STRENGTH, DEFORMATION AND COMPRESSION BEHAVIOR OF TUNGSTEN CARBIDE, KRYPTON, AND XENON UNDER QUASI-STATIC LOADING

By

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ABSTRACT

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Strength and deformation are fundamental material responses to stress that are important to multiple scientific disciplines. The response of materials to thermodynamic conditions affects geologic and planetary processes and the structure, chemical behavior, and rheology of planetary interiors, as well as the outcome of accretionary impacts. These same properties are applied in defense science and are important industrially for the development of novel materials and the manufacture of strong tools and parts. In this dissertation, I determine the high-pressure strength, compression and deformation behavior of tungsten carbide, and solidified krypton and xenon – simple materials that exhibit very different strength and compression properties.

Material properties are examined in this work with synchrotron radiation in the diamond anvil cell, which allows a variety of X-ray and complementary optical techniques to be used on materials under quasi-static stress loads. Synchrotron radiation is brilliant, tunable, and highly focused, allowing precision measurements of small samples. Pressure media may be used to minimize the effects of non-hydrostatic stress, or if non-hydrostaticity is required, the sample may be compressed without a medium. By using both the axial and radial diffraction geometries, materials may be probed under a range of stress conditions.

Tungsten carbide is a hard, ultra-incompressible ceramic used widely in industry. The reported bulk modulus of WC was discrepant by more than 125 GPa. This is attributed to grain size dependence, though measurement techniques may also be important. Quasi-static compressive strength and deformation behavior of WC at high pressure have not been previously

studied. I compressed bulk and nano-crystalline hexagonal WC to 66 GPa in the diamond anvil cell. Nano-WC is softer than bulk WC. Yielding at \sim 30 GPa is accommodated by prismatic slip up to 40-50 GPa, at which pressure pyramidal slip along a different direction also becomes activated. WC supports \sim 12-16 GPa differential stress, the difference between stress aligned with the load axis and stress in the direction of the gasket, at yielding but its strength is anisotropic and the (001) plane supports a \sim 68-70% higher differential stress at yielding.

Solidified noble gases are prototypical solids that crystallize with simple structures and low strength. Heavy rare gas solids Ar, Kr, and Xe undergo a martensitic fcc-hcp phase transition as pressure is increased. At 300 K the metastable fcc phase persists over a wide pressure range. I compressed Kr and Xe in the diamond anvil cell to 115 GPa to determine phase equilibria, strength, and deformation. The phase transition progresses more quickly in Xe than in Kr. Both Kr and Xe crystallize as large fcc crystals and develop preferred crystallite orientation (texture) in the fcc and hcp phases. Xe peaks are highly textured and broad to at least 101 GPa. Non-hydrostaticity is observed at 15-20 GPa in both Kr and Xe and increases with pressure, with both materials supporting at least 5-7 GPa differential stress above 40 GPa.

This work examines the strength, compression and deformation behavior of WC, Kr, and Xe, extremes in the range of possible mechanical responses to stress. Strength in WC is overestimated when determined by lattice strain due to plastic deformation and is anisotropic, possibly due to the position of C atoms blocking slip systems dislocation motion. Grain size may affect incompressibility. The phase transition progresses more slowly in both Kr and Xe than previously reported. Radial diffraction can reveal more about material properties than axial diffraction and may be especially useful when multiple phases are present because texture and stress orientation can bias axial patterns.

To my husband W. David Brunnemeyer IV, my parents Ron & Sheila Brugman, my brother Dan Brugman, my advisor Dr. Susannah M. Dorfman, and in memory of Tommy Clonts

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KEY TO ABBREVIATIONS

ANL	Argonne National Laboratory
APS	Advanced Photon Source
bcc	body-centered cubic
bct	body-centered tetragonal
CDAC	Chicago-DOE Alliance Center
COMPRES	Consortium for Materials Properties Research in Earth Sciences
CRSS	Critical resolved shear stress
DAC	Diamond anvil cell
DFT	Density functional theory
EOS	Equation of state
EVPSC	Elasto-viscoplastic self-consistent
fcc	face-centered cubic
fco	face-centered orthorhombic
GSECARS	GeoSoilEnviro Center for Advanced Radiation Sources
hcp	hexagonal closest-packed
HPCAT	High Pressure Collaborative Access Team
LLNL	Lawrence Livermore National Laboratory
LPO	Lattice preferred orientation
m.r.d.	Multiples of a random distribution
pPv	post-Perovskite
RGS	Rare gas solid
XRD	X-Ray Diffraction
Z	Atomic number

CHAPTER 1: Introduction

Strength and deformation behavior are important properties for understanding the behavior of naturally occurring materials under the extreme pressure conditions of planetary interiors, the high stresses involved in accretionary impacts, detonations and defense applications, and in industry for the improvement of tools and parts. Strength is a fundamental material property describing resistance of a material to deformation under applied stress. It is a result of chemical bonding and the internal atomic structure of the material. Deformation may be elastic and/or plastic, and results from the orientation of the applied stresses and the physical properties of the material. Elastic deformation is reversible, and includes hydrostatic compression, which is described by the pressure-volume Equation of State (EOS) of the material, and elastic strain in response to loading forces. The new experimental results presented in this dissertation characterize elasticity, strength, and plasticity of solids. Accurate measurements of material strength and deformation behavior at high pressure are important for a thorough and fundamental understanding of the mechanics of solids under varying thermodynamic conditions.

1.1 Significance of elasticity, strength, and plastic deformation in Earth

Elastic properties of Earth materials govern the response of Earth's interior to seismic waves and the density structure of the planet. Inferences about structures within the Earth, including the layers of the Earth and regional structures in the mantle, subducting tectonic plates (slabs) and thermochemical heterogeneities associated with Earth's early history come predominantly from seismic waves. These properties vary with thermodynamic conditions, in particular pressure and temperature which reach up to ~363 GPa and ~6000 K in Earth's modern interior and range up to hundreds of GPa and 2000-10000 K (Melosh, 1989; Kraus *et al.*, 2012) during the accretion and evolution of planets and other rocky bodies. In Earth, the mechanical properties of prominent

mineral phases at these extreme pressure-temperature conditions affect mantle viscosity (Meade and Jeanloz, 1990). This has important implications for the evolution of the Earth as it affects mantle convection, but also acts on plate tectonics by modifying slab subduction.

Pressure in planetary interiors increases with depth and materials inside planets are subjected to compressive deformation, resulting in changes in the density or in some cases the atomic structure of the material (e.g. phase transitions). Elastic volumetric compression is described by the EOS. Phase transitions may or may not induce a change in the density of a material but may alter the elastic properties substantially. Density changes, whether from volumetric compression or phase equilibria, affect transport of materials within planetary bodies and are a major component of planetary differentiation and accretion.

Yield strength, the maximum elastic stress supported by a material before it deforms plastically, controls the occurrence of earthquakes, the boundary between the lithosphere and asthenosphere, and the deformation of planetoids during accretionary impacts. Accretion is the result of impact processes. Strength is thus important to the dynamics and evolution of the interior of the Earth and other planets.

Strength and EOS measurements may be incorporated into hydrocode models for planetary impacts along with other types of collisions and detonations, an area of overlap between planetary and defense science. The mechanical response of materials is relevant to the development of energetic materials (explosives) and damage-resistant materials such as armor and building materials. Material strength may also play a role in hazard mitigation. The use of the yield strength and the elastic properties of metals and silicate minerals in asteroid impact hazard mitigation models is an ongoing project at US national labs and NASA (Bruck Syal, Michael Owen and Miller, 2016; Cotto-Figueroa *et al.*, 2016).

The plastic flow of solid minerals controls the dynamics and anisotropy of Earth's mantle and possibly the solid inner core (Wenk et al., 2011; e.g. Lincot et al., 2016). Changes in the deformation mechanisms (i.e. changes in dominant slip systems during plastic deformation) in forsterite drive thermal convection and development of lattice preferred orientation (LPO) in the upper mantle (Raterron *et al.*, 2011), associated with seismic anisotropy. In the lower mantle, slip systems in MgO affect viscosity and can result in stagnation of subducting slabs (Marquardt and Miyagi, 2015; Mao and Zhong, 2018), and the relative strengths of dominant mineral phases in the lower mantle may promote the perseverance of geochemical reservoirs by localizing deformation and mixing to boundary layers (Girard et al., 2016). The rheology of hcp iron has also been used to infer viscosity and rotation of the inner core (Ritterbex and Tsuchiya, 2020). Plasticity also occurs under short timescales of accretionary impacts on Earth and other rocky bodies. The yield strength of impactors is important for understanding asteroid collisions and crater development on Earth and other rocky bodies (Nolan et al., 1996; e.g. Kimberley and Ramesh, 2011; Timms et al., 2012; Rae et al., 2019). The rheology of planetary interiors and the mechanics of accretion and impacts are controlled by the strength of a material and the mechanics of its deformation.

1.2 Significance of materials in this work

Mechanical properties of materials at high pressure are poorly understood. The strength and deformation properties of even high-symmetry, simple materials such as metals and salts are difficult to determine precisely at extreme pressures relevant to Earth's interior and depend on strain rates that cannot be replicated in the laboratory. Equation of state measurements at Mbar pressures relevant to the base of Earth's mantle and core suffer from uncertainty in the stress state and calibration at ~few percent level (Dorfman et al. 2012). Onset of plasticity in materials

at high pressure confounds measurements of elasticity (Weidner *et al.*, 2004). Many materials exhibit heterogeneity and complex crystal structures, making experimental determination of their properties challenging. WC as well as Xe and Kr cover a wide range of materials properties, from hard to soft. All are simple materials; the rare gas solids (RGS) are considered the prototypical van der Waals solids and WC is a hard ceramic commonly used in industry. Observing strength and deformation of simple materials at high pressure provides a foundation for work on more complex materials, whether geologic or industrial (Figure 1).

1.2.1 Tungsten carbide

Tungsten carbide is a transition metal carbide and a hard, ultra-incompressible ceramic. Hard ceramics are relevant to the manufacture of strong and durable parts in industry. Transition metal carbides may be important for the Earth's carbon cycle by facilitating carbon transport to the deep Earth. In particular, carbides such as Fe_3C and Fe_7C_3 are found in superdeep diamonds (Kaminsky, 2012) and understanding their elastic properties may help constrain the density and seismic velocity observed in Earth's core materials (Nakajima et al., 2011; Chen et al., 2018). These carbides, along with rarer naturally occurring carbide phases like qusongite (WC) have been found in exhumed ophiolites (e.g. Q. Fang et al., 2009; Shi et al., 2009; Kaminsky, 2012). Transition metal carbides are important catalysts in redox reactions (Levy and Boudart, 1973; e.g. Abdelkareem et al., 2020), and WC is used as a redox buffer in high-pressure experiments (Taylor and Foley, 1989). High hardness and incompressibility help resist surface damage (Yeung, Mohammadi and Kaner, 2016) and WC has widespread use in industry for this purpose - it is used in the manufacture of protective coatings for tools and chemical containers, as well as in the manufacture of durable cutting tools, and strong components. Because of these same useful physical properties, WC is also used in high-pressure experiments for support and as an

anvil material, and as such is fundamental to scientific state-of-the-art in understanding physical properties of mantle minerals. New constraints on the high-pressure elasticity, strength and deformation mechanisms of WC will help to develop techniques for measuring these physical properties, and to improve design of anvils for experimental mineral physics.



Figure 1: Strength of geologic and selected materials with pressure. Black squares, diamond, (Wang, He and Duffy, 2010), Gray circles, heterodiamond (Dong et al., 2009), blue squares, ringwoodite (Kavner and Duffy, 2001), green diamonds, olivine (Uchida et al., 1996), open gold triangles, MgO (Uchida et al., 1996), closed gold triangles, MgO (Merkel et al., 2002), red hourglasses NaCl (open – with annealing, closed – without annealing, (Funamori, Yagi and Uchida, 1994), orange triangles SiO₂ (Shieh, Duffy and Li, 2002), pink diamonds, neon (Dorfman et al., 2012).

WC exhibits impressive physical properties that make it a popular choice in industrial applications and important for research technology. It is very strong, ultra-incompressible, and has a high hardness. Nevertheless the incompressibility (1-bar bulk modulus) reported in the literature is discrepant and may be affected by grain size, with nano-crystalline WC reported to have incompressibility on par with diamond (Lin *et al.*, 2009). Despite widespread use of WC, its compressive yield stress and deformation mechanisms at high pressure have not been studied. Accurate constraints on the equation of state and knowledge of the strength and deformation mechanisms of WC under high stress conditions will lead to a better understanding of its response to extreme pressure and stress conditions, as well as support improvements in durable parts made from WC.

1.2.2 Heavy rare gases krypton and xenon

Like carbides, the inert gases (a.k.a. rare gases and noble gases) are important to a range of disciplines, including physics, materials science, and Earth and planetary science. Rare gases are extremely important geochemical and cosmochemical tracers (e.g. Jephcoat, 1998; Mandt *et al.*, 2015), offering insight into the evolution of Earth and the solar system. They are present in Earth and other bodies such as asteroids and comets. The gas planets (e.g. Jupiter and Saturn) are composed of hydrogen and helium, and understanding the strength and deformation of gas solids at high pressure will be necessary for understanding the interiors of these planets as well.

