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Super Rapid Crystal Growth and Quench of Monoclinic Bi-II* During Dynamic Compression

Zachary Allen Fussell

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SUPER RAPID CRYSTAL GROWTH AND QUENCH OF MONOCLINIC
BI-II* DURING DYNAMIC COMPRESSION

By

Zachary Allen Fussell

Bachelors of Science - Physics
University of Nevada Las Vegas
2015

A thesis submitted in partial fulfillment
of the requirements for the

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Department of Physics and Astronomy
College of Sciences
The Graduate College

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This thesis prepared by

Zachary Allen Fussell

entitled

Super Rapid Crystal Growth and Quench of Monoclinic BI-II* during Dynamic Compression

is approved in partial fulfillment of the requirements for the degree of

Master of Science - Physics
Department of Physics and Astronomy

Victor Kwong, Ph.D.
Examination Committee Chair

Kathryn Hausbeck Korgan, Ph.D.
Graduate College Dean

Oliver Tschauner, Ph.D.
Examination Committee Member

Ashkan Salamat, Ph.D.
Examination Committee Member

Paul Forster, Ph.D.
Graduate College Faculty Representative

Abstract

We show that monoclinic Bi-II* forms during a dynamic compression regime with crystal growth rates from melt of ≈ 70 m/s. This extreme quench rate implies crystallization by non-diffusive processes and indicates that the liquid had a high degree of pre-ordering. Using ambient condition single crystal structure analysis we show for the first time that the monoclinic distorted phase of Bi (Bi-II) exists at ambient pressure, albeit bound to formation under dynamic compression. We review the pressure, temperature, and time conditions for formation and growth of this structure.

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Chapter 1 Introduction

Ten crystalline phases of bismuth (Bi) are as yet known to occur between ambient conditions and 12 GPa [1]. This includes bismuth II (Bi-II), a monoclinic distortion of the simple cubic α polonium (α -Po) structure. [2] The Bi-II structure was initially proposed as simple cubic [3], but static compression experiments [4,5] combined with more advanced X-ray diffraction techniques [6] showed Bi-II to be monoclinic. Here we report the first recovery of monoclinic distorted Bi-II* to ambient conditions using dynamic compression. Formation of high-pressure phases of Bi under dynamic compression is interesting under more than one aspect: Firstly, there is the question of kinetic overriding of the static phase boundaries. Recently, it was shown for Si that dynamic phase boundaries are shifted to lower rather than higher pressure [7] despite kinetic effects are generally believed to shift boundaries to higher pressure upon dynamic compression [8]. Secondly, entirely different structures may occur upon dynamic than under static compression [9]. These questions are centered around the effect of short stress duration and fast ramp on formation and growth of phases. This is further discussed in the Background.

A single stage light gas gun is used to launch projectiles at a recovery target chamber which allows the sample to be recovered to ambient conditions for post shock analysis where

electron microscopy and X-ray diffraction are used to identify irreversible changes in the chemical and crystalline structure. The projectile velocity and its material are varied to tune peak pressure, duration, and release paths. (See Methods) Here we explore if high pressure phases of bismuth can be recovered to ambient conditions from dynamic compression experiments. (See Results) If confirmed, this will shed light onto the behavior of materials under dynamic compression and their kinetics. (See Discussion) In general this would open new paths for material synthesis.

Chapter 2 Background

Shock recovery studies look for features observed post shock at and around impact sites. In nature this can be observed on meteorites and at crater sites [10,11]. Light gas gun based shock recovery experiments can mimic the compositions and conditions of these large scale events [12]. However, unlike studies of shock impact craters, the material composition and experimental conditions are controllable. Bismuth is known by its unique features in the field of high pressure physics, e.g. the solid state is less dense than liquid state up to 2.2 GPa. Upon compression, the sequence of crystallographic phase transformations of this group 15 semimetal have been much debated [3, 4, 5, 6, 13].

2.0.1 Bismuth Crystal Structure

In a solid, atoms reside at the nodes of a periodic lattice. There are seven primitive and seven non primitive lattice types in three spatial dimensions. Lattices can be defined by three sets of parameters; Lattice vectors along crystallographic directions a , b and c , angles between lattice vectors α , β and γ , and fractional coordinates defining atomic positions relative to the lattice vectors. Consider a cube with $a = b = c$, $\alpha = \beta = \gamma = 90^\circ$ and an atom located at each corner. This is the simple or primitive (P) cubic lattice. Adding one atom to the midpoint of each face diagonal is the non-primitive face centered (F) cubic lattice. Adding

an atom to the midpoint of a body diagonal is the body centered (I) cubic lattice. These three structures are visualized below using PowderCell. [14]

Figure 2.1: Cubic unit cells generated in Powdercell. [14] Starting with the simple or primitive cubic (a) there is an atom located at each corner of the cube. (b) Body centered cubic where atoms are located at each corner and at the midpoint of the body diagonal. (c) Face centered cubic where an atom is located at each corner of the cube as well as the midpoint of each face diagonal.

The group 15 elements (nitrogen group) contain 5 valence electrons, 2s and 3p in the ground state. The third, fourth and fifth row elements of this group are closely related semimetals arsenic, antimony and bismuth, respectfully. At ambient conditions, As, Sb and Bi form in the rhombohedral As-I structure space group 166 [5, 15, 16, 17]. At 2.4 GPa the structure of Bi-II was initially proposed as simple cubic [3], but static compression experiments [4, 5] combined with more advanced X-Ray diffraction techniques showed that Bi-II is a monoclinic distortion of the simple cubic α -Po structure [6]. Bismuth transforms into phase three at 2.8 GPa, an incommensurate host - guest structure [13]. Bismuth assumes a BCC structure at 7.8 GPa [4]. While a similar sequence is followed by As and Sb, the transitions occur at different pressures. E.g. at 300 K the bcc phase forms in Bi at 7.7 GPa [13], Sb at 28 GPa [15] and As at 97 GPa [16]. Monoclinic and tetragonal As structures have been recovered

to ambient conditions using rapid vapor and liquid quenching [18], but only the rhombohedral structure has been observed at ambient conditions in Sb and Bi. Bridgman observed a large change of resistivity in bismuth upon compression and identified this change as a transition from Bi-I to Bi-II [19]. Bismuth became a subject of debate when static and dynamic studies of phase transition pressures disagreed [20, 21]. The invention of Velocity Interferometer System for Any Reflector (VISAR) [22] for measuring surface velocities and later a correction in strain gauge finite strength [23] revealed agreement between the static work by Bridgman and those dynamic studies. This agreement is generally not found in other materials, where compression strain rate shifts phase transitions to higher pressures [24]. Recent experimental work on dynamic phase boundaries using laser driven shock with free electron laser (FEL) in-situ diffraction identified lowering of the transition pressure as a function of shear stress introduced during planar impacts [7]. Cox developed a multiphase equation of state for bismuth [25] including one liquid and five solid phases. A large hysteresis has been observed in the transition from Bi-II to Bi-I upon decompression with some dependence on the decompression rate [26]. In order to compare dynamic results with static data it is necessary to make accurate measures and / or calculations of state variables such as pressure and temperature.