On Earth, RGS exist both dissolved in magma, where their solubility is affected by magma chemistry, temperature, and pressure (Chamorro-Pérez *et al.*, 1998; Shibata, Takahashi and Matsuda, 1998) as trapped gases and possibly as solid phases or bonded with iron and other elements within the Earth (e.g. Ono, 2020; Peng *et al.*, 2020), or may be stored withing the lattice structure of other materials (Ono, 2020; Rosa *et al.*, 2020). The role of noble gases in the

Earth's core is an active area of research. Xe has been shown both computationally and experimentally to form stable alloy structures with Fe and Ni at conditions of the Earth's core (Zhu *et al.*, 2014; Dewaele *et al.*, 2017; Stavrou *et al.*, 2018), which has been proposed as a potential reservoir for Xe in the Earth, approximately 90% of which is missing relative to Ar and Kr (Anders and Owen, 1977; Jephcoat, 1998), based on solar and chondritic measurements (e.g. Caldwell, 1997; Lee and Steinle-Neumann, 2006). More recently, the Earth's core has been proposed as a reservoir for other noble gases, including He and Ne (Bouhifd *et al.*, 2020).

Rare gas solids are prototypical simple solids and determining their physical properties may improve our understanding of the compression of solids and the effects of pressure on interatomic potentials in van der Waals materials. Lighter rare gas solids He, Ne, and Ar are often used as pressure-transmitting media in high-pressure experiments (e.g. Angel *et al.*, 2007; Klotz *et al.*, 2009). Ar, Kr, and Xe are known to undergo a kinetically inhibited martensitic fcc-hcp phase transition (Figure 2), in which the Gibbs free energy of the two phases are very similar, but the activation energy required to drive the transition is relatively high, resulting in a wide pressure interval in which both the fcc and hcp phases co-exist (Caldwell, 1997; Boehler *et al.*, 2001; Cynn *et al.*, 2001; Errandonea *et al.*, 2002, 2006; Rosa *et al.*, 2018). The quality of Kr or Xe as a pressure medium will depend on their respective strengths and on the strength of the two-phase fcc-hcp mixture during their respective phase transitions. Studying the strength, deformation, and phase equilibria of Kr and Xe may provide insight into their behavior in the deep Earth, while improving our understanding of solids and discovering novel alloys.



Figure 2: Schematic of the fcc-hcp phase transition. The two structures can be represented as displaced layers of atoms, where A, B, and C are not equivalent closest-packed layers. The fcc structure is ordered ABCABC and the hcp structure is ordered ABABAB. Closest-packed planes (represented here by the orange diamond) shared between the two structures, result in the continuation of some diffraction lines throughout the transition.

1.3 Dissertation purpose and structure

In this dissertation, I consider a range of strength and deformation responses in simple materials by examining a hard, ultra-incompressible ceramic, WC, and two soft solidified inert gases, Kr and Xe. WC is a strong ceramic which is widely used in industry and research technology, yet its quasistatic yield strength and plastic deformation mechanisms are not known. The reported EOS in the literature varies substantially. The pressure-dependence of the single-

crystal elastic constants cij for WC has never been measured experimentally. Experiments are needed to resolve differences in the EOS and to determine strength, deformation behavior and to test theoretical elasticity. Rare gas solids are simple, inert van der Waals materials which are important tracers of geological processes (e.g. Burnard, Zimmermann and Sano, 2013). They are prototypical solids, but are known to form compounds, become metallic, and undergo sluggish phase transitions at high pressure (Caldwell, 1997), behavior which is important to determining the role of RGS in planetary interiors and for understanding bonding in solids (Jephcoat, 1998; Sanloup, 2020). RGS are frequently used in high-pressure experiments as pressure-transmitting media. Despite their importance across a range of disciplines, the strength of Kr and Xe as a function of pressure has not been studied, and the effect of the martensitic fcc-hcp phase transition on strength is not known. Understanding simple, high-symmetry materials lays the groundwork for measuring strength and deformation properties of lower-symmetry mineral phases prominent in the Earth. Precision in measurements of physical properties for materials with simple structures will make determination of these properties in more complex phases, such as orthorhombic bridgmanite and post-perovskite (pPv) in the lower mantle less challenging. The results presented in this dissertation will improve the results of high-pressure experiments. Improved loading methods described are important for more successful experiments at higher pressures. Oriented WC anvils may extend the capabilities of modern high-pressure apparatuses. The effects of phase equilibria on RGS improve our understanding of quasi-hydrostatic pressure media.

In Chapter 2, I review methods used in quasi-static high-pressure experiments, highlighting the axial and radial diffraction geometries, which provide different means of assessing stress and strain at high pressure. In Chapter 3, I determine the compressive yield

strength, deformation properties, and Equation of State of tungsten carbide, and assess the effects of crystallite size on its EOS. Dr. Lowell Miyagi and Dr. Feng Lin at the University of Utah provide an Elasto-viscoplastic self-consistent (EVPSC) model to determine plastic deformation mechanisms, which provides insight into the effects of plasticity on strength. Chapter 4 explores of the strength and deformation of solid noble gases Kr and Xe determined from multiple complementary methods and examines the effect of the martensitic fcc-hcp phase transition on their respective strengths. In Chapter 5, I discuss the implications of the findings in Chapter 3 and Chapter 4. I consider the importance of grain size effects, elasticity, strength, and deformation behavior for future work in Earth science and materials research.

CHAPTER 2: Methods for measuring strength and deformation at high pressure

2.1 Introduction

The mechanical response of materials to thermodynamic conditions such as pressure and stress can be either studied experimentally or inferred through theoretical calculations from first principles. Experimental measurements may be conducted under quasi-static conditions, where the thermodynamic conditions remain stable throughout the experiment, or they may be dynamic Quasi-static experiments such as the use of X-ray diffraction or optical (time-resolved). spectroscopy in the diamond anvil cell provide information on the material under approximately consistent stress conditions, whereas dynamic experiments include strain-rate effects. The diamond anvil cell is the only method by which conditions at Mbar pressures, relevant to the lower mantle and core of Earth, may be obtained. Gaskets are used to stabilize the anvils and provide confining stress. Pressure-transmitting media are needed to produce quasi-hydrostatic conditions in the diamond anvil cell. Pressure within the cell chamber is calibrated by a material within the chamber or from the anvil culets. Synchrotron radiation is ideal for X-ray diffraction measurements in the diamond anvil cell because it is bright, focused and tunable. The axial diffraction geometry may allow for a higher maximum pressure, but strain and texture evolution are more clearly observed in the radial geometry. Measurements in the radial geometry may be more sensitive to phase transitions in plastically deforming materials because a range of stress orientations and texture intensities are observed, some of which may be invisible in the axial geometry. A smaller gasket hole helps stabilize the cell chamber for radial experiments to Mbar conditions. In this work, quasi-static compression methods are used to probe the strength in a range of materials.

2.2 Quasi-static compression in the diamond anvil cell

Diamond anvil cells (DACs) of various configurations have been used to generate pressures up to ~10 Mbar (1000 GPa), approximately the stability of the diamond phase of carbon (Ruoff, Xia and Xia, 1992; Dubrovinsky *et al.*, 2015; Dubrovinskaia *et al.*, 2016; Dias and Silvera, 2017; Dewaele *et al.*, 2018), a pressure greatly exceeding those generated in Earth's interior and relevant to gas giants and larger rocky planets such as super-Earths. The DAC is one of a family of opposed, rigid anvil devices, some of which employ other materials for anvils, such as sapphire or WC (Furuno, Onodera and Kume, 1986; e.g. Besson *et al.*, 1992; Rüetschi and Jaccard, 2007), and which date back to the Bridgman cell (Bridgman, 1952). The DAC is also currently the only method by which quasi-static stress at Mbar pressures may be achieved. The underlying principle of the DAC includes a cell defined by a chamber constrained by the anvil culets and a gasket, and contains the sample, any internal pressure standards, and the medium (if any) used to transmit pressure. Pressure in the DAC is generated by applying a force to a sample or pressure transmitting medium with opposed diamond anvils.

Diamond anvils are optimal for high-pressure experiments because of their high strength and optical transparency, which allows a range of techniques to be used on materials inside the cell, including diffraction, spectroscopic analyses, and laser heating. The surface of the anvil which applies force to the cell chamber is called the culet. The maximum attainable pressure for a given DAC experiment is limited primarily by the surface area of the diamond culets (O'Bannon *et al.*, 2018) and the strength of the anvils. Single-crystal anvil culets as small as 30 µm with a beveled edge have been used in experiments approaching 500 GPa (Dias and Silvera, 2017), whereas culets up to 800 µm in diameter are appropriate for experimental pressures below 15 GPa. The anvils are glued to tungsten carbide or X-ray transparent cubic boron nitride (cBN) seats with a strong epoxy and placed in an opposed piston-cylinder arrangement, which maintains alignment while allowing the application of force by tightening the cell with screws. Force in the DAC is moderated by spring-cushioning provided by Bellville washers, and balanced by opposed threading (right- and left-handed) in the screws (Figure 3).



Figure 3: Standard symmetric diamond anvil cell. Bellville washers provide cushioning as hexscrews are tightened. X-rays or optics are admitted through an aperture, are scattered by the sample, and exit an aperture on the opposite end.

A gasket stabilizes the anvil alignment further, prevents anvils from coming into contact directly. Diamonds are brittle, superhard, and highly incompressible. Stress from contact is isolated to a very small surface area and would cause them to fracture and fail. The gasket distributes stress across a broader area and provides confining pressure for materials inside the cell. Gaskets materials are typically made from metals that exhibit a high-strength such as rhenium or tungsten (Duffy, 2007), or from X-ray transparent materials such as beryllium (Hemley, 1997),

cubic boron-nitride (cBN), boron-mica, and/or with Kapton epoxy for radial experiments (Merkel and Yagi, 2005; Miyagi *et al.*, 2013). Materials such as Be and cBN may be hazardous, more difficult to use, or add additional signal to collected data. However, they are the only means by which radial experiments can be conducted in the DAC. Stronger materials provide better stability and allow access to higher pressures but are not X-ray transparent and can only be employed in axial experiments where access through the gasket is not required. Regardless of experimental geometry, gaskets provide support for anvil alignment at high pressure and exert confining pressure for materials inside the DAC as the chamber is compressed (Figure 4).



Figure 4: Diamond anvil cell schematic. Two opposed anvils press on a cell chamber defined by the anvil culets and a gasket. The sample is loaded inside the chamber along with a pressure-transmitting medium or other internal markers (if desired).

2.3 The stress state in the DAC

Uniaxial forces generated by the opposed anvils combined with radial confining stress from the gasket induces differential and shear stresses within the cell chamber which increase with pressure. The stress state in the DAC can be described in tensor notation (Ruoff, 1975; and e.g. Singh and Takemura, 2001):

$$\sigma_{ij} = \sigma_P + D_{ij},\tag{1}$$

where σ_{11} is the radial stress component, σ_{33} is the axial stress component, σ_P is the hydrostatic component of stress defined by:

$$\sigma_P = \begin{bmatrix} P & 0 & 0 \\ 0 & P & 0 \\ 0 & 0 & P \end{bmatrix},$$
 (2)

where mean normal stress $P = \frac{2\sigma_{11} + \sigma_{33}}{3}$, and the stress deviator D_{ij} is given by:

$$D_{ij} = \begin{bmatrix} -t/3 & 0 & 0\\ 0 & -t/3 & 0\\ 0 & 0 & 2t/3 \end{bmatrix},$$
(3)

with differential stress $t = (\sigma_{33} - \sigma_{11})$, such that:

$$\sigma_{ij} = \begin{bmatrix} \sigma_{11} & 0 & 0\\ 0 & \sigma_{11} & 0\\ 0 & 0 & \sigma_{33} \end{bmatrix} = \begin{bmatrix} P & 0 & 0\\ 0 & P & 0\\ 0 & 0 & P \end{bmatrix} + \begin{bmatrix} -t/3 & 0 & 0\\ 0 & -t/3 & 0\\ 0 & 0 & 2t/3 \end{bmatrix}.$$
 (4)

This results in both a stress gradient throughout the chamber, and a non-hydrostatic stress condition in all materials loaded in the DAC. Depending on the goal of the experiment, this may or may not be desired. For experiments in which only volumetric compression is desired, hydrostatic stress conditions are preferable.

Samples compressed in the DAC in a liquid medium will experience hydrostatic stress. Common media for this purpose include methanol-ethanol mixtures, silicone oil, or He gas. No media are liquid above the room-temperature freezing pressure of helium (~12 GPa) however, so for pressures exceeding this range, pressure-transmitting medium are selected for their ability to maintain quasi-hydrostatic, or low non-hydrostatic stress. Since the non-hydrostaticity of pressure-media like methanol-ethanol and silicone oil rises rapidly above 12-15 GPa (Angel *et al.*, 2007; Klotz *et al.*, 2009), noble gases such as He, Ne, and Ar are used for experiments approaching or extending into the Mbar regime. He and Ne are known to diffuse into anvils and sample materials and can cause anvil failure and measurement errors (Dewaele *et al.*, 2006; Sato, Funamori and Yagi, 2011; Shen *et al.*, 2011), and the strength of Ar increases rapidly above 15-20 GPa (Mao *et al.*, 2006). All solid pressure media are non-hydrostatic and subject the sample to non-uniform stresses, which introduces uncertainty into DAC measurements, so careful decisions about appropriate pressure-transmitting media must be made depending on the needs of the experiment. To observe the hydrostatic compression of a sample material, pressure transmitting media are required. If deviatoric stresses are desired, as is the case in experiments probing the yield strength and plastic deformation behavior of materials, then no pressure medium needs to be employed, and non-hydrostatic stress will be maximized.

2.4 Pressure calibration, stress markers, and ruby fluorescence

Because the stress-state inside the DAC is non-uniform, the pressure at a given point within the DAC results from a combination of the loading inside the cell, the stress gradient, mechanical properties of the gasket material, and the distribution of the force over screws and washers that drive uniaxial load. The non-uniform stress conditions in the DAC are a source of systematic experimental uncertainty in pressure calibration (e.g. Meng, Weidner and Fei, 1993; Wu and Bassett, 1993), so obtaining an accurate measurement of pressure inside the cell chamber requires an internal barometer. Such a pressure-standard could be sample itself, if the equation of state (EOS) is known, or an internal pressure standard may be loaded with the sample (e.g. Ag and ruby in Figure 5). Line shift analysis of Raman scattering from the diamond culet may also be used to determine pressure within the cell, as can the EOS of the pressure-transmitting medium. Internal measurements of pressure may be accomplished in several ways.



Figure 5: View of the DAC chamber through the anvils before loading compressed gas. The cell is pre-loaded with an Ag pressure standard and a ruby ball for gas-loading of Kr or Xe gas. The anvils are 300 um culets appropriate for pressures up to \sim 70 GPa. The Re gasket has a 150 µm hole drilled to contain the standards and the gas sample.

Each method of pressure-determination has benefits and limitations, depending on the individual experiment. Direct determination from the EOS of the sample or pressure transmitting medium obviates the need for loading other materials and can reduce signal not associated with the sample. In many cases, the P-V relationship of the sample is not known however, or the sample

may undergo a structural transition to a different phase, making pressure determination in this way unreliable. Standards are therefore usually a well-characterized material loaded with the sample.

Pressure scales from internal standards are based on the equation of state (EOS) of a material loaded with the sample. This EOS is determined from independent measurements of volume or density and pressure, elasticity, or compressibility. These measurements can come from temperature-reduced shock wave (e.g. Nellis, 2007) measurements, or the combination of measurements of elasticity with ultrasonic interferometry or Brillouin measurements and compressibility measurements from neutrons or X-ray diffraction (Poirier, 2000). The ruby pressure-scale is particularly well-known and frequently reviewed (Forman *et al.*, 1972; Mao, Xu and Bell, 1986; Dorogokupets and Oganov, 2006; Syassen, 2008a; Shen *et al.*, 2020). The ruby pressure scale has been benchmarked against reduced shock isotherms and ultrasonic measurements of several metals (Dewaele, Loubeyre and Mezouar, 2004; e.g. Dewaele *et al.*, 2008), and a metal with a well-characterized EOS may be loaded in small quantities with the sample and its EOS used to calculate pressure. Foils are often employed for this purpose as their thickness can be constrained and the chances of bridging the anvils is minimized. Internal barometers provide a reliable means of calculating pressure as it occurs inside the DAC.

Pressure can be considered the hydrostatic component of stress. To constrain the nonhydrostatic stresses inside the DAC chamber, internal stress markers are required as well. If the elastic deformation of a material inside the cell can be constrained, it may be used to determine the stress state of the surrounding medium. Internal barometers such as metal foils loaded with the sample may double as an internal stress marker in this way, provided they do not deform plastically. An effective stress marker must therefore be stronger than the pressure-transmitting medium and bridging of the marker must be avoided. If the internal standard generates an X-ray diffraction pattern, a stress analysis may be performed on the pattern of the stress marker similarly to the sample and this provides a constraint on the stresses exerted on the marker.

Because diamonds are optically transparent, spectroscopic methods such as ruby fluorescence (Mao et al., 1978, 1986) and Raman (Dubrovinskaia et al., 2010) can be used in DAC experiments as a complementary analysis to X-Ray diffraction or stand-alone experiments to characterize the stresses affecting the sample (e.g. Piermarini, 1973; Klotz et al., 2009). This can be accomplished with fluorescence line shift analysis, or pressure gradients analysis.

2.5 Synchrotron radiation

Synchrotron X-rays are ideal for diamond anvil cell experiments because they provide a high density of coherent photons focused to a small beam size, and desired energy can be selected. A small beam size is critical as the surface area of the anvils is small so that pressure is maximized and samples must not only be smaller than the anvil culets but must also be small enough to fit inside the gasket chamber, which must 1/3 - 1/2 the diameter of the culet to avoid closure of the gasket hole while stabilizing anvil alignment. Synchrotron radiation provides sufficient brilliance such that well-resolved patterns may be collected from very small samples, using short collection times (as low as ~30s). In a synchrotron, charged particles (electrons or positrons) are accelerated around the accelerator ring by bending magnets and insertion devices, resulting in emission of photons that are collected at stations tangent to the ring. Each station has instrumentation suitable to the preferred or specialized techniques of the work conducted at that beamline, such as powder or single-crystal diffraction, time-resolved experiments, or low angle/surface diffraction. Synchrotron radiation provides X-rays with a beam diameter small enough to probe the inside of the chamber, and brilliant enough to produce a signal from small sample volumes.
2.6 X-Ray diffraction, diffraction geometry, and texture evaluation

X-rays transmitted through the diamond anvils and the sample chamber are diffracted by the sample. Photons are scattered according to the Bragg law: $n\lambda = 2dsin\theta$, where *n* is a positive integer, λ is the X-ray wavelength, *d* is the lattice-spacing, a function of *hkl*, and θ is the scattering angle. The high photon intensity at characteristic angles may be analyzed as thermodynamic conditions are varied to observe changes in material properties such as unit cell volume or structure. Because the diamond anvil cell restricts optical access to the sample and limits sample size, all of the diffraction experiments in this work utilize high-energy, highbrilliance synchrotron angle-dispersive diffraction at a fixed energy ~25-40 keV, resulting in typical Bragg angles $\theta < 15^{\circ}$.

If the sample is a powder with random crystallite orientation, diffracted X-rays produce Debye-Scherrer rings when collected on a 2D detector such as an image plate. Each ring is representative of an individual lattice plane *hkl*, which can be related to the lattice parameter of the sample through the diffraction angle and X-ray wavelength. Changes in diffraction rings may be analyzed to determine physical properties, for example the unit cell volume of a material under a specific thermodynamic condition, such as temperature or pressure, may be determined from lattice parameter (a function of the diffraction ring position) at that condition. The analysis used will vary depending on the diffraction geometry employed.

X-ray diffraction is used in DAC studies to characterize structure and determine changes in the lattice spacing of a sample as thermodynamic conditions such as temperature or pressure are varied. Diffraction may be conducted in either axial (sometimes referred to as "polar") or radial (sometimes referred to as "cross-axial") geometry. In axial diffraction, the X-ray probe is transmitted through the diamond anvils (Figure 6). There is no need for an X-ray transparent

gasket, and maximum pressures may be achieved. In this configuration, the beam is approximately parallel to the loading axis. The angle ψ between the diffracting planes and the loading axis (Figure 6) is maximized in this case and the direction of minimum strain is sampled.

Diffraction patterns collected in the axial geometry are integrated to 1D line patterns and fit with Voigt or Lorentzian line profiles. Peak positions from the line fits are used to determine lattice parameters. Volumes for EOS calculations may be determined from lattice parameters of diffraction patterns collected under hydrostatic conditions. In the absence of a pressure medium, non-hydrostatic stress is maximized – the material being studied is effectively its own pressuretransmitting medium. Variability in the lattice parameter for different *hkl* arises from nonhydrostatic compression and can be used to derive strength from lattice strain theory if the elastic anisotropy (a function of the single-crystal elastic constants) of the material is known (Singh, 1993). This is theoretically possible for any crystal system, however in practice it is difficult to apply to many materials in axial patterns because knowledge of the lattice parameter under hydrostatic stress conditions is required. This can be determined from non-hydrostatic compression data for cubic materials because of the linear relationship between orientation and lattice parameter for these materials (Singh, 1993), but a priori knowledge of this parameter is required to apply the lattice strain theory to lower-symmetry materials using the axial diffraction geometry, and this may not be readily available for the material in question.

2.6.1 Axial geometry

In the axial diffraction geometry, the X-ray probe is transmitted through the length of the DAC and the angle of conical openings in the seats to which the diamonds are mounted limits k-space availability. Typical angular ranges in the axial geometry are limited to $2\theta <~30^{\circ}$. This can be alleviated somewhat by small rotations of the DAC relative to the beam. This limitation

also ensures that most of the diffracted planes are ~parallel to the beam and load axis, which is the direction of minimum strain. Sampling only planes in the direction of minimum strain may cause structural changes to be detected at incorrect pressures. Development of preferred orientation (texture) during plastic deformation of the sample may induce minimize diffracted intensity in any direction relative to the stress load. If these minima occur in the direction of minimum strain (i.e. parallel to the stress load), it is possible peaks may be absent from the collected pattern.

2.6.2 Radial geometry

In the radial geometry (Figure 6), the beam is transmitted through an X-ray transparent gasket, and is normal to the loading axis. Radial diffraction generates diffraction patterns that sample strain in all orientations relative to the stress axis. This allows characterization of the deviatoric strain and observation of texture development (i.e. development of variation in diffraction line intensity) as pressure is increased. Nevertheless, the maximum pressure accessible with the diamonds may be further limited in the radial configuration by the need for expensive and sometimes toxic X-ray transparent gaskets, which are weaker and more brittle than gaskets used in the axial geometry. Panoramic DACs are optimized for radial diffraction experiments. The piston and cylinder are separated by long posts, so the X-ray transparent gasket is the only detectable signal between the cell chamber and the detector. This provides wide access to k-space, but panoramic DACs can be very difficult to align. Radial experiments to high-pressure can therefore be especially challenging. For this work, use of a smaller gasket hole (with diameter ½ of the culet diameter, rather than ½) helped stabilize the panoramic cells to reach Mbar pressures.



Figure 6: Diffraction geometries using the diamond anvil cell. In the axial geometry (top) the Xray beam is parallel to the loading axis the angle ψ between the plane normal and the load axis is a function of the diffraction angle 2θ . Due to the structure of the DAC, most diffracted planes which reach the detector have small 2θ and ψ is close to 90°, the minimum strain condition. In the radial geometry (bottom) the beam is normal to the loading axis, and ψ varies from 0° to 90°, so the full range of strain is sampled.

In this work, radial diffraction is analyzed with full-profile Rietveld refinement of 2D diffraction patterns. Each pattern is divided into 5° wedges using Fit2D software (Hammersley, 1997, p. 2). The wedges are aggregated in Materials Analysis Using Diffraction (MAUD)

software (Lutterotti, Matthies and Wenk, 1999). Instrument parameters such as detector distance and beam position are calibrated from CeO_2 or LaB_6 standards. In addition to refinement of structural parameters, crystallite size, and microstrain, MAUD allows for refinement of deviatoric strain by fitting eccentricity in the diffraction rings with Q-values. Lattice strain theory can thus be applied more readily to radial patterns as diffraction ring Q-values can be fit for individual *hkl*. For radial lattice strain analysis, the shear modulus of the material must be known, either from previous experiments or from theoretical computations.

Upon compression, plastically deforming materials may exhibit a preferred crystallite orientation or texture. Texture is a function of orientation and may cause diffraction line intensity to be biased in the axial geometry. In the radial geometry, texture produces intensity variation around the diffraction rings. Various models for fitting and analyzing texture in MAUD are available. Texture in this work is fit using the Entropy-modified Williams-Imhof-Matthies-Vinel (E-WIMV) texture model (Lutterotti *et al.*, 2004; Chateigner, Lutterotti and Morales, no date).

2.7 Conclusion

Experimental high-pressure techniques provide a means to constrain the physical response of materials to varying thermodynamics, which is important for advancing scientific research and finding novel materials and applications for industry. The diamond anvil cell enables these properties to be examined under quasi-static conditions to Mbar pressures, using a variety of X-ray and optical techniques. In this dissertation, I use these techniques to study mechanical properties in a range of materials.

CHAPTER 3: Strength, deformation, and equation of state of tungsten carbide to 66 GPa

This chapter has been submitted and is under minor revisions as: "Strength, deformation, and equation of state of tungsten carbide to 66 GPa" Benjamin Lee Brugman, F. Lin, M. Lv, C. Kenney-Benson, D. Popov, L. Miyagi, and S.M. Dorfman

Abstract

Strength, texture, and equation of state of hexagonal tungsten monocarbide (WC) have been determined under quasi-hydrostatic and non-hydrostatic compression to 66 GPa using angledispersive X-ray diffraction in the diamond anvil cell. Quasi-hydrostatic compression in a Ne pressure medium demonstrates that nanocrystalline WC is slightly less incompressible than bulkscale WC, with respective bulk moduli of $K_0 = 397 \pm 7$ and 377 ± 7 GPa and pressure derivatives $K_0^* = 3.7 \pm 0.3$ and 3.8 ± 0.3 . This decrease in incompressibility with grain size is similar to behavior observed in other ceramics. Under nonhydrostatic compression, WC supports a mean differential stress of ~12-16 GPa at plastic yielding, which occurs at ~30 GPa. Strength in WC is anisotropic, with the (001) plane supporting 68-70% higher stress than stresses calculated from mean strain. Simulations using an Elasto-ViscoPlastic Self-Consistent model (EVPSC) indicate that strength inferred from lattice strain theory may be an overestimate due to effects of plastic deformation. Plastic deformation generates a texture maximum near $\langle \overline{2}110 \rangle$ in the compression orientation, initially through prismatic slip on the $\{10\overline{1}0\}\langle\overline{1}2\overline{1}0\rangle$ and $\{10\overline{1}0\}\langle0001\rangle$ slip systems, followed by activation of pyramidal slip on $\{10\overline{1}1\}\langle\overline{2}113\rangle$ at ~40-50 GPa.