2.1 Shock Waves

The term "shock wave" defines not a wave, but a discontinuous transition from some initial state to a high pressure state. Hooke's law describes the linear elastic region of compression where stress and strain are proportional giving a linear relationship between the modulus of

elasticity ($k = -v \frac{dp}{dv}$) and pressure. For a large increase in pressure, beyond the hugoniot elastic limit, a non linear increase in k leads to an increase in the wave velocity. Further increase in wave velocity may cause the wave to form a discontinuous jump from initial state to the high pressure state [27], and this establishes a shock compression state. Consider a large increase in pressure across a compression wave front as shown in (Figure 2.2).

Figure 2.2: Steepening of wave front in a finite thickness pressure wave for pressures beyond the hugoniot elastic limit leading to an increase in velocity with increasing pressure.

By allowing one micro-second to pass all three points will form a vertical line (discontinuity) where the material is nearly instantaneously compressed from the initial state to the high pressure state.

2.1.1 Equation of State (EOS)

Equations of state establish a relationship between thermodynamic variables; pressure P , volume V , temperature T , entropy S , etc. Considering a system in equilibrium with N

particles, contained by a volume V at temperature T , the partition function defines the population of energy states by the particles of this system [28]

$$Z(V, T, N) = \sum_n \exp(-E_n/kT). \quad (2.1)$$

The free energy, entropy and pressure can be defined in relation to the partition function with $F = -kT \ln Z$, $S = -\partial F / \partial T|_{V,N}$ and $P = -\partial F / \partial V|_{T,N}$. We are specifically interested in the relationship between pressure and volume during compression. Here the Birch-Murnaghan functional form is used to represent isotherms [29] over extended range of pressure and volume. Ahrens and Jeanloz derived an equation for the adiabatic curve [30] from the Hugoniot. Using bismuth EOS parameters from Johnson et al. [31], the isotherm and adiabat are plotting along with the principal Hugoniot of bismuth [32] in Figure 2.3.

Figure 2.3: Pressure volume relations along isotherm (blue diamonds), adiabat (red squares) and principal hugoniot (black circles).

The isotherm (blue) gives a reversible thermodynamic path where temperature is held con-

stant. The adiabat (red) gives a reversible thermodynamic path where temperature is allowed to increase, but no heat transfer. The Hugoniot (black) gives a locus of states achievable through shock compression. It is an important distinction that the Hugoniot does not represent a thermodynamic path, instead compression is along Raleigh lines as shown in Figure 2.4.

Figure 2.4: Pressure volume compression path due to shock compression given Hugoniot (black), the Raleigh line to 5 GPa (cyan) and the Raleigh line to 10 GPa (purple).

Compression to 5 GPa (cyan line) and 10 GPa (purple line) is represented by a straight line from the initial state to the final state on the hugoniot at peak pressure.

2.1.2 Rankine-Hugoniot Equations

The Rankine-Hugoniot or sometimes referred to as Hugoniot equations are used to relate thermodynamic and kinematic variables across a jump discontinuity. The Rankine-Hugoniot equations were developed near the end of the 18th century, where previously such discon-

tinuity was considered a "queer kind of motion" doubted by Sir George Stokes and Lord Rayleigh [33]. A detailed mathematical description is given in the Zel'dovich Raizer [34] and Landau Lifschitz [35] textbooks. In the impact of two flat plates a one dimensional approximation is used to calculate peak pressure and shock durations. Considering this impact, beyond the shock wave front is the ambient equilibrium material and immediately behind the shock front is the compressed high pressure state [32]. The high pressure state is defined by the three Hugoniot equations describing the mass, momentum and energy exchange across the shock front.

Mass

$$\frac{\rho_1}{\rho_0} = \frac{U_s}{U_s - U_p}. \quad (2.2)$$

Momentum

$$P_1 = \rho_0 U_s U_p. \quad (2.3)$$

Energy

$$e_1 - e_0 = 1/2(P_0 + P_1)(V_1 - V_0) \quad (2.4)$$

Equations 2.2, 2.3 and 2.4 make up the Hugoniot equations where ρ is density, P is pressure, U_s is the shock velocity, U_p is the particle velocity and e is the energy [36]. A linear relationship has been measured between the shock velocity and particle velocity in most materials and is given in the form

$$U_s = C_0 + sU_p. \quad (2.5)$$

Here C_0 is the adiabatic sound speed and s is a constant. Constant s is a function of the derivative of the elastic modulus $(K'_s + 1)/4$ [37], relating the particle velocity to the shock

velocity.

2.1.3 Shock Impedance

Consider the collision of two disks where the first disk (flyer) is moving with some initial velocity and the second disk (driver) is at rest and attached to a third disk (sample) as shown in Figure 2.5.

Figure 2.5: Experiment layout with flyer (1) impacting the driver (2) attached to the sample (3). Shock impedance and the thickness of disk 1, 2 and 3 alter the pressure duration and release profile.

Upon impact two shockwaves are formed, one propagating backward into the flyer and a second propagating forward into the driver. The initial shockwaves formed upon impact are governed by the equation

$$\rho_{01}(U_f - U_p)(C_{01} + s_1(U_f - U_p)) = \rho_{02}U_p(C_{02} + s_2U_p). \quad (2.6)$$

U_f is the flyer or projectile velocity and all other variables are the same as previously defined [37]. The left hand side of the equation represents the shockwave propagating backward into the flyer (subscript 1) and the right hand side represents the shockwave propagating forward into the driver (subscript 2). When the backward moving wave reaches the free rear surface of the flyer pressure is released through a wave traveling with a velocity of two times the initial

particle velocity (leading edge) [38]. It is important to note this release wave is moving from a lower pressure to a higher pressure region (Shock Wave Decompression). This pressure release will spread in time with the slowest component (trailing edge) moving at the ambient sound speed and releases pressure to ambient conditions. The fastest component (leading edge) of the rarefaction wave starts the pressure release process as it passes through the assembly. In this work multiple experiments used an impedance matched flyer and driver (Case 1) and two experiments used impedance mismatched flyer and driver (Case 2). In Case 1 the initial density, sound speed and s parameters of the flyer and driver equal and remain in contact with zero relative terminal velocity following the release outlined above. The pressure duration is determined by the thickness of the flyer. In Case 2, the initial density, sound speed and s parameters are different between the flyer and driver. The higher impedance flyer produces a greater peak pressure in the driver and reduced particle velocity U_p in the flyer, calculated by Equation 2.5. The reduced particle velocity in the flyer leads to only a partial release of pressure from the rarefaction wave. An additional compression wave propagates backward into the flyer and another partial release of pressure occurs. Ultimately a combination of these partial release waves release the sample to ambient pressure. The reduction in pressure from each partial release depends on the relative difference in shock impedance. When the shockwave interacts at the driver / sample interface a reflected and transmitted wave result. The particle velocity of the reflected and transmitted waves are dependent on the relative change in shock impedance between the driver and sample, dependent on Equation 2.6.