3.1 Introduction

Tungsten monocarbide is a transition metal carbide used extensively in industrial and research technology because of an abundance of useful physical properties, including high strength and hardness, ultra-incompressibility, wear resistance, and high melting temperature

(Amulele et al., 2008; Lin et al., 2009; Golovchan, 2010; Roebuck, Klose and Mingard, 2012; Yeung, Mohammadi and Kaner, 2016). Because of its high strength, synthetic WC is used as a sturdy backing for abrasives on modern industrial cutting tools, in wear-resistant coatings (Cook and Bossom, 2000; Lee and Gilmore, 1982; Li et al., 2010; Benea and Benea, 2015), and in the manufacture of anvils and support structures in high-pressure apparatuses^{1,10 and e.g. 11}. Improving the strength of parts made from WC and extending the pressure range accessible by highpressure devices are active areas of research (Yamazaki et al., 2019; e.g. Silvestroni et al., 2020). WC is also one of the least compressible materials known, with a bulk modulus comparable to other incompressible materials such as Os-borides, cBN, and cRuO₂ (Lee and Gilmore, 1982; Haines, Léger and Bocquillon, 2001; Gilman, Cumberland and Kaner, 2006; Gu, Krauss and Steurer, 2008). WC has also been useful to high-pressure/temperature redox chemistry: it was originally discovered by reduction of tungsten oxide (Z. Z. Fang et al., 2009; Borovinskaya, Vershinnikov and Ignatieva, 2017), a reaction that defines the WC-WO redox buffer used in geochemistry (Taylor and Foley, 1989), and also occurs naturally in Earth's reduced mantle as the rare mineral qusongite (Q. Fang et al., 2009). Despite these remarkable properties and widespread applications, the strength and deformation mechanisms of WC under extreme quasistatic stress have not been studied.

Constraints on the equation of state (EOS) of WC are important for understanding its response to extreme conditions and chemistry (Cheng *et al.*, 2012). Experimental work on WC has reported values of the ambient bulk modulus, K_0 , ranging from 329-452 GPa (Brown, Armstrong and Kempter, 1966; Lin *et al.*, 2009) depending on method and grain size of WC. EOS measurements for WC based on X-ray diffraction of samples compressed in a multianvil device under hydrostatic conditions with high-temperature annealing have been reported to 30

GPa (Litasov et al., 2010). Relative to these measurements, experiments conducted in the diamond anvil cell (DAC) have yielded systematically higher volumes and incompressibility under pressure, possibly due to nonhydrostatic stress. Nano-grain-size WC was also suggested to be much more incompressible than bulk-grain-size WC, with $K_0 \sim 452$ GPa, similar to diamond (Lin et al., 2009). In general, effects of nanoscale grain sizes on bulk incompressibility are not clearly systematic: a few-10s-nm grain size cubic BN (Le Godec et al., 2012), Al₂O₃ (Chen et al., 2002) and TiO₂ (Al-Khatatbeh, Lee and Kiefer, 2012) have been observed to be less incompressible than bulk samples, while nano-grain-sized noble metals Au, Ag, and Pt appear more incompressible than micron-scale grain sizes (Gu, Krauss and Steurer, 2008; Mikheykin et al., 2012; Hong et al., 2015). For other materials such as Fe, TiC, and TiN, observations suggest that grain sizes have either no effect or nonmonotonic effects on bulk modulus (Chen et al., 2001; Q F Gu et al., 2008; Wang et al., 2014). Recent first-principles studies provide values for K_0 for WC that mostly cluster in the center of the experimental range for bulk WC ~380-390 GPa. Additional experiments are needed to reconcile these differences in observed and predicted bulk compression behavior.

Anisotropic elasticity of WC has also been studied by both experiments and theory, but limited high-pressure constraints are available. The elastic stiffness coefficients c_{ij} for WC have been studied at ambient conditions experimentally (Gerlich and Kennedy, 1979) and computationally [2,8,32-36]. Theoretical predictions for c_{ij} s as a function of pressure have been computed to 100 GPa (Liu *et al.*, 2013; Li *et al.*, 2014), and agree well with previous experimental values at ambient conditions, with the exception of c_{13} , which is consistently predicted to be ~100 GPa lower than the experimental value (Gerlich and Kennedy, 1979). The

pressure-dependence of the c_{ij} s of WC has not been measured experimentally, and experimental tests of theory are required.

The high strength, i.e. maximum stress before transition from elastic to plastic deformation of WC and other strong metal-light element compounds is linked to covalent bonding which impedes deformation mechanisms common in metals. In hexagonal P6m2 WC, carbon atoms are positioned as interstitial layers in what would be an otherwise softer (though among the strongest of all metals) hexagonally closest-packed sub-lattice of W atoms (Goldschmidt, 1967; Liu, Wentzcovitch and Cohen, 1988). This interstitial positioning combined with the density of valence electrons promotes strong covalent W-C bonding (Liu, Wentzcovitch and Cohen, 1988; Yeung, Mohammadi and Kaner, 2016). In addition, the incomplete 5d band in W atoms promotes replacement of the softer metallic W-W bonds by W-C covalent bonds, increasing the hardness and incompressibility of WC relative to WN, which has similar structure but different valence states (Shein, Suetin and Ivanovskiĭ, 2008). The interstitial C atoms also impede the movement of dislocations within the lattice during strain and act to prevent basal slip, which is commonly observed in hexagonal materials (Bolton and Redington, 1980). Slip at ambient conditions activates in the closest-packed directions and is prismatic on $\{10\overline{1}0\}(0001)$ and $\{10\overline{1}0\}(2\overline{1}\overline{1}0)$, and Burgers vector (2113) has been noted as dislocation decomposition of $(2\overline{1}\overline{1}0)$ (Takahashi and Freise, 1965; Bolton and Redington, 1980). This blocking of common slip systems and of dislocation motion in general increase hardness and strength by resisting plasticity (Yeung, Mohammadi and Kaner, 2016). Ultimately, there is still sufficient metallic character such that WC only reaches a Vickers hardness of ~30 GPa (Teter, 1998; Haines, Léger and Bocquillon, 2001), making WC harder than many industrial ceramics, but substantially softer than superhard (Vickers hardness > 40 GPa) materials like

diamond (e.g. Irifune *et al.*, 2003) and cubic boron nitride (Sumiya, Uesaka and Satoh, 2000; Dubrovinskaia *et al.*, 2007). However, at high pressures, the strength, hardness, and slip mechanisms of WC have not been studied. Because the high-pressure compressive yield strength is related to both hardness and bulk modulus, WC is expected to yield at lower stress relative to superhard materials, but comparable or higher stress than yielding in other ultraincompressible ceramics. Elastic and plastic anisotropy induced by interstitial carbon layers may translate into slip strength anisotropy in the WC lattice.

To characterize the strength, deformation, and the equation of state of WC with pressure, we compressed hexagonal WC powder of bulk (microcrystalline) and nanocrystalline grain size to 66 GPa with X-ray diffraction in the diamond anvil cell (DAC). Complementary Elasto-ViscoPlastic Self Consistent (EVPSC) simulations on textures and lattice strains were carried out to infer the plastic deformation mechanisms and strength at high pressures. Our results extend the pressure range of the quasi-hydrostatic EOS of WC to 59 and 64 GPa for bulk and nanocrystalline WC, respectively, and offer new constraints on strength and plastic deformation mechanisms of WC.

3.2 Experimental details

3.2.1 Sample preparation and loading

Microcrystalline (Alfa Aesar) and nanocrystalline (Inframat) hexagonal WC powders were used as sample materials. Initial grain sizes of these materials were determined to be 1.2 µm and 54 nm using hkl-dependence of size and strain broadening (Popa, 1998) based on peak widths for ambient X-ray diffraction (XRD) patterns collected using a Bruker DaVinci D8 powder diffractometer with Cu Kα source at the Michigan State University Center for Material Characterization. Volumetric compression under hydrostatic conditions and strain and texture development under non-hydrostatic conditions were investigated in WC in diamond anvil cells. For hydrostatic experiments, WC powder was loaded with internal standards Au (Alfa Aesar) and ruby within a Ne medium using the COMPRES/GSECARS gas-loading apparatus (Rivers *et al.*, 2008). Each sample was enclosed by a rhenium gasket pre-indented to ~40-µm thickness with ~150-µm sample chamber and compressed in symmetric DACs with anvils of 300-µm culets. For nonhydrostatic experiments, WC powder was packed without a medium and an Au foil standard was placed on top. An X-ray transparent beryllium gasket pre-indented to 32 µm with a 100-µm-diameter sample chamber hole was used with a 2-pin panoramic DAC with 300-µm anvil culets. Gaskets were machined using the HPCAT laser cutting facility (Hrubiak *et al.*, 2015). Samples were compressed in 2-10 GPa steps up to maximum pressure of 66 GPa, with pressure at each step calculated using the equation of state for Au (Dewaele, Loubeyre and Mezouar, 2004).

3.2.2 X-ray diffraction in the DAC

Upon compression, synchrotron X-ray diffraction was obtained using both axial diffraction geometry in a symmetric DAC in which the X-ray probe was parallel to the loading axis (both grain sizes), and the radial diffraction geometry in a panoramic DAC in which the incident X-rays were perpendicular to the loading axis (bulk WC only). Angle-dispersive X-ray diffraction (ADXD) was conducted at the High-Pressure Collaborative Access Team (HPCAT) beamline at Argonne National Lab, Sector 16-BM-D. X-rays monochromatized to 40 keV (axial experiments) or 37 keV (radial experiments) were focused to 4-6-µm spot size using Kirkpatrick-Baez focusing mirrors and collimated using a 90-µm pinhole. Diffraction patterns were collected

for 60-80s on a MAR2300 image plate detector and detector geometry was calibrated using a CeO₂ standard.

Diffraction patterns were masked to eliminate saturated intensity and integrated to 1-D profiles using Fit2D (Hammersley et al., 1996) or Dioptas software (Prescher and Prakapenka, 2015). For data collected in the axial geometry, diffraction peaks were fit to Voigt lineshapes using the IgorPro MultipeakFit module. For analysis of data collected in the radial geometry, each pattern was divided into 5° azimuthal wedges over the full 360° azimuthal range for fullprofile Rietveld refinement with Materials Analysis Using Diffraction (MAUD) software (Lutterotti et al., 1997; Lutterotti, Matthies and Wenk, 1999). The synchrotron instrument parameters in MAUD were refined using the CeO₂ standard. Sample parameters, including polynomial backgrounds, lattice constants, grain size, and microstructure were refined at each pressure step. Strain was fit at each step for WC and Au using the "Radial Diffraction in the DAC" model. To include the maximum number of diffraction lines from WC in our calculations and to minimize the effects of peak overlap, Q-values for higher-order parallel planes were fixed equal to the lowest order plane to which they were parallel. Be and BeO phases (at 1 bar) were included in the refinement to model diffraction from the gasket peaks. Texture in all phases was fit using the Entropy-modified Williams-Imhof-Matthies-Vinel (E-WIMV) texture model (Lutterotti et al., 2004; Chateigner, Lutterotti and Morales, no date) with an imposed fiber symmetry. The orientation distribution function (ODF) was exported from MAUD and inverse pole figures were plotted using the BEARTEX software (Wenk et al., 1998). Pressure was calculated from unit cell volumes of Au determined by fitting the (111) diffraction peak in the 5° azimuthal wedge containing the hydrostatic angle ($\psi = 54.7^{\circ}$).

3.3 Results and interpretation

Representative diffraction patterns for bulk and nano-crystalline WC compressed in Ne are presented in Figure 7. All observed diffraction peaks correspond to the WC sample, Ne medium, Au pressure standard, and Re gasket. Ne peaks (highly textured spots) and diamond



Figure 7: Representative synchrotron X-ray diffraction patterns of bulk and nano-crystalline WC compressed in Ne pressure medium with Au pressure standard and Re gasket in the axial diffraction geometry.

spots were masked to remove overlap with WC sample. Only non-overlapped WC and Au diffraction lines were used to determine unit cell parameters. Lattice spacings for WC (001), (100), (101), (110), and (111) and Au (111), (200), and (220) were fit by least squares with

UnitCell Software (Holland and Redfern, 1997). The resulting unit cell volumes for both nanocrystalline WC and bulk WC are presented in Figure 8.



Figure 8: Compression of bulk (blue circles, with 3rd order Birch-Murnaghan equation of state fit in blue line) and nanocrystalline (yellow circles, with EoS fit in yellow line) WC in Ne compared with other studies. Pressure was determined from the EOS of Au, using the (111), (200), and (220) Au peaks and the pressure scale of Dewaele (Dewaele, Loubeyre and Mezouar, 2004). Data from previous studies were obtained in the multi-anvil press (Litasov et al., 2010) (black open circles) and in the DAC for bulk (red open squares (Amulele et al., 2008)) and nano-crystalline WC (green open triangles (Lin et al., 2009)). Ultrasonic measurements (Amulele et al., 2008) are displayed in red solid line and extrapolated with red dashed line.

3.3.1 Equation of state and linear compressibility

Volume-pressure data collected in the axial geometry for WC compressed in Ne medium (Figure 8) were fit to a 3rd order Birch-Murnaghan equation of state (BME), yielding EOS parameters of $V_0 = 20.77 \pm 0.01$ Å³, $K_0 = 397 \pm 7$ GPa, and $K_0' = 3.7 \pm 0.3$ for bulk WC and $V_0 = 20.74 \pm 0.01$ Å³, $K_0 = 377 \pm 7$ GPa, and $K_0' = 3.8 \pm 0.3$ for nano-crystalline WC. With V_0 fixed at observed ambient values of 20.74 Å³ and 20.72 Å³ for bulk and nano-WC respectively, the fit

results in higher K_0 and lower K_0 ', with $K_0 = 412 \pm 4$ GPa, and K_0 ' = 3.3 ± 0.2 for bulk WC, and $K_0 = 388 \pm 5$ GPa, and $K_0' = 3.5 \pm 0.2$ for nano WC. These values are tabulated with previous work in Table 1. Previous studies in the DAC report higher K_0 but lower K_0 ' than calculated in our work or the work by (Litasov et al., 2010). In addition to non-hydrostatic stress, the tradeoff between K_0 and K_0 ' during EOS fitting is responsible for some of the discrepancy between the values for the EOS parameters (Figure 9). Combined with independent measurements of elasticity from ultrasonic (Lee and Gilmore, 1982; Amulele et al., 2008) and shock wave (Dandekar, 2002) studies, the consensus value for K_0 is ~380-400 GPa, which is consistent with our data particularly with the bulk fit where $V_0 \sim 20.77$ Å³. The range of K_0 ' most consistent with our data and the consensus K_0 is ~3.6-4.3. In comparison, density functional theory (DFT) predictions using both the local density approximation (LDA) and generalized gradient approximation (GGA) all obtain a higher V_0 than that measured in our samples at 1 bar, and accordingly suggest K_0 ' > 4, consistent within uncertainty with our results (Figure 9). Our experiments indicate that the bulk modulus of nano-crystalline WC is lower than that of the bulk material, and consistent with the consensus of ultrasonic, shock wave, and DFT EOS.

The ratio of the hexagonal lattice parameters c/a can indicate a convolution of anisotropic elasticity and anisotropic stress. Our experimental values for c/a in bulk WC compressed hydrostatically in Ne medium indicate a systematically lower ratio than other DAC XRD studies (Figure 10). Again, note that the axial XRD in the DAC samples crystallites oriented near the direction of minimum stress. Anisotropic stress combined with anisotropic elasticity will result in systematic differences in lattice parameters c and a calculated from diffraction lines at the minimum stress orientation. Systematically higher c/a ratio from studies of WC under nonhydrostatic compression in the axial geometry indicates anisotropy in linear compressibility.

V_0 (Å ³)	Ko (GPa)	<i>K</i> ₀ '	Grain Size	Method	Reference
20.4667	329	-	not specified	US	(Brown, Armstrong and Kempter, 1966)
20.707-20.747	383	-	not specified	SW	(Dandekar, 2002)
-	390.3	-	not specified	US	(Lee and Gilmore, 1982)
20.806 ± 0.020	383.8 ± 0.8	2.61 ± 0.07	Bulk	US	(Amulele et al., 2008)
20.806 ± 0.020	411.8 ± 12.1	5.45 ± 0.73	Bulk	DAC XRD, NaCl, silicone oil, and 4:1 methanol-ethanol solution	(Amulele et al., 2008)
20.749	452.2 ± 7.8	1.25 ± 0.53	Nano	DAC XRD, silicone oil	(Lin et al., 2009)
20.750 ± 0.002	384 ± 4	4.65 ± 0.32	Bulk	MAP XRD, MgO	(Litasov et al., 2010)
$20.75{\pm}~0.00$	387 ± 5	4.38 ± 0.40	Bulk	MAP XRD, MgO	BM-EOS fit to (Litasov <i>et al.</i> , 2010)
20.77 ± 0.01	397 ± 7	3.7 ± 0.3	Bulk	DAC XRD, Ne	This study
20.74 (fixed)	412 ± 4	3.3 ± 0.2	Bulk	DAC XRD, Ne	This study
20.75 ± 0.01	377 ± 7	3.8 ± 0.3	Nano	DAC XRD, Ne	This study
20.72 (fixed)	388 ± 5	3.5 ± 0.2	Nano	DAC XRD, Ne	This study

Table 1: Experimental and theoretical values for the equation of state parameters for hexagonal tungsten monocarbide. US =ultrasonic, SW = shock wave, DAC = diamond anvil cell, MAP = multi-anvil press, XRD = X-ray diffraction, LDA = local-densityapproximation, GGA = generalized gradient approximation, PWP = plane wave potential, PBE = Perdew, Burke, and Ernzerhof,LMTO = linear muffin-tin orbital.

Table 1 (continued)

V_0 (Å ³)	Ko (GPa)	<i>K</i> 0'	Exchange-correlation functional	Reference
-	655	-	not specified	(Zhukov and Gubanov, 1985)
				(Christensen, Dudiy and
	404	-	GGA	Wahnström, 2002)
				(Suetin, Shein and Ivanovskii,
20.5267	382.4	-	GGA	2008)
				(Shein, Suetin and Ivanovskiĭ,
-	382.4	-	GGA	2008)
-	392.5	-	LDA	(Su et al., 2009)
20.749	390.2 ± 0.5	4.19 ± 0.04	LDA	(Lin et al., 2009)
20.6558	393	-	GGA	(Li et al., 2010)
20.6558	400.9	4.06	GGA	(Li et al., 2010)
21.240	356	-	GGA	(Kong et al., 2010)
21.33	373	4.40	GGA	(Cheng et al., 2012)
-	389.4	4.16	GGA	(Liu et al., 2013)
20.99	389.6	4.27	GGA	(Li <i>et al.</i> , 2014)



Figure 9: Ellipses representing 95.3% confidence in K_0 and K_0' obtained from Birch-Murnaghan equation fit to pressure-volume data for bulk (blue, this study and black, room temperature data from multi-anvil (Litasov et al., 2010)), and nano-grained WC (yellow). Dashed ellipses with open circles are with V₀ fixed to ambient XRD measurements, solid ellipses with solid circles are with V₀ fit. The open gray circle indicates reported values from multi-anvil, high-temperature/pressure EOS (Litasov et al., 2010). Solid gray squares are from other DAC studies on nano-crystalline (Lin et al., 2009) and bulk (Amulele et al., 2008). Red triangles indicate values obtained from theoretical calculations (Lin et al., 2009; Li et al., 2010, 2014; Cheng et al., 2012; Liu et al., 2013). The solid red diamond is the adiabatic bulk modulus from ultrasonic experiments (Amulele et al., 2008). Dashed lines are from shock wave (black line (Dandekar, 2002)) and ultrasonic interferometry experiments (gray line (Zhukov and Gubanov, 1985)), which only constrain K_0 but not K_0' .



Figure 10 The ratio c/a vs P for bulk- and nano-grain WC from experimental measurements. Values obtained using nonhydrostatic media (open circles) are systematically higher than with hydrostatic media (filled circles, this study).

The linear compressibilities χ_a and χ_c may be determined from their relations to the bulk modulus and the pressure dependence of the *c/a* ratio in a hexagonal material (Singh, Mao, *et al.*, 1998; Duffy *et al.*, 1999):

$$2\chi_a + \chi_c = \frac{1}{K} \tag{5}$$

$$\chi_a - \chi_c = \left(\frac{\partial \ln(c/a)}{\partial P}\right)_T \tag{6}$$

Under hydrostatic conditions, the c/a ratio of WC increases non-linearly with pressure, so the slope of its pressure dependence cannot be accurately represented with a constant value. To determine the pressure dependence of c/a, we determined lattice parameters a and c and K(P)from the quasi-hydrostatic diffraction data and fit a least-squares 3^{rd} order BME to parameters a and *c* to obtain parameters a(P) and c(P) and computed numerical derivatives of the ratio c/a at each pressure step.

Experiments and theoretical computations agree that the *a* direction of WC is more compressible than *c*. Our BME fit of lattice parameters for WC yields linear ambient bulk moduli of $K_a = 366$ GPa and $K_c = 456$ GPa for bulk WC and $K_a = 359$ GPa and $K_c = 407$ GPa for nanocrystalline WC. The value of K_c for nanocrystalline WC compressed in Ne medium is lower than for bulk WC, and lower than the value reported in previous experiments on nanocrystalline WC (Lin *et al.*, 2009).

3.3.2 Differential stress and elastic stiffness coefficients

Without a hydrostatic medium, a sample in an opposed anvil device such as the DAC sustains approximately uniaxial compressive stress, with a maximum stress σ_3 parallel to the direction of the compression by the diamonds, and a radial minimum stress σ_1 (Ruoff, 1975). The difference between these stresses is termed the differential stress. In order to characterize the effects of non-hydrostatic stress on deformation of anisotropic materials, the radial diffraction geometry allows observation of strains at a wide range of orientations relative to the orientation of maximum stress. Unrolled radial "cake" patterns obtained at selected pressures upon compression of WC are presented in Figure 11.

Diffraction lines of WC under anisotropic strain exhibit varying *d*-spacing along the azimuthal angle. The measured d-spacing d_m deviates from the hydrostatic d-spacing d_p as a function of the angle ψ between the diffracting plane normals and the loading axis as quantified



Figure 11: X-ray diffraction pattern data (lower half of each image) and full-profile refinements (upper half of each image) for selected pressures a) 16 GPa, b) 34 GPa, c) 48 GPa and d) 66 GPa. The Debye-Scherrer rings are transformed to azimuth vs 2θ and Miller indices for WC are labeled in each pattern. WC peaks exhibit increasing sinusoidal curvature with pressure due to non-hydrostatic strain. Systematic variation in intensity in individual diffraction lines is indicative of plastic deformation and also increases with pressure in WC. Diffracting planes from gasket materials Be and BeO at ambient conditions are also observed and exhibit no strain.

by the non-hydrostatic lattice strain Q(hkl) for individual lattice planes hkl (Singh and Balasingh, 1994; Singh, Balasingh, *et al.*, 1998):

$$d_m(hkl) = d_p(hkl)[1 + (1 - 3\cos^2\psi)Q(hkl)].$$
(7)

Our detection limit for Q(hkl) is ~8-9×10⁻⁴, with typical uncertainty up to 6-7×10⁻⁴, exemplified by the strain observed in the (201) plane at 16 GPa. For materials in the hexagonal crystal system such as WC, Q(hkl) is a quadratic function (Singh and Balasingh, 1994; Singh, Balasingh, *et al.*, 1998; Singh, Mao, *et al.*, 1998) of lattice plane orientation B(hkl), relative to the loading axis:

$$Q(hkl) = m_0 + m_1 B + m_2 B^2, (8)$$

where $B(hkl) = \frac{3a^2l^2}{[4c^2(h^2+hk+k^2)+3a^2l^2]}$, in which *a* and *c* are the measured lattice parameters at pressure, and the m_i are the coefficients of the quadratic relationship between Q and B.

In the elastic regime, the strain Q(hkl) is a function of the differential stress, *t*, the elastic shear moduli G_R and G_V under isostress (Reuss bound) and isostrain (Voigt bound) conditions, respectively, and α , a constant between 0.5 and 1 which determines the weight between Voigt and Reuss conditions, i.e. stress vs. strain continuity at grain boundaries (Singh, 1993; Singh and Balasingh, 1994; Singh, Balasingh, *et al.*, 1998).

$$Q(hkl) = \frac{t}{3} \left[\frac{\alpha}{2G_R(hkl)} + \frac{1-\alpha}{2G_V} \right],\tag{9}$$

The mean strain $\langle Q(hkl) \rangle$ and range of Q(hkl) for different diffraction lines indicate lattice strain due to increasing anisotropic stress, change in anisotropic elasticity, or both. Above the yield stress, in the viscoelastic regime, Q(hkl) will be modified by plasticity as well.

We used full-profile refinement in MAUD (Figure 11) with the "Radial Diffraction in the DAC" stress model to determine *Q*-factors for each *hkl* (Figure 12). With increasing pressure



Figure 12: Strain obtained for WC lattice planes Q(hkl) at selected pressures plotted vs. the orientation function B(hkl) (eqn 8) relative to the stress axis (a-d) and for all planes as pressure increases (e). In (a-d), red curves are quadratic fits to strain Q(hkl) vs. B(hkl). Strain anisotropy increases with pressure (scaling is constant for Figures a-d). Error in Q(hkl) at individual pressures represents the error of the refinement to the experimentally observed curvature. In e), the mean strain $\langle Q \rangle$ (red circles and dashed line between points for emphasis) increases monnotonically, and the shape of the Q vs P curve is similar for all Q(hkl), however values diverge in Q as pressure increases, indicating an increase in anisotropy as pressure increases.

(and differential stress), Q(hkl) increases for all diffraction lines, and the range of Q(hkl) observed increases, with maximum lattice strain in WC at (001) and (100) directions, and minimum lattice strain near (101) and (112). Up to ~30 GPa, strain is increasingly anisotropic for WC (Figure 12e). At ~30 GPa, the effect of pressure on Q tapers off, and anisotropy in Q values is due to both elastic and plastic deformation.

Figure 13a illustrates the range of differential stress values obtained for analysis assuming Reuss and Voigt bounds. In the Reuss limit ($\alpha = 1$, implying stress continuity across



Figure 13: Differential stress t in WC obtained from lattice strain analysis and EVPSC model of experimental measurements. Figure 12a (left): Average Voigt (red triangles) and Reuss (teal circles) values for differential stress computed from Q(hkl) and elastic constants obtained from theoretical calculations (Liu et al., 2013), with values obtained using aggregate shear modulus (gold squares (Amulele et al., 2008)). Also shown is differential stress obtained from EVPSC simulation incorporating texture and plasticity (solid black line). Stress accounting only for elastic strain diverges from stress accounting for both elastic and plastic strain at the yield point near 30 GPa. Figure 12b (right): Reuss stresses computed for individual lattice planes hkl using purely elastic strain. (001) supports the largest differential stress ~28 GPa, ~68-70% larger than differential stress values of ~16-20 GPa at yielding, which use the aggregate and Reuss-limit shear modulus, respectively, and 65-89% larger than the stress from the EVPSC model.

crystallite boundaries), mean strain $\langle Q(hkl) \rangle$ and prior constraints on the shear modulus G

(Singh, 1993) may be used to determine *t*:

$$t = 6G\langle Q(hkl)\rangle f(x), \tag{10}$$

where f(x) is a function of α and elastic anisotropy factor x. Across a range of materials and crystal systems *f* has been shown to have a value close to 1 (e.g. Singh, 2009), so we adopt *f*=1 in analysis of WC. Aggregate shear modulus *G*(*P*) was constrained by extrapolation of a linear fit of ultrasonic data obtained up to 14 GPa (in Amulele *et al.*, 2008). Based on these assumptions, elastic differential stress sustained by WC is reported in Figure 14, with error bars computed based on the standard deviation of *Q*(*hkl*) at each pressure.