2.1.4 Shock Wave Decompression

During decompression pressure is released along a continuous adiabat. Consider the impact of a flyer plate onto an infinitely thick driver plate. A release wave is formed when the shockwave propagating backward into the flyer plate reaches the rear surface. The fastest moving portion of the release wave will propagate forward through the compressed at two times the velocity of the initial wave [38]. Since pressure is released to ambient the slowest moving portion of the release wave will propagate at the ambient sound speed. The release wave will catch up to the shock front reducing the pressure duration until it eventually reduces the amplitude. As time progresses, the shock wave will be reduced to a sound wave (Fig. 2.6.)

Figure 2.6: Attenuation of shockwave following the onset of rarefaction. The rarefaction will cause a ramp down in pressure limiting the length of the shocked state eventually cutting down the pressure until the wave is reduced to a sound wave.

Release rarefaction is not only limited to forming at the flyer rear surface in layered targets, see further discussion in Methods.

Chapter 3 Methods

Laboratory based shock compression provides safe repeatable measurements used to study materials and their properties subject to shockwaves. A number of different techniques have been developed, in this work we use a single stage light gas gun. [40, 41, 42, 43] Light gas guns are used to produce planar shock waves with peak pressures and time scales constrained by the projectile velocity, material type and material thickness. In nature shockwaves occur when high velocity meteorites impact earth or space debris collides with satellites. In these meteorite impacts scientists have identified features in the shocked terrain to understand the conditions of the impact such as meteorite size, velocity and composition. In our work we use a light gas gun equipped with a recovery chamber to drive a shockwave through the sample, then recover it back to ambient conditions. X-ray and electron based tools are used pre and post shock to identify shockwave effects.

3.1 UNLV Gas Gun

A helium driven single stage light gas gun launches projectiles up to 1 km/s in Oliver Tschauner's lab at UNLV. Peak pressure, shock duration and the release pathway are determined by projectile velocity, thickness and composition of the target assembly layers. The

experimental configuration is shown below in Figure 3.1.

Figure 3.1: UNLV Light gas gun layout. (1) Launch tube, (2) Sabot, (3) Flyer disk, (4) Optical beam break, (5) Flange, (6) Driver disk, (7) Sample, (8) Momentum trap (Stainless Steel S.S.), (9) Guide ring (S.S.), (10) Capture Tank.

The sabot and flyer disk (projectile) (2,3) are launched down the steel launch tube (1) and cross an optical beam break (4) mounted perpendicular to the projectile path, measuring the projectile velocity. The flyer disk (3) impacts the driver disk (4), driving a shockwave through the recovery chamber (6, 7, 8). The recovery chamber consists of a driver disk (6), sample (7) and stainless steel momentum trap (8) held in place by a guide ring (9) mounted inside the catch tank (10). The momentum trap ensures the bismuth sample is not destroyed by a release rarefaction wave. Rags are placed behind the target assembly inside the capture tank (10) along with foam behind the capture tank to absorb residual momentum transferred by the projectile or gas. The catch tank is connected to the launch tube via slip fit through a flange (5). An example of the optical beam break readout is given in Figure 3.2. Voltage

threshold is manually set and optical intensity variation is monitored to ensure the sabot and flyer have not separated.

Figure 3.2: Optical beam break read out for recording projectile velocity. Optical intensity is measured as a function of time with diode 1 (yellow) and diode 2 (blue).

The time difference is measured and averaged at the steepest slope at the projectile arrival (voltage drop) and projectile departure (voltage rise). Both Lexan and cork have been used as sabots. These materials are soft so they will not damage the launch tube, they are inexpensive and available. Initially Lexan was used, but launch velocity was highly dependent on projectile diameter ($\pm 10 \mu m$), making the machining process difficult and timely. When the projectile diameter is too narrow, helium escapes past the projectile, reducing the velocity. Too wide a diameter runs risk the projectile is wedged stuck in the barrel. The Poisson ratio of cork is nearly 0, that is, upon axial compression there is nearly no radial expansion [44]. Cork projectiles are tight fit into the barrel without risk of getting stuck. Shots following experiment GG119 were completed using cork projectiles with tight

fits allowing for greater velocities. A calibration curve of helium pressure vs. velocity is measured in order to repeat velocities from previous experiments.

3.1.1 Gas gun calibration

If two shots are ran at the same helium pressure will the projectile reach the same velocity?

All experiments are ran using the operating procedure given in Appendix A, results are shown in Table 3.1.

Table 3.1: Calibration test results

Shot Number	GG120	GG121	GG122	GG124	GG125	GG126	GG127
Gas Pressure (psi)	810	850	850	600	500	410	300
Flyer Velocity (km/s)	0.66	1.00	0.92	0.64	0.77	0.82	0.63
Sabot Mass (g)	0.102	0.104	0.102	0.134	0.103	0.128	-
Sabot diameter (mm)	7.98	8.36	8.13	8.2	8.2	8.2	8.3

With increasing gas pressure we expect to see an increase in velocity. (Fig. 3.3)

Figure 3.3: Calibration curve distorted by extraneous variable, likely the solenoid gas release valve.

The first three shots GG120, GG121 and GG122 were ran back to back using similar pressure and different diameter to determine the significance of projectile diameter on launch velocity. All projectiles are tight fit, therefore little He gas is expected to blow past the projectile, but the velocities have nearly a 40 % difference. It is most significant between the first and second shot. A second set of calibration shots were ran further constraining the experiment, using matched diameter sabots and recording the mass. From shot one (GG124) to shot two (GG125), He pressure was decreased, mass was increased, and velocity also increased. In shot three (GG126) He pressure was further reduced and velocity increased. These three shots were separated by less than a 15 minute time interval. Shot four (GG127) was ran following a 45 minute delay, pressure was reduced and projectile velocity was reduced. Temperature inside the barrel is expected to increase due to friction. Temperature in the solenoid valve is also expected to increase because of current ran through the coil. Temperature can be constrained by waiting for 0.75 to 1 hour between shots. Variation in the solenoid could be eliminated by changing the experimental configuration to use a burst valve that opens after pressure reaches a predetermined threshold. Considering only the first shot in each series limits temperature induced variability. Line $y = (9.5 \cdot 10^{-5})x + 0.58$ crosses the GG120 and GG124 shot velocities evaluated at helium pressures 600 and 800 psi.