Average values of differential stress obtained from lattice strain increase with pressure throughout the entire range of this study, to a maximum of 27 (Voigt, α =0) to 33 (Reuss, α =1) GPa at the maximum pressure measured, 66 GPa. The slope of *t*(*P*) decreases at ~30 GPa, at which pressure the observed differential stress is ~12 GPa. A decrease in slope of *t*(*P*) is consistent with expected behavior at initiation of plastic flow.

Figure 13b illustrates Reuss stresses for individual lattice planes in which t(hkl) is calculated using equation 10 with Q(hkl) for (001), (100), (110), (101), and (111) and the X-ray shear modulus $G_R^X(hkl)$, given by (Singh, Balasingh, *et al.*, 1998):

$$\left[2G_{R}^{X}(hkl)^{-1} = \frac{1}{2}(2S_{11} - S_{12} - S_{13}) + B^{2}(-5S_{11} + S_{12} + 5S_{13} - S_{33} + 3S_{44}) + B^{4}(3S_{11} - 6S_{13} + 3S_{33} - 3S_{44})\right],$$
(11)

where the *Sij* are the elastic compliances. Differential stress t(001) is substantially higher than t(hkl) for other planes, supporting 26 GPa of differential stress at the yield stress, 40-43% higher than the Reuss bound differential stress calculated from $\langle Q(hkl) \rangle$ with theoretical G_R , 68-70% higher than the differential stress determined from $\langle Q(hkl) \rangle$ and the aggregate shear modulus.

Below the yield pressure of ~30 GPa, in the elastic regime, the strain anisotropy from Q(hkl) can also be used to compute elastic compliances S_{ij} . S_{ij} at a given pressure may be



Figure 14: Differential stress observed in WC and other hard ceramics compressed uniaxially with no pressure-transmitting medium. Stress in WC is computed with both lattice strain theory (solid circles) and EVPSC simulation (dashed line). Dynamic yield strength from shock wave data are open gold circle, calculated after (Feng, Chang and Lu, 2016). Previous studies on all other hard ceramics (open symbols) use lattice strain theory. Blue squares are WB (Dong et al., 2012), green triangles are γ -Si₃N₄ (Kiefer et al., 2005), black diamonds are TiB₂ (Amulele, Manghnani and Somayazulu, 2006), teal hexagons are B₆O (He, Shieh and Duffy, 2004), and magenta triangles are BC₂N heterodiamond (Dong et al., 2009). Uncertainty is calculated as ± the standard deviation in mean Q at each pressure, propagated through equation 10. Differential stress increases with uniaxial load until yielding, where the change in slope of the t(P) indicates strain is accommodated by both elastic and plastic deformation. In WC, yielding at 30 GPa is supported by the development of texture at the same pressure (Figure 16). The flow stress of WC above yielding is higher than flow stresses observed in WB and Si₃N₄. Flow stress obtained from EVPSC simulation is systematically lower than that derived from lattice strain analysis only, though the results of the two methods remain within uncertainty of each other.

determined by the vector product of the inverted coefficient matrix of the lattice strain equations (Singh, Balasingh, *et al.*, 1998) with their solution matrix for the hexagonal system (Singh, Balasingh, *et al.*, 1998; Singh, Mao, *et al.*, 1998):

$$\begin{bmatrix} 2 & -1 & -1 & 0 & 0 \\ -5 & 1 & 5 & -1 & 3 \\ 3 & 0 & -6 & 3 & -3 \\ 1 & 1 & 1 & 0 & 0 \\ 0 & 0 & 2 & 1 & 0 \end{bmatrix}^{-1} \begin{bmatrix} 6m_0/t \\ 6m_1/t \\ 6m_2/t \\ \chi_a \\ \chi_c \end{bmatrix} = \begin{bmatrix} S_{11} \\ S_{12} \\ S_{13} \\ S_{33} \\ S_{44} \end{bmatrix}$$
(12)

Equations (5-10) and (12) may thus be used to combine Q(hkl) with independent constraints on the linear incompressibilities in *a* and *c* directions χ_a and χ_c derived from hydrostatic data, and an average G(P) or t(P), to determine $S_{ij}s$. The elastic stiffness coefficients ($c_{ij}s$) are obtained from equivalence relations between $c_{ij}s$ and $S_{ij}s$ (Nye, 1985).

Calculated c_{ij} values are shown in Figure 15. Values for c_{11} and c_{13} increase monotonically throughout the pressure regime. The values for c_{33} and c_{12} decrease with pressure until the yield stress. Values for c_{44} increase with pressure to the yield strength. Above 30 GPa, apparent c_{ij} are modified by convolved effects of plasticity with elasticity on strain behavior. Our calculated values for c_{11} and c_{13} agree well with theoretical predictions from 18 to 66 GPa, but c_{12} , c_{33} , and c_{44} diverge from theory rapidly as plasticity progresses (Figure 15). Specifically, c_{12} decreases to ~30 GPa, and then remains approximately constant with pressure, c_{33} decreases until it becomes similar to c_{11} at ~30 GPa, and c_{44} increases rapidly and remains ~200 GPa higher than predicted. For similar behavior observed in rhenium, Duffy *et al.* (1999) note the c_{ij} s are in agreement correspond to basal planes, but this is not the case in WC. Our experimental c_{ij} s are in best agreement with theory below the plastic yield pressure at ~30 GPa, but significant discrepancies remain between experimental and theoretical c_{33} and c_{44} even in the elastic regime, and more work is needed to resolve these discrepancies.



Figure 15: Elastic stiffness coefficients for experimental data as calculated from equations 5-10, and 12 (closed symbols: this study). Open symbols are experimental zero-pressure values (Gerlich and Kennedy, 1979). Solid and dashed lines are from theoretical calculations (Liu et al., 2013; Li et al., 2014). Our values for c_{11} and c_{13} agree well with theoretical predictions. Other c_{ij} s deviate from predicted values rapidly as plastic deformation increases. Above yielding at 30 GPa, values for c_{44} is substantially higher than predicted, and c_{33} and c_{12} diverge from predicted values. Values for c_{33} appear to converge with c_{11} , while c_{12} varies only slightly from a constant value of 200 GPa throughout the experimental pressure interval.

3.3.3 Plastic Deformation

Plasticity may be evaluated based on the texture (non-random orientation distribution of crystallites) of the sample and lattice strains of a series planes as observed as systematic azimuthal variations in diffraction intensity and d-spacing variation with azimuth (Figure 11). The E-WIMV model implemented in MAUD software fits intensity variation (texture) in the Debye-Scherrer rings by generating an orientation distribution function that describes the frequency of crystallite orientations within the sample coordinate system (Wenk, Lutterotti and Vogel, 2010). The "Radial Diffraction in the DAC" stress model in the MAUD software fits the

d-spacing variation with azimuth to obtain lattice strains. Deformation mechanisms can be investigated using EVPSC simulations, which model lattice strains and texture as a function of slip system activities and strength.

3.3.3.1 Texture analysis

To determine crystallite orientation in WC, the E-WIMV texture model was applied to each phase at each pressure step. Upon compression of WC up to 16 GPa, texture remained random. At 16 GPa, weak texture develops (Figure 11 and Figure 14). Texture strength scaled in multiples of random distribution (m.r.d.) is observed to increase with pressure, particularly above 30 GPa, the pressure at which yielding was inferred from lattice strain. The development of texture supports the onset of plasticity at ~30 GPa (Figure 16).



Figure 16: Inverse pole figures reconstructed from experimental ODF data fit with fiber texture at selected pressures. A texture maximum is observed at \sim 30 GPa near the 2-1-10 planes (symmetrically equivalent to 100 planes in *hkl* notation), indicating plastic deformation. This value increases to \sim 1.9 multiples of a random distribution at the maximum pressure of 66 GPa.

At the maximum pressure examined in this study, 66 GPa, the texture maximum in the inverse pole figure of the compression direction is near the $2\overline{110}$ pole, which is the pole to the (100) in 3-coordinate *hkl* notation (Figure 16). In the case of WC, (001) is the lattice plane supporting the highest strain and exhibiting the highest strength. Note that WC is a layered structure, with layers of C-atoms (graphene) orthogonal to 001, between hexagonal W layers (Goldschmidt, 1967). The covalent C-C bonds within the layer are very strong, making deformation in the $\langle 001 \rangle$ direction extremely difficult. To determine which deformation mechanism(s) is consistent with generating this preferred orientation in WC, modeling elastoviscoplastic response of a polycrystalline WC aggregate is necessary.

3.3.3.2 Plasticity simulation

Plasticity was simulated with an elasto-viscoplastic self-consistent (EVSPC) (Wang *et al.*, 2010) model, modified for application to high-pressure experiments (Lin *et al.*, 2017). The model simultaneously reproduces refined Q values (lattice strain) and texture development at each pressure step and accounts for both elastic and viscoplastic deformation (Figure 17). For our models we used theoretical elastic properties for WC (Liu *et al.*, 2013). The EVPSC model treats individual grains in a polycrystalline material as inclusions in an anisotropic homogeneous effective medium (HEM). The average of contributions from all grain inclusions determines the properties of the HEM matrix. Plasticity of a grain in the HEM matrix is then described by rate-sensitive constitutive equation for multiple slip systems:

$$\dot{\varepsilon}_{ij} = \dot{\gamma}_0 \sum_s m_{ij}^s \left\{ \frac{|m_{kl}^s \sigma_{kl}|}{\tau^s} \right\}^n sgn(m_{kl}^s \sigma_{kl}),$$
(13)

where $\dot{\varepsilon}_{ij}$ is the plastic strain rate, $\dot{\gamma}_0$ is the reference shear strain rate and τ^s is the critical resolved shear stress (CRSS) of the slip system *s* at the reference strain rate under conditions in



Figure 17: Strain and texture in WC. *Left*: Experimental and modeled strain (Q-factors) for selected planes of WC vs. pressure. *Right*: Experimental (top) and modeled (bottom) inverse pole figures illustrating non-random texture at 66 GPa.

the HEM. The grains are subject to local stress tensor σ_{kl} , the symmetric Schmid factor m_{kl}^s describes the straining direction of slip system s. When the stress resolved onto a given slip system is close to or above the threshold value, plastic deformation will occur on that slip system. The empirical stress exponent *n* describes strain rate sensitivity to applied stress, where infinite *n* implies rate-insensitivity. Deformation of WC appears to be rate insensitive (Mandel, Radajewski and Krüger, 2014) and consequently we assume a high stress exponent of n = 30 (Lin *et al.*, 2017).

The parameter τ^{s} represents the effective polycrystal CRSS and includes both strain hardening and pressure hardening. Pressure hardening and strain hardening effects on CRSS cannot be separated because both pressure and strain increase simultaneously in DAC experiments. Both are included in the pressure dependence of CRSS calculated by:

$$\tau^{s} = \tau_{0}^{s} + \frac{\partial \tau^{s}}{\partial P} P, \qquad (14)$$

where τ_0^s is the initial CRSS value, and $\frac{\partial \tau^s}{\partial P}$ is its pressure-dependence. Values of CRSS and its pressure dependence for WC are presented in Table 2. The CRSS effectively controls slip

Slip System	Slip Mechanism	CRSS (GPa)	d(CRSS)/dP
{1010}(1210)	Prismatic	4.0	0.065
$\{10\overline{1}0\}(0001)$	Prismatic	2.6	0.065
{10 <u>1</u> 1}(<u>2</u> 113)	Pyramidal	14.0	0.08

Table 2: CRSS and pressure dependence values for active slip systems in WC under nonhydrostatic compressive stress.

system activity and different active slip systems (Lin *et al.*, 2019) result in different lattice strains and texture and must be matched to experimental observations.

Lattice strain and texture evolution in WC are modeled simultaneously to determine deformation mechanisms such as slip system activity and slip system strength and are used to calculate yield stress from reproduced Q-values and texture (Figure 13 and Figure 16). Slip is activated at ~30 GPa on the $\{10\overline{1}0\}\langle\overline{1}2\overline{1}0\rangle$ prismatic slip system. From 30-40 GPa, this system converges towards ~50% of the slip system activity with the other 50% supported by $\{10\overline{1}0\}\langle0001\rangle$ prismatic slip (Figure 18). Above 50 GPa, these systems each account for ~45% of the slip system activity, with the remaining 10% contributed from $\{10\overline{1}1\}\langle\overline{2}113\rangle$ pyramidal system (Figure 18), which activates at ~40 GPa, and increases to 10% activity by 50 GPa. This slip system is needed to induce yielding on Q(001) and occurs in $\{10\overline{1}1\}$ rather than in $\{10\overline{1}0\}$ as described in previous work (Takahashi and Freise, 1965; Bolton and Redington, 1980).

3.3.3.3 Crystallite size and microstrain

Refined values of grain size and microstrain in radial XRD patterns of bulk WC support the observed texture and modeled deformation mechanisms (Figure 19). Mean anisotropic grain



Figure 18: Modeled slip system activities as determined from the EVPSC simulation. Based on experimental texture, below 8 GPa, deformation is entirely elastic, and no plastic deformation occurs. Between 8-30 GPa, a small amount of plastic strain is accommodated by prismatic slip activation on $\{10\overline{1}0\}(0001)$. At 30 GPa, bulk plastic yielding occurs, accommodated by continued prismatic slip on $\{10\overline{1}0\}(0001)$ and activation of prismatic slip on $\{10\overline{1}0\}\langle\overline{1}2\overline{1}0\rangle$ A third (pyramidal) slip system is activated between 40-50 GPa on $\{10\overline{1}1\}\langle\overline{2}113\rangle$.



Figure 19: Crystallite size and microstrain vs pressure from full-profile refinement in WC under non-hydrostatic compression. Crystallite size decreases and microstrain increases up to ~30 GPa, the pressure at which lattice strain suggests yielding and texture indicates activation of prismatic slip on $\{10\overline{1}0\}\langle\overline{1}2\overline{1}0\rangle$ and $\{10\overline{1}0\}\langle0001\rangle$. Reduction in crystallite size below plasticity onset is attributed to lattice-bending, which reduces the size of the coherently diffracting regions contributing to crystallite size in MAUD software. Above 30 GPa, microstrain drops and then resumes increasing, while grain size remains ~constant at ~80 - 90 nm. A second dip in microstrain at ~50 GPa follows the activation of pyramidal slip on $\{10\overline{1}1\}\langle\overline{2}113\rangle$.

size decreases rapidly until plastic yielding, after which the grain size decreases slowly. Anisotropic crystallite size represents the size of coherently diffracting regions within the sample. Lattice bending can reduce the refined grain size by reducing the size of these regions, which can explain grain size reduction below plastic yielding. Microstrain increases with pressure until yielding, where it drops sharply and then begins to increase again. A second drop in microstrain may follow activation of slip on $\{10\overline{1}1\}\langle\overline{2}113\rangle$. Both microstrain and elastic macrostrain behavior as a function of pressure support elastic stress release in WC through plastic slip.

3.4 Discussion

3.4.1 Equation of state

Observed volumes for bulk WC obtained in this study under quasi-hydrostatic conditions are similar to data obtained in multi-anvil experiments on annealed WC, but systematically lower than volumes observed in previous DAC studies (Amulele *et al.*, 2008; Lin *et al.*, 2009) (Figure 8). Previous DAC studies employed less hydrostatic pressure-transmitting media: NaCl, methanol-ethanol solutions, and/or silicone oil are known to sustain significantly non-hydrostatic stress particularly at pressures above ~10 GPa (Funamori, Yagi and Uchida, 1994; Angel *et al.*, 2007; Klotz *et al.*, 2009). Under nonhydrostatic axial compression, diffraction in axial geometry samples the crystallites near the orientation of minimum compression, and so obtains systematically larger calculated volumes and a correspondingly higher apparent incompressibility. The neon medium used in this study supports < ~1 GPa differential stress through the 64 GPa maximum pressure investigated here (e.g. Dorfman *et al.*, 2012), resulting in reliable quasi-hydrostatic volumes for constraining the EOS of WC. Although previous work had suggested nano-WC is highly incompressible (Lin *et al.*, 2009), data obtained under quasi-hydrostatic compression in this study demonstrate that nano-WC is not more incompressible than bulk WC. Observed volumes for bulk and nano-crystalline samples are indistinguishable at ambient conditions and remain similar upon compression. With increasing pressure, volumes obtained for nano-WC diverge to slightly smaller volumes relative to those for bulk WC. Previous work on nano-WC used silicone oil pressure medium (Lin *et al.*, 2009), and as for bulk WC, may have overestimated incompressibility due to effects of non-hydrostatic stress. Based on our results for both bulk- and nano-WC compressed in Ne medium, we conclude there is no significant stiffening due to grain size; if anything, nano-WC is slightly less incompressible than bulk WC. This decrease in incompressibility with decreasing grain size in the nano-regime is consistent with observations for other ceramics cBN, TiO₂ and Al₂O₃ (Chen *et al.*, 2002; Al-Khatatbeh, Lee and Kiefer, 2012; Le Godec *et al.*, 2012).

Understanding the effects of grain size on incompressibility is important for assessing overall elasto-viscoplastic responses of polycrystalline materials. Our bulk modulus value of 397 ± 7 GPa is in agreement with both theory and other hydrostatic experimental studies on WC. For nanocrystalline WC, our bulk modulus value of 377 ± 7 is lower than the bulk value, and substantially lower than previous values reported for nano WC. A growing body of evidence indicates that while nano-scale grain size increases strength (e.g. the Hall-Petch effect), it decreases incompressibility for multiple incompressible materials, now including tungsten carbide. WC is among the least compressible materials, with incompressibility on par with cBN and cRuO₂ (cf. Haines, Léger and Bocquillon, 2001), but neither the bulk nor the nanocrystalline phase is as incompressible as diamond or higher- K_0 osmium borides (Haines, Léger and Bocquillon, 2001; Yeung, Mohammadi and Kaner, 2016).

3.4.2 Strength, elasticity, and deformation

The strength of bulk WC determined from lattice strain is comparable to other hard ceramics below 30 GPa pressure and ~12-16 GPa differential stress is supported at the yield point of 30 GPa. The strength of WC determined by lattice strain is similar to that of TiB₂ and B_6O (He, Shieh and Duffy, 2004; Amulele, Manghnani and Somayazulu, 2006, p. 2) (Figure 14). It supports less differential stress than doped diamond (Dong *et al.*, 2009), but is stronger than tungsten boride (Dong *et al.*, 2012). Reuss stresses provide information on strength anisotropy in WC, with (001) supporting the highest strength. Oriented WC crystals may provide a means of producing stronger parts without the need for binders. Lattice strain assumes purely elastic deformation however, and the determination of strength based on EVPSC modeling suggests a lower overall yield strength and flow stress when plasticity is considered. Plasticity affects the experimental results, and as noted by previous studies on other materials (Weidner *et al.*, 2004; Raterron and Merkel, 2009) strength from inferred elasticity may be overestimated in previous studies when not accounting for plasticity.

Deformation of WC above the yield stress includes both plastic and elastic components. The elastic stiffness coefficients calculated from our results only agree in part with theoretical calculations. This is consistent with observations of other materials in which plasticity is expected to occur. Previous experimental studies of elasticity based on radial diffraction have similarly observed that only some elastic constants agree with density functional theory predictions, while others diverge (e.g. Duffy *et al.*, 1999; Merkel and Yagi, 2006). This is attributed to the effects of plasticity (Weidner *et al.*, 2004; Merkel, Tomé and Wenk, 2009). In the case of rhenium (Duffy *et al.*, 1999), c_{11} and c_{12} , which describe stress and strain in the basal planes of the hexagonal system, agree well with computations. In hcp cobalt (Merkel and Yagi,
2006; Merkel *et al.*, 2006), only c_{12} and c_{13} are in modest agreement with theory. In WC, c_{11} and c_{13} , representing stress and strain in both the basal and meridional planes, agree with theory but c_{12} , c_{33} , and c_{44} do not. Q-values are a function of both plasticity and elasticity and more work is needed to successfully solve for elastic stiffnesses in X-ray diffraction experiments on materials undergoing plastic deformation. Experimental values for the bulk and shear moduli at pressures > 15 GPa are needed to minimize error in calculations of c_{ij} s measured in X-ray diffraction experiments. New theoretical computations accounting for experimental measurements of c/a with pressure are necessary to better constrain the pressure-dependence of the c_{ij} s, and to assess the effect of non-hydrostatic stress on hexagonal materials like Re and WC.

3.5 Conclusion

Our results demonstrate the mechanical response of WC under quasi-hydrostatic and nonhydrostatic compressive loads up to 66 GPa. As determined by our data and modeling, the strength of the (001) plane in WC is ~68-70% larger than the mean strength of WC. Plastic deformation in WC above yielding at 30 GPa is accommodated by prismatic slip on $\{10\overline{1}0\}\langle\overline{1}2\overline{1}0\rangle$ and $\{10\overline{1}0\}\langle0001\rangle$, and pyramidal slip on $\{10\overline{1}1\}\langle\overline{2}113\rangle$. WC anvils should be oriented to the strongest direction to maximize strength performance under pressure. The new constraints provided by this study on the strength, deformation, and EOS of WC can help inform production of WC parts, and potentially applications of polycrystalline materials more broadly, for research and industry.

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CHAPTER 4: Phase equilibria, strength, and deformation of Kr and Xe to Mbar pressures *This chapter to be submitted as: "Phase equilibria, strength, and deformation of Kr and Xe to Mbar pressures" Benjamin Lee Brugman, M. Lv, J. Liu, A. Farmer, E. Greenberg, V.B. Prakapenka, D.Y. Popov, C. Park, and S.M. Dorfman*

Abstract

Phase transformations, strength, and plastic deformation of heavy rare gas solids krypton and xenon have been investigated using compression in the diamond-anvil cell. Strength determined from stress measurements in Pt and ruby standards at pressures up to 115 GPa is complemented by observations of strain and texture measurements obtained by synchrotron angle dispersive x-ray diffraction in the radial geometry to 100 GPa. Stacking faults indicative of the martensitic fcc-hcp phase transition are observed at pressures at and above 2.3 and 2.2 GPa in Kr and Xe, respectively. The strength and pressure dependence of Kr and Xe are compared with other rare gas solids He, Ne, and Ar. Non-hydrostaticity determined by calibrant materials within Kr and Xe media indicates stiffening at 15-20 GPa. Above 15-20 GPa, deviation from ideal fcc d-spacing ratios is observed in both Kr and Xe, indicating stress computed for these materials with the cubic lattice strain theory is not reliable. Lattice strain computed for Pt compressed in Kr and Xe indicates a differential stress of at least 5-7 GPa above 40 GPa, in agreement with non-hydrostaticity observed in ruby R1-R2 separation. Texture obtained from radial diffraction data indicates the persistence of broad highly-textured fcc diffraction lines to 101 GPa in Xe, suggesting axial measurements may underestimate the metastable persistence of the fcc phase due to preferred crystallite orientation.

4.1 Introduction

Rare gas solids (RGS) are prototypical van der Waals solids, composed of atoms with filled electron shells which impart an approximately spherical atomic geometry and make them chemically inert at ambient conditions. Another consequence of this electronic configuration is the relatively high freezing pressures of RGS, which crystallize into simple, high-symmetry structures with low strength and high compressibility. The simple structures and systematic behavior of RGS with atomic number make them particularly useful for understanding the role of interatomic potentials and many-body forces in van der Waals bonding under increasing pressure (Hama and Suito, 1989; Polian, Itie, et al., 1989; Boehler et al., 2001; Errandonea et al., 2006). He is hcp at 300 K above its freezing pressure (Franck and Daniels, 1980; Mao et al., 1988), while Ne crystallizes in an fcc structure and is expected to remain fcc to hundreds of terapascals (He, Tang and Pu, 2010), though partial fcc-hcp structure has been proposed based on Raman experiments (Schuberth, Creuzburg and Müller-Lierheim, 1976). Ar, Kr, and Xe undergo a kinetically inhibited, martensitic fcc-hcp phase transition, which may include intermediate structures, as pressure increases (Asaumi, 1984; Jephcoat et al., 1987; Caldwell, 1997; Kim et al., 2006). Both He and Ne retain low strength to multi-Mbar pressures (Takemura, 2001; Takemura et al., 2010; Dorfman et al., 2012; Singh, 2012a), but the progression and mechanism of the fcc-hcp phase transformation of heavy RGS affects physical properties at high-pressure (Rosa et al., 2018; Stavrou et al., 2018; Sanloup, 2020). Effects of pressure on bonding and reactivity in rare gas solids are also important to constraining the roles of these elements in planetary interiors (Jephcoat, 1998; Sanloup, 2020).

Physical properties such as low strength, high freezing pressures, and inert chemistry (Angel *et al.*, 2007) make RGS attractive for experimental purposes, such as pressure-

transmitting media for DAC experiments. The utility of He, Ne, and Ar as pressure media is well-established (Bell and Mao, 1981; Meng, Weidner and Fei, 1993; Klotz *et al.*, 2009; Dorfman *et al.*, 2012; Singh, 2012b and references therein), and Xe has been proposed as a pressure medium because of apparent hydrostaticity observed in ruby fluorescence R1-R2 peak splitting (Asaumi and Ruoff, 1986). Relatively little is known about the strength of either Kr or Xe, or the effect of the fcc-hcp transition on the physical properties of bulk RGS, though stiffening in Kr at ~20 GPa has been observed (Rosa *et al.*, 2018). The strength and deformation mechanisms of rare gas solids (RGS) with pressure can provide important tests of theory for compression of simple solids and yield insight into the nature of bonding and phase equilibria in condensed matter (Kittel, 1996; Errandonea *et al.*, 2006).