3.1.2 Experiment Design

The experimental assembly (Flyer/Driver/Sample/Backer) composition and thickness along with the flyer impact velocity determines the peak pressure and shock duration. Hugoniot parameters for the materials used in the work are given in Table 3.2 [32].

Table 3.2: Hugoniot parameters for tungsten, 304 steel and bismuth used for flyers, drivers and samples.

Material	ρ_0 (g/cm ³)	C_0 (km/s)	s
Tungsten	19.224	4.029	1.237
304 Steel	7.896	4.569	1.490
Bismuth	9.836	1.826	1.473

We probe the dynamic phase transitions in bismuth by using two different assembly configurations giving distinct pressure-temperature release pathways. The setup for experimental configuration 1 consists of a 250 μm thick steel flyer plate, 250 μm thick steel driver plate and and 300 μm thick bismuth sample. The sample thickness was set so the release wave from the flyer plate arrives at the driver - sample interface when the forward propagating shockwave reaches the sample - backer interface. (See Figure 3.4) The sample itself consists of a brass washer with 4 mm inside diameter, 8 mm outside diameter polished down to a final thickness of 300 μm using 100 - 10 micron polishing film. Bismuth poly-crystals of 99.9 % purity with a length ranging from 0.2 - 1 mm are then placed in the washer and hand pressed locking them into place. A light microscope image of the sample GG111 is given in Figure 3.8. Using the layered Target assembly given in Figure 3.1, four interfaces are considered: flyer rear surface, flyer - driver, driver - sample, and sample - backer. In configuration one, the flyer and driver materials are both stainless steel. The impedance of these two materials is matched, and upon impact one shockwave is driven forward through the sample and another is driven backward toward the flyer rear surface. Using equation 2.6, the impedance of steel is greater than bismuth and therefore pressure is reduced in the shockwave crossing this driver - sample interface. A reflected wave is produced and reduces pressure in the steel driver. A transmitted shockwave passes from bismuth back to steel

at the sample - backer interface, impedance goes up along with the pressure. A reflected wave is produced and increases pressure in the bismuth sample. A transmitted shockwaves propagates through the backer. When the backward propagating shockwave reaches the rear surface of the flyer pressure begins to release through the sample via rarefaction wave. The rarefaction wave front will catch up to the compression front within the steel backer. The complete process is shown in Figure 3.4 with position of shockwave in assembly vs time. Reflected waves at driver - sample and sample - backer are not shown.

Figure 3.4: Position of shockwave in target assembly versus time. Impact at flyer driver interface is at position (0,0) (red line). At the rear surface of the flyer (gray line) a release rarefaction wave will propagate back into the flyer with leading velocity (solid red line) and trailing sound speed velocity (red dashed line).

Flyer, driver and sample thickness can be varied to change the shock duration. Here thickness was set to match the compression wave arrival time at the sample - backer interface with the release wave front arrival time at the driver - sample interface . In configuration two, a tungsten flyer plate is used instead of stainless steel. The shock impedance difference between flyer and driver leads to a considerably different stepwise pressure release. Pressure is maintained between the flyer and driver during this stepwise release, so reverberative shocks and cavitation effects are also considered. Due to the added complexity of tracking the additional shockwaves, pressure calculations were provided by our collaborator Cameron Hawkins from Mission Support and Test Services LLC., using the program MACRAME (Fig. 3.5) [45].

Figure 3.5: Time versus position of shockwaves in the target assembly from collaborator Cameron Hawkins using MACRAME [45]. Flyer driver interface at $x=0$, driver sample interface at $x = 0.25$ mm and sample backer interface at $x = 0.55$ mm.

This program tracks the multiple compression and release waves throughout the assembly as well as the separation of material under tension known as spall. About every 30 ns pressure is partially released at the flyer driver interface. The second pressure state interacts with the reflected wave from the steel / bismuth interface leading to the formation of a new interface at (1.5,0.7). A 2D simulation is used to further evaluate the release pathway in conjunction with the effect of edge release due to finite crystal dimensions. Our collaborator, Cameron Hawkins, from MSTS provided compression and release pathway for both configurations from a 2D simulation using CTH [45]. CTH is finite element based code developed by Sandia National Laboratories and here a $3 \times 3 \mu m^2$ mesh is used with 10 ns time steps.

Figure 3.6: CTH simulation from collaborator M. C. Hawkins at MSTS [45] on configuration one, experiment GG119, pressure and temperature conditions at a flyer velocity of 880 m/s.

Figure 3.7: CTH simulation from collaborator M. C. Hawkins at MSTs [45] on configuration two, experiments GG111 and GG137, pressure and temperature conditions at a flyer velocity of 540 m/s.

In Figures 3.6 and 3.7 (a) pressure versus time is given over a 10 microsecond period nearest the center of the sample where pressure and temperature conditions are maximized. (b) zooms in on the first few hundred nanosecond to show the initial compression wave. (c) gives temperature versus time over a 12 microsecond period and (d) shows pressure vs temperature for the compression and release. A total of 12 experiments were ran, where 10 experiments used stainless steel flyers and two used tungsten flyers. A summary of experimental conditions for 5 characteristic experiments is given in Table 4.1 including: shot number, flyer velocity, maximum pressure in sample, maximum temperature in sample, helium gas pressure, flyer thickness, driver thickness, and flyer type. In configuration 1 peak pressure and temperature correspond to the initial shockwave. In configuration 2 peak pressure corresponds to the initial shockwave, but peak temperature is due to additional

shocks later in time.

Table 3.3: Experiment shot log including shot number, projectile velocity, max pressure, max temperature, gas pressure, flyer thickness, driver thickness, sabot diameter.

Shot Number	GG106	GG111	GG119	GG128	GG137
Flyer Velocity (km/s)	0.63	0.54	0.88	0.66	0.54
Max Pressure (GPa)	9.3	11.6	18	10	11.6
Max Temperature (K)	480	520	760	500	520
Gas Pressure (psi)	500	800	810	250	300
Flyer thickness (μm)	0.21	0.07	0.25	0.26	0.07
Driver thickness (μm)	0.24	0.23	0.25	0.27	0.24
Flyer type	S.S.	W	S.S.	S.S.	W

3.1.3 Post Shock Sample

Compression of bismuth beyond the hugoniot elastic limit (Pressure > 10 MPa) will lead to plastic deformation. In some experiments additional compression caused the sample to melt and recrystallize, further changing the sample. A light microscope image of experiment GG137 sample post shock is given in Figure 3.8 (left) and similarly loaded GG111 pre shock (right).

Figure 3.8: Left: Experiment GG137 bismuth sample post shock optical image. Bismuth recrystallizes within the brass ring and a number of different grains are still present. Right: Experiment GG111 sample pre shock.

Post shock the GG111 sample was mounted on a microscope slide, set in epoxy and polished with 15, 10, 5, 2 and 1 μm polishing film before final vibro-polish to ensure the surface finish was free of scratches. High resolution electron back-scatter diffraction and energy dispersive spectroscopy were performed at Caltech.

3.2 Electron Microscopy

Field emission scanning electron microscopes (FE SEM) at Caltech GPS division and UNLV collect secondary electron images, backscatter electron images, electron back scatter diffraction (EBSD) and energy dispersive spectroscopy (EDS) to characterize the samples. In field emission microscopes an electron beam is emitted from a sharp tungsten tip and accelerated

toward the sample with characteristic energies 10-100 keV. Secondary electrons are emitted by the sample due to ionization. If core electrons are ejected, characteristic X-rays are emitted and detected using EDS. Back scatter electrons are elastically scattered by the sample and for a highly polished sample the back scatter electrons produce diffraction of individual crystals [46].

3.3 X-Ray Diffraction

X-Ray diffraction was performed at the Sector 16 HPCAT IDB micro-diffraction beamline. This undulator beamline [47] utilizes a silicon monochromator to produce light from 18 - 60 keV with a resolution of $1 \times 10^{-4} \frac{\Delta E}{E}$ and $\approx 1 \times 10^{12}$ photons per second. Kirkpatrick-Baez (KB) mirrors are used to focus the X-ray beam down to $3 \times 6 \mu m^2$ and detectors (MAR165 CCD, PILATUS 1MF) capture diffraction patterns. A cerium dioxide standard was used to calibrate the detector distance and tilt at set wavelength $\lambda = 0.0406305$ nm using the automated fitting procedure in Dioptas [48] from the pattern given in Figure 3.9.

Figure 3.9: Cerium dioxide standard characteristic diffraction pattern.

Gaussian and Lorentzian profile parameters were extracted from a Rietveld refinement of this pattern using a Pseudo-Voigt profile and were used as the initial profile parameters for structural refinements of the powder-like bismuth. (Fig. 3.10.)

Figure 3.10: Cerium dioxide standard Rietveld refinement (red) using PowderCell, with integrated diffraction pattern (black) and residual (green) given below.

Each bismuth sample was removed from the momentum trap and driver plate then fixed with

a piece of clay on top of an optical post, still within the brass retainer ring. The sample was centered on the calibrated position and aligned using one dimensional radiography scans over three angles in ϕ . A coarsely scanned 2D radiography image was recorded over a 3.9×3.9 mm² grid with 13×13 μm^2 spacing using a silicon pin diode and the Diptera [49] program. As shown in Figure 3.11, the radiographic map identifies regions that could generate local temperature or stress excursion during shock [50].

Figure 3.11: Bismuth sample pre shock X-Ray radiography image taken in transmission geometry. High count (red) regions indicate high transmission. X and Y axis dimensions are in length (mm).

The radiography is set in transmission geometry and high count regions (red) indicate high transmission in Figure 3.11. The x and y axis are length given in mm. Diffraction grid scans are then taken over a range of angles at regions of interest to include locations in the bulk of the crystals and near the edge of individual grains. The GG111 polycrystalline pre shock

characteristic pattern is given in Figure 3.12. The large single crystal peaks were masked before integration.

Figure 3.12: Bismuth GG111 pre shock characteristic diffraction pattern.

Figure 3.13: LeBail refinement [12] of integrated bismuth GG111 pre shock characteristic diffraction pattern with Bi-I peak locations identified by red lines and Miller indices given.

A LeBail refinement of the pre shock GG111 sample gave an R_p value of 12.32 and a R_{wp} of 18.12. Large single crystals were recovered to ambient conditions from shock experiments GG111 and GG137. A 20 μm sliver of the bismuth sample was removed and placed in the beam centered by radiography scans over three angles in ϕ . Experiments GG111 and GG137 required single crystal diffraction analysis, which is beyond the scope of this thesis and was performed by Oliver Tschauner. This analysis was done using GSE-ADA [51] for peak fitting, intensity and angles $(\theta, \chi, \phi, 2\theta)$, which are input into Reciprocal Space Viewer (RSV) [52] and exported to CellNow [53] for indexation. The indexation is loaded back into RSV where a hkl file is generated and is then used to solve the structure by SIR92 [54] and Endeavour [55].

Chapter 4 Results

In experiments with impedance matched flyer and driver, the ambient Bi-I structure was recovered. In the two experiments with impedance mismatched flyer and driver large single crystals of a monoclinic structure similar to the high pressure Bi-II structure were recovered from 11.6 GPa peak pressure. This structure belongs to the same space group as previously reported monoclinic Bi-II observed at high pressure, but the lattice parameters and β angle are slightly larger, therefore we refer to this new structure as Bi-II*. See Table 4.1 for a list of experiments, the analysis performed and a summary of the result. The first experiment GG106 was not analyzed because of a non planar impact. Experiments GG119, GG128, GG130 and others were run using impedance matched configuration and only to the ambient Bi-I structure was recovered. Experiment GG111 was ran using mismatched impedance and a high pressure monoclinic phase of bismuth was recovered to ambient conditions. Experiment GG137 was performed using the same experimental configuration and projectile velocity as experiment GG111. Both experiments resulted in the recovery of monoclinic Bi-II* structure to ambient conditions. The GG111 sample was characterized by a full suite of diagnostics to look for signs of melt, confirm the chemical composition, confirm the structure. Scanning electron microscopy identified the formation of spherical droplets, indicating melting of the sample surface. Energy dispersive spectroscopy verified the chemical composition as bismuth

and X-Ray identified the presence of Bi-I and Bi-II* crystal structures.

Table 4.1: Experiment, characterization methods and result summary.

Experiment	Analysis Methods	Result Summary
GG106	N/A	N/A non planar impact
GG111	XRD, SEM, EBSD, EDS, AFM, Scanned probe	High pressure Bi-II* recovery, melt, Bi chemical composition
GG119	XRD	Bi-I
GG128	XRD	Bi-I
GG129	XRD	Bi-I
GG130	XRD	Bi-I
GG137	XRD	Bi-II*

Impedance matched experiments were ran over a range of pressures (7 GPa - 18 GPa) compared with the impedance mismatched flyer and driver setup ran at 11 GPa. In GG119 we loaded 99.99 % pure bismuth powder with 1-10 μm grain size into a 4 mm diameter brass ring and used impedance matched flyer and driver to give a single shockwave compression and release. Figure 4.1 shows the bismuth phase diagram with GG119 pressure temperature curve calculated in CTH [45] overlaid (black dashed line). Experiment GG111 and GG137 were both ran at a velocity of 540 m/s within 1 % difference are also given in Figure 4.1 (black solid line).

Figure 4.1: Bismuth phase diagram with GG119 (dashed black line) and GG111 and GG137 (solid black line) pressure temperature curves calculated using CTH [45] overlaid.

Experiment GG119 sample was shocked up to 18 GPa and 760 K, where it would release through liquid phase stability upon release from pressure. In GG128 and other impedance matched experiments pressure and temperature conditions were lower, maintaining the solid state. For GG111/137 along the principal hugoniot to 11 GPa, 500K was achieved before releasing to ambient pressure. Additional shocks drive the sample to the maximum temperature of 520 K at 1.2 GPa. Additional shocks compressing into the liquid stability region are unique to the impedance mismatched experimental configuration.

4.1 Scanning Electron Microscopy

Spherical droplets were observed near grain boundaries throughout the GG111 sample indicating the bismuth had melted. Pressure is reduced near grain boundaries due to edge release, therefore it is expected this melting was due to local hot spot formation upon shock. Initial SEM images were taken prior to polish to avoid risk of polishing away these droplets. Droplets range in size from 2 to 20 micrometers in diameter. In Figure 4.2 a $1.5\ \mu\text{m}$ spherical melt droplet is shown near a grain boundary.

Figure 4.2: SE-SEM image of $1.5\ \mu\text{m}$ spherical melt droplet identified near edge of grain in GG111.

Additional droplets are observed throughout the sample ranging in size up to $20\ \mu\text{m}$ in diameter. Energy dispersive spectroscopy (EDS) records chemical composition within the droplet. (Fig. 4.5.)

Figure 4.3: a.) SE-SEM image of spherical melt droplet. b.) Energy Dispersive Spectroscopy (EDS) taken on 1.5 mm spherical droplet near void in shock recovered GG111.

Primarily bismuth was present according to this analysis. A characteristic spectrum was recorded throughout the sample.

Figure 4.4: EDS taken at two different points on bismuth sample with varying electron intensity from grain to grain. Despite highly intense regions, the EDS spectrum remains constant with only the presence of bismuth.

Despite variations in intensity, EDS confirms the presence of bismuth throughout the sample. Some traces of carbon were found in the sample and are likely contamination from pre-shock polishing (diamond powder). Since the intensity is dependent on the surface geometry, the unpolished surface leads to a skewed intensity representation, as can be seen by the bright white and dark regions. The sample was polished and quantitative grain to grain analysis was performed using Electron Back Scatter Diffraction (EBSD).

4.1.1 Electron Back Scatter Diffraction

Following the SEM work, the GG111 sample was polished and brought to the system at Caltech. A number of images were taken throughout the sample over a range of magnifications. A representative image is given in Figure 4.5 with 1.5×10^3 zoom and accelerating voltage 15 kV.

Figure 4.5: Secondary electron image of GG111 sample taken at Caltech containing fluctuations of intensity over small grains throughout the entire sample.

The dark lower region is due to a void and the straight lines that appear to cut through the entire length of the image are likely scratches induced during the polishing process. Different crystal structures may have unique intensity distributions, but the intensity distribution for each individual structure is dependent on the orientation. The overlap of intensity distributions render these images qualitative for phase proportion identification. Initial EBSD

identified Bi-I phase along with possible Bi-II grains, but further work showed those grains to be another orientation of the Bi-I phase. The grain and phase distribution is shown in Figure 4.6 pole figure diagram.

Figure 4.6: SEM band contrast image (left) and pole figure diagram (right). Scratches visible in band contrast led to poor something.

Near scratches the high pressure phase was selected by the software initially, but additional analysis throughout those regions showed either the ambient Bi-I structure was present, or the result was inconclusive due to a poor fringe resolution. One of the diffraction patterns with the Bi-I phase overlaid is given below.

Figure 4.7: Electron back scatter diffraction interference image with fit overlaid and miller indices given.

Further EBSD analysis identified only the ambient Bi-I phase, however, previous experiments have struggled to identify metastable phases through EBSD because of the intense electron beam back converting the sample to its stable ambient phase. [18]

4.2 X-Ray Diffraction (XRD)

The heterogeneous nature of the polycrystalline samples led to both powder-like bismuth crystals and large single crystals in the sample. Experiment GG119 used a powder-like Bi-I starting material, and a similar powder-like Bi-I was found throughout the sample post shock.

Figure 4.8: Bismuth GG119 diffraction pattern from Sector 16 IDB with beamsize $3\ \mu\text{m} \times 6\ \mu\text{m}$ and $\lambda = 0.4066\ \text{\AA}$.

Figure 4.9: Lebail refinement [14] of integrated bismuth GG119 diffraction pattern post shock.

This refinement gave a R_p value of 12.20, (R_{wp} of 19.27). There are some very weak peaks not fit in this pattern between (012) and (104) peaks. Previous work using transmission electron microscopy and synchrotron radiation has attributed peaks over this range to the coexistence of metastable polymorphs at ambient conditions [56]. GG111 contained very weak powder-like peaks in this region not belonging to any of the previously recorded metastable polymorphs or the ambient oxide phases BiO or Bi₂O₃. (See Appendix B) In addition to these peaks, large single crystal peaks of a monoclinic bismuth structure were present in the diffraction patterns.

4.2.1 Single Crystal XRD

The diffraction pattern of a 20 μm crystal of bismuth removed from GG137 sample is given in Figure 4.10.

Figure 4.10: Bi GG137 Diffraction Pattern.

Figure 4.11: Bi GG137 integrated diffraction pattern with single crystal peaks masked.

This phase was determined to be a monoclinic bismuth II like structure using reverse-Monte Carlo methods in Endeavor [55] and direct methods in SIR92 [54]. In the integrated pattern single crystal peaks are masked with Bi-I peak locations given in orange, located at the powder fringe angles.

Table 4.2: Monoclinic SG 12 (C1 2/m 1) Bi-II* Crystallographic Parameters.

S.G.	a (Å)	b (Å)	c (Å)	$\beta(^{\circ})$
C1 2/m 1 (12)	8.167 ± 0.175	4.526 ± 0.009	4.727 ± 0.008	121.9 ± 0.632
Volume (Å ³)	B_{iso}			
148.3	1.30			
Atom	Wyck.	x	y	z
Bi	4i	0.599	0	0.279

This monoclinic structure was visualized using Vesta [57] and is presented in the Discussion.

Chapter 5 Discussion

The recovery of Monoclinic Bi-II* from dynamic compression for the first time is interesting in multiple aspects: Firstly, a monoclinic Bi-II structure has been reported at high pressure, but has never been recovered to ambient conditions. Secondly a single crystal 20 μm in length of this structure formed, an unexpected result for the short time scale of these experiments. Thirdly this structure was only formed using impedance mismatched flyer and driver configuration even with impedance matched experiments ran under similar Pressure-Temperature conditions.

5.1 Monoclinic Bismuth II* Structure

The monoclinic structure recovered belongs to the same space group as the high pressure structure (SG 12 C1 2/m 1), but is distorted in bond length and angle β . This distortion could be due to the full release of pressure. X-ray diffraction pattern is shown in Figure 5.1 with Miller indices overlaid.

Figure 5.1: Monoclinic Bi-II like structure with Miller indices given at each peak.

The monoclinic distortion changes the coordination of Bi from octahedral 6-fold to 2+4 with two shorter distances which establish zigzag chains of Bi atoms while the four longer distances establish connections between these chains. 2-D projections along the a-c and a-b planes show these bonds in Figure 5.2.

Figure 5.2: (a) 2D projection along the a-c plane showing bonds of $\delta = (3.24(8) \text{ \AA}, 3.17(6) \text{ \AA}, \text{ and } 2.25(5) \text{ \AA})$. (b) 2D projection along the a-b plane.

In shock-synthesized monoclinic Bi the intra-chain Bi-Bi distances are $2.25(5) \text{ \AA}$ and $3.17(6) \text{ \AA}$ and the inter-chain distances are $3.24(8) \text{ \AA}$ which are close to the range of Bi-Bi distances of $3.2 \text{ \AA}$ to $3.48 \text{ \AA}$. A 3-dimensional representation of the diffraction image is given using Fit2D [59] (Fig. 5.3).

Figure 5.3: 3D representation of GG137 XRD detector using Fit2D software [58]. Intensity is logarithmic and position is linear.

In the 3D representation it is easier to see the difference between the highly intense Bragg peaks and low intensity connecting them.

Figure 5.4: In (a) 2D projection of peak directly above the beam stop (-202) in Figure 5.3 at $2\theta = 9.833$ is shown. Intensity vs 2θ is given in (b) along a cross-section through the peak.

The full width half maximum (FWHM) was calculated by first determining the pixel to 2θ ratio along the distance of the detector. A cross section of the peak was then taken halfway between the peak maximum and background floor (40 counts) and for the peak directly above the beam stop (-202) is $\approx 0.44^\circ \Delta 2\theta$. The FWHM along the direction connecting the (-313) and (020) peak is $\approx 0.49^\circ \Delta 2\theta$. The highly intense peak nearest the beam center (0-2-1) at $2\theta = 11.833$, the FWHM is $0.08^\circ \Delta 2\theta$ with no intensity linking to adjacent peaks. An interesting aspect to our recovery of high pressure bismuth is the large single crystal formed on the short time scale of a shock experiment. Shock experiments are known to produce small grains and have been used for generating nanomaterials [60]. Previous work has studied the formation and growth of crystals in non-equilibrium thermodynamic conditions.

5.2 Monoclinic Bismuth II* Synthesis

Ostwald looked beyond thermodynamically stable crystallization and observed a tendency in nature known as the Ostwald Step Rule. He observed crystallization occurred through indirect transitions or "steps", which minimizes the entropy [61]. Schreinemakers studied metastability through the geometric interpretation of phase diagrams. He then developed rules for the metastable extension of phase boundaries. Under equilibrium conditions Gibbs phase rule describes a geometric interpretation of phase diagrams given by $F = 2 - P + C$, with F the thermodynamic degrees of freedom (e.g. Pressure and Temperature, Volume and Entropy), P the number of phases and C the number of chemical species [62]. In the case of a pure metals system $F = 3 - P$, and P varies based on location in phase space. At triple points $P = 3$ giving zero degrees of freedom. Along the line separating two phases $P = 2$ giving one degree of freedom. Within the region of a single phase $P=1$ giving two degrees of freedom. Considering a triple point and two of the phase lines starting at this point there exists a third line between them defining the metastable boundary and the angle formed between the stable phase boundary, the triple point and this new metastable boundary can be at most 180° [63]. Applying these rules to the bismuth phase diagram gives Figure 5.6, where the blue dotted line represents a Bi-II metastable extension line into the melt and the purple dotted line represents a Bi-II metastable extension into the Bi-I phase.

Figure 5.5: Pressure vs Temperature plot with initial hugoniot compression along the green dashed line, release isentropes along the blue dotted line and recompression before final release along red solid line. Compression and release profiles provided by our collaborator at MSTs [45]. Metastable melt line extension (purple dashed line) and metastable Bi-II extension (light blue dashed line) are overlaid.

The final compression reaches a peak pressure of 1.2 GPa and a temperature of 520 K just within the region of stability for the metastable extension of Bi-II into the melt. The pressure and temperature are then released to ambient conditions recovering a single crystal of the high pressure monoclinic bismuth II* phase. Time is not given in this plot explicitly, but is given in the Pressure vs Time plot given in Methods. It takes 40 ns to release from the peak temperature down to the red arrow followed by another 250 ns to ambient pressure. The 20 μm long recovered crystal would have to grow at a rate of nearly 70 meters per second. Using a Bridgman apparatus growth rates in bismuth have been observed up to 1.1 mm per second [64], four orders of magnitude lower than what is presented here. Crystal growth rates of 1-

10 m/s have been found in other systems [65] including growth of quasi-crystals from metallic melt [66]. Their growth rates have been found to scale with the particle velocity. Rapid grain growth on the order of 100 m/s has been studied experimentally [67] and theoretically [68], but with a caveat: the pure metal must be supercooled. Advanced equipment has been developed to achieve this in static experiments, but in shockwave studies it is common for liquids to become supercooled before solidifying [69]. If the liquid is supercooled down to the red arrow at 504 K and 0.4 GPa there was ≈ 200 K of undercooling from the blue dashed metastable extension line in Fig. 5.5. The single crystal grows at a rate of 80 m/s to 20 μm in length before ambient pressure was reached. In addition, it is conceivable the melt already exhibited atomic order beyond typical short range order, thus removing the kinetic barrier for crystal growth [67]. Overall, we have shown monoclinic Bi-II* single crystals form during dynamic compression with crystal growth rates from melt of ~ 80 m/s.

Chapter 6 Conclusions

In conclusion we recovered monoclinic Bi-II* to ambient conditions using shockwave recovery experiments. This recovery was only successful when launching a tungsten flyer plate at a stainless steel driver plate. The impedance mismatch between flyer and driver led to cavitation and reverberative shocks compressing the solid bismuth to 1.2 GPa and into the liquid state at 520 K. The liquid state was supercooled and began to rapidly solidify at 0.3 GPa and 470 K in the metastable monoclinic Bi-II structure. Additional compression maintained finite pressure for 280 ns and the crystal grew to 20 μm length giving a growth rate of 70 m/s. This growth rate is compatible with previous theoretical and experimental super rapid growth rates in supercooled metals. [58].

Appendix A

UNLV Gas Launcher Experiments - Operations Checklist

Pre Shot Measurements

1. Record date and shot number in shot record
2. Measure and Record flyer thickness, driver thickness, sabot diameter and projectile weight in shot record

Preparing Firing Operations

3. Load sample into capture tank along with wood disk and towels for dampening
4. Secure metal back onto capture tank with 3 bolts a few threads in
5. (Optional) Attach gas tube
6. (Optional) Clear particles along launcher tube using remaining gas in line
7. (Optional) Detach gas tube
8. Mount capture tank and slide into position
9. Secure flyer to the center of sabot with a small piece of clay or optical gel
10. Place sabot/flyer into the launcher tube

11. Switch on laser diodes
12. (Optional) Test velocimeter with pin

Performing Firing operations

13. Connect launcher gas line to barrel breach
14. Open helium cutoff valve
15. Open launcher cutoff valve
16. Open pressure regulator valve and Set to desired pressure
17. Close launcher cutoff valve
18. Close pressure regulator valve
19. Close helium cutoff valve
20. Record gas pressure in shot record
21. Plug in solenoid
22. Switch on and reset scope
23. Check LED lights
24. Trigger system

Post Shot Shutdown

25. Record velocity in lab book
26. Switch off scope

27. Disconnect power from solenoid
28. Disconnect launcher from barrel breach
29. Shut off power for lasers
30. Ensure He gas tank valve is closed

Appendix B

Initial XRD of GG111 sample post shock taken at 16-IDB synchrotron source revealed intensities within the shoulder of intense Bi-I peaks. The intense peaks were masked and the intensity was rescaled over the region between the third and fourth quadrant (See Fig. 6.1), with the origin at the center of the beam stop.

Figure 6.1: GG111 sample post shock diffraction pattern with powder-like fringes identified in green.

Very weak powder-like peaks were found and occurred at 2θ values matching with both the

ambient Bi-I structure and the Bi-II monoclinic high pressure structure. Diffraction patterns were collected throughout the GG111 sample to search for additional regions of the sample displaying peaks at these angles. In other regions of the sample more intense powder-like regions were found, but contained no peaks from the high pressure Bi-II structure (Fig. 6.2).

Figure 6.2: GG111 Sample post shock diffraction pattern at fine grained region giving powder-like pattern.

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Curriculum Vitae

Zachary Allen Fussell

Email : zfussell70@hotmail.com

Research Interest

Nucleation, growth and stability of solid states formed during dynamic compression.

Research Experience

Salaried Research Staff, University of Nevada Las Vegas **2015 - 2018**

External research and development project: Correlating hot spots to 3-D defect structures in single and poly-crystalline high-explosive materials. Supervised by Dr. Oliver Tschauner utilizing the UNLV shockwave lab and the Sector 16 APS X-Ray micro diffraction beam-line.

- Design and execute light gas gun experiments at UNLV
- Analyze samples with XRD and associated software (Matlab, Powdercell, etc.)

Guest Scientist, Los Alamos National Lab **2017 - 2018**

Measured phase distribution in shock recovered bismuth using scanning probe microscopy at the Center for Integrated Nano Technologies to complement phase identification from X-Ray Diffraction (XRD) at the Advanced Photon Source (APS)

Associate in Research, National Security Technologies

2011 - 2017

Aid in the research and development of multiple high-speed diagnostic systems used to study material response. Tasks included:

- Build high-speed optical diagnostic systems from the prototype stage through completion, including MPDV, which lead to a Defense Programs Award of Excellence
- Field imaging, MPDV and BLR diagnostics on light gas gun shots
- Use LaTeX, Office, C++, and R to analyze, plot and display data

Education

University of Nevada Las Vegas | Las Vegas, NV

2010 - 2015

B.S. Physics, Research Project: First-Principles density functional theory based approach to study Phase Transitions in Titanium.

University of Nevada Las Vegas | Las Vegas, NV

2016 - 2019

M.S. Physics, Research Project: Super Rapid Crystal Growth and quench of monoclinic Bi-II* during dynamic compression.

Publications

- C. Hawkins, O. Tschauner, Z. Fussell, et al., Correlation between hot spots and 3-

D defect structure in single and polycrystalline high-explosive materials, Proc. Eng. (2017)

- D. Smith, K. Lawler, M. Martinez-Canales, et al., Post Aragonite phases of CaCO_3 at lower mantle pressures, Phys. Rev. Mat. 2, 013605 (2018)

Presentations

- Pressure-induced phase transitions in titanium: A first-principles study: 2016 SSAP
- Novel pre-shock diagnostic tools for defects in heterogeneous materials: 2016 MetSoc
- Shock Recovery of High Pressure Bismuth Phases: 2017 SCCM APS Topical Meeting
- Correlating hot spot to defects in High Explosives: 2017 SCCM APS Topical Meeting

Miscellaneous

- Featured in NNSA press release <https://nnsa.energy.gov/blog/academic-symposium-promotes-fundamental-science-stockpile-stewardship>
- Z. Fussell, A. Daykin, M. C. Hawkins, et al., Titanium Dynamic Properties, Summary of Test Data SDRD Project: Characterization of Shock Propagation and Failure Mechanisms in Composite and Additive Manufactured Materials, NSTec STIP Report (2015)
- Z. Fussell, A. Luttman, M. Misch, et al., Analysis of Cygnus Anodization 2014-2015 Test Series, NSTec STIP Report (2016)