The fcc-hcp transition in heavy RGS is anticipated at lower pressures with higher Z (Caldwell, 1997), but the energy difference between the two structures is small (Kwon *et al.*, 1995), and the onset pressures for the transition in the available literature are not in good agreement due to hysteresis along a decompression pathway or heating, which accelerates the phase transition (Eremets *et al.*, 2000; Cynn *et al.*, 2001; Errandonea *et al.*, 2002). At room temperature, stacking faults associated with onset of the fcc-hcp phase transition have been observed at 2.7 GPa in Kr (Rosa *et al.*, 2018) and at 3.7 GPa in Xe (Cynn *et al.*, 2001). These stacking faults have also been observed in Ar after high-temperature annealing at 49.6 GPa (Errandonea *et al.*, 2006). The transition may be further complicated by multiple phase transition mechanisms such as fcc-fco-hcp have not been observed in all models (Li *et al.*, 2017), and the reported XeII phase was not matched to any structures (Jephcoat *et al.*, 1987). The pressure ranges associated with onset of transition have been reported from 5 to 29 GPa for Xe (Cynn *et al.*).

al., 2001; Dewhurst *et al.*, 2002) and 0.8 to 3.2 GPa for Kr (Cynn *et al.*, 2001; Chen *et al.*, 2014), with theoretical prediction of the transition occurring in Kr at 130 GPa (Kwon *et al.*, 1995). The transition in Xe was observed in experiments to be complete at ~70 GPa at 300 K on the basis of disappearance of fcc diffraction lines (Cynn *et al.*, 2001), but is not complete in Kr at pressures up to 140 GPa at 300 K (Rosa *et al.*, 2018). The initiation of the phase transition in Ar is observed with annealing at 49.6 GPa (Errandonea *et al.*, 2006), but experiments have been conducted to at least 80 GPa without observation of hcp Ar (e.g. Mao, Xu and Bell, 1986; Ross *et al.*, 1986) and theory places the upper bound on initiation of the transition at 230 GPa (McMahan, 1986), while completion is expected at 310 GPa (Errandonea *et al.*, 2006). The low-pressure onset of hcp Kr and Xe means that the utility of Kr or Xe as a pressure-transmitting medium in DAC experiments will need to include careful consideration of the strength of both fcc and hcp phases, and the effect of the incomplete phase transition on net physical properties.

Modeling deformation and phase equilibria of the heavy RGS is difficult relative to their lower-Z counterparts because they exhibit increasingly complex electronic interactions as pressure increases (Tsuchiya and Kawamura, 2002; Troitskaya, Val. V. Chabanenko, *et al.*, 2012; Tian *et al.*, 2012). Strength of RGS is generally expected to increase with Z because more electrons are involved in the dipole moment of the respective atoms, which would act to strengthen van der Waals forces within the material. Kr and Xe are therefore expected to be stronger than Ar. The slow kinetics of the fcc-hcp phase transition allow for the presence of both fcc and hcp phases, as well as intermediate structures, across a wide pressure regime in the heavier RGS, and the strength of a mixture of these phases may differ from that of single phases. Deformation and phase equilibria of solid noble gases can be studied with X-ray diffraction and

spectroscopic methods in the diamond anvil cell (DAC). Experimental results may be used to test theoretical models and constrain systematics of the mechanical properties of RGS.

To date, no experimental studies have addressed the effect of the fcc-hcp phase transition on the strength of a multi-phase aggregate of RGS. In this study, we examine the strength of fcc Kr and Xe, and the effect of the fcc-hcp phase transition using analysis of X-ray diffraction and ruby fluorescence in the DAC, supported by theoretical elasticity from density functional theory (DFT) predictions (e.g. Cohen, Stixrude and Wasserman, 1997; Tsuchiya and Kawamura, 2002) for behavior of RGS under high pressure.

4.2 Methods

Compression of sample materials Kr (Praxair or Airgas) or Xe gas (Ingas) was performed in diamond anvil cells. Gases were loaded using the Consortium for Materials Properties Research in Earth Sciences (COMPRES)/GeoSoilEnviro Center for Advanced Radiation Sources (GSECARS) gas loading device at the Advanced Photon Source (APS) at Argonne National Lab (Rivers et al., 2008). Rhenium gaskets pre-indented to thicknesses from ~30-40 µm were used for diffraction and ruby fluorescence experiments conducted in the axial geometry and X-ray transparent beryllium gaskets pre-indented to ~20 µm were used for radial diffraction experiments. Gaskets were drilled onsite using either the GSECARS or the High-Pressure Collaborative Access Team (HPCAT) laser drill facilities (Hrubiak *et al.*, 2015), the GSECARS laser drill, or at MSU using a Hylozoic electronic discharge machine. Pt (Goodfellow) and Ag (Fisher Scientific), and ruby were loaded as internal pressure standards, and Pt and Ag were also used as stress markers. Table 3 provides a summary of experimental runs.

4.2.1 X-ray diffraction

Phase transitions, strain and texture development were measured using angle-dispersive X-ray diffraction obtained in both the axial diffraction geometry in symmetric DACs with X-rays

Run	Sample	Geometry	Pressure Range	Step size (GPa)	Standard	λ (nm)
Kr Al	Kr	Axial	1 bar - 94 GPa	0.5-1	Pt	0.4246
Kr A3	Kr	Axial	1 bar – 47 GPa	3-5	Pt	0.31
Kr P1 Kr R2	Kr Kr	Axial Radial	1 bar - 52 GPa 1 bar - 100 GPa	1-3 1-3	Ruby Ruby	450 0.31
Xe A1	Xe	Axial	1 bar - 83 GPa	3-5	Pt	0.2952
Xe A2a	Xe	Axial	1 bar - 48 GPa	3-5	Ag	0.3344
Xe A2b Xe A3	Xe Xe	Axial Axial	55- 115 GPa 1 Bar - 17 GPa	3-5 0.5-1	Ag Ag	0.31 0.31
Xe P1	Xe	Axial	1 Bar - 33 GPa	1-3	Ruby	532
Xe R3	Xe	Radial	1 Bar - 100 GPa	1-3	Ruby	0.31

Table 3: Summary of experimental runs for Kr and Xe.

parallel to the load axis, and in the radial geometry in a 2-post panoramic DAC with the X-ray beam normal to the loading axis. Axial and radial experiments were conducted at the HPCAT beamline at Argonne National Lab, Sector 16-BM-D. Axial experiments were also conducted at GeoSoilEnviro Center for Advanced Radiation Sources (GSECARS) at Argonne National Lab, Sector 13-ID-D. The X-ray beam at HPCAT was monochromatized to 40 keV (axial experiments) or 37 keV (radial experiments). X-rays were focused to 4-6-µm spot size using Kirkpatrick-Baez focusing mirrors and collimated using a 90-µm pinhole to block tails in beam diameter and minimize diffraction from gasket materials. Diffraction patterns were collected for 60-300s on a MAR2300 image plate detector, which was calibrated using a CeO₂ standard. At GSECARS, a monochromatized 37 keV X-ray beam was focused to 2.5-3- μ m and collected on either the MARCCD 165 or Pilatus detector, calibrated with an LaB₆ standard.

Saturated intensity in each diffraction pattern was masked and diffraction patterns were integrated using Dioptas software (Prescher and Prakapenka, 2015) for axial experiments and Fit2D (Hammersley *et al.*, 1996) for radial data. Axial diffraction peaks were fit with Lorentzian lineshapes using the IgorPro MultipeakFit module (WaveMetrics Inc., Lake Oswego, OR, USA). Radial patterns were divided into 5° azimuthal wedges across a 360° azimuthal range with Fit2D and Fit2D2MAUD for Rietveld refinement. Full-profile refinement of radial patterns was conducted with Materials Analysis Using Diffraction (MAUD) software (Lutterotti, Matthies and Wenk, 1999). Be and BeO phases from the gasket were included in the refinement in addition to sample and internal standards. Global background intensities, as well as phase fraction, unit cell parameters, microstructure and texture for all phases were fit with MAUD. Strain was fit for Xe, Kr, and Pt using the "Radial Diffraction in the DAC" model in MAUD. Texture in all phases was modeled with the a refinable orientation distribution function (ODF) using the extended WIMV (E-WIMV) texture model (Lutterotti *et al.*, 2004).

Pressure in axial diffraction experiments was calculated from the equation of state of Ag (Dewaele *et al.*, 2008) or Pt (Dewaele, Loubeyre and Mezouar, 2004) and unit cell volumes for these metals derived from the (111), (200), (311), and (222) planes for Pt, and the (111) and (200) planes for Ag. Pressure for radial diffraction experiments was determined from fcc Kr and Xe directly by fitting the volumes determined from the refined lattice parameters of the fcc phases to EOS of fcc Kr (Polian, Besson, *et al.*, 1989) or fcc Xe (Cynn *et al.*, 2001).

4.2.2 Ruby fluorescence.

Ruby is a well-characterized stress sensor (Piermarini, 1973; Mao, Xu and Bell, 1986; Syassen, 2008b). Symmetric DACs with 300 µm anvils were loaded with a grid of 8-9 rubies (Figure 20) and the cell chamber was filled with Kr or Xe gas at APS. Xe was compressed in



Figure 20: Photomicrographs of diamond anvil cell sample chambers inside Re gaskets loaded with ruby grids prior to gas-loading. The cell in figure A (left) was loaded with Xe and the cell in figure B (right) was loaded with Kr. Fluorescence measurements for each cell are plotted in Figure 26 and compared with similar measurements for other RGS.

1-3 GPa pressure increments to 33 GPa. Kr was compressed in 1-3 GPa steps to 52 GPa. Fluorescence spectra for each ruby at each pressure step were collected at either the offline ruby system at 16-BM-D (HPCAT) or with an Optiprexx ruby fluorescence system at MSU. The R1 and R2 ruby fluorescence peaks were fit using Lorentzian lineshapes and the local pressure for each ruby was calculated from the R1 and R2 peak positions at ambient temperatures, using the ruby pressure scale of Dewaele et al. (2004).

4.3 Results and discussion

4.3.1 The fcc-hcp phase transition in Kr and Xe

Based on our X-ray diffraction data, we identified the fcc-hcp transition proceeding over a wide pressure range as observed in previous studies of Kr and Xe compressed at room temperature (Jephcoat et al., 1987; e.g. Cynn et al., 2001; Errandonea et al., 2002; Rosa et al., 2018) and peaks from both phases are present through the majority of our diffraction data. All observed diffraction peaks in axial diffraction patterns correspond to either sample (fcc and hcp Kr or Xe) or internal pressure standards (Pt or Ag). In radial diffraction data, additional peaks were observed that correspond to either gasket materials (Be and BeO) or to a previously reported Xe peak related to an as yet undetermined high-pressure phase (Jephcoat et al., 1987). Selected axial 1D diffraction patterns and lattice spacings for Kr and Xe are presented in Figure 21a and Figure 21b and 2D radial diffraction patterns are presented in Figure 22-Figure 26. In our radial data, the onset of the transition to hcp occurs as diffusely scattered intensity which may extend over a range of diffraction angles, up to $\sim 1^{\circ}$ -width in 2 θ , which sharpen into hcp peaks as pressure increases. This signal appears as weak and broad hcp peaks in 1D patterns, and are interpreted as stacking faults and dislocations as in previous reports (e.g. Rosa *et al.*, 2018).

The appearance of these stacking faults on compression is observed at 1.9 and 2.3 GPa in Kr and Xe respectively in axial patterns and at 2.2 GPa in both Xe and in Kr in the radial diffraction patterns. Stacking faults have transformed completely to hcp peaks by 101 GPa (Figure 22a-b). No stacking faults were observed in fcc Xe at 0.7 GPa in the axial geometry or 1.5 GPa in the radial geometry, indicating onset of hcp occurs between 1.5 and 2.2 GPa in Xe, with pressure calibrated on the Xe EOS (Cynn *et al.*, 2001). In Kr, 1.9 GPa was the lowest pressure at which

fcc Kr peaks could be identified in the axial geometry, and 2.2 GPa was the lowest pressure pattern collected for Kr in the radial geometry, with pressure calibrated on the Kr EOS (Polian, Besson, *et al.*, 1989). Our observations are consistent with the onset of stacking faults associated with the martensitic fcc-hcp phase transition previously observed at 2.1-2.7 GPa in Kr (Cynn *et al.*, 2001; Rosa *et al.*, 2018) and ~1 GPa lower than observations at 3.7 GPa in Xe (Cynn *et al.*, 2001). Raman shifts associated with the hcp phase in Xe have been observed at 5 GPa (Sasaki *et al.*, 2009). On decompression, coexistence of the hcp phase has been observed to persist down to 3.2 GPa in Kr and down to 1.5 GPa in Xe (Errandonea *et al.*, 2002).

A weak extra peak that matches neither fcc nor hcp structures appears in Xe at ~57 GPa and increases in intensity to 101 GPa (Figure 26). This peak appears to be consistent with previous identification of a Xe-II phase, though no structure was matched to this peak (Jephcoat *et al.*, 1987). The peak does not match dhcp or bct structures, nor does it match the bcc structure indicated by (Krainyukova, 2011) or the fco structure indicated by (Kim *et al.*, 2006) to be possible intermediate metastable structures formed during the Xe fcc-hcp transition. D-spacing ratios for twinning in the fcc structure (cf. Pashley and Stowell, 1963) also do not explain this peak. It has been proposed that this peak would not occur under quasi-hydrostatic compression (Belonoshko, Ahuja and Johansson, 2001). No extra peaks are present in Kr.

The phase transition from fcc to hcp proceeds more completely at lower pressures in Xe than in Kr (Figure 21, Figure 23-Figure 26). The progress of the transition from fcc to hcp is quantified based on increasing intensity of hcp peaks with decreasing intensity of fcc peaks, with completion of the transition indicated by the disappearance of the fcc 200 diffraction peak. 1D patterns emphasizing the appearance of 100 and 101 hcp peaks and their development with



Figure 21: Axial synchrotron X-ray diffraction patterns for a) Xe (left) and b) Kr (right) with Ag and Pt internal pressure standards, respectively. Intensities of peaks shared between the fcc and hcp phase: fcc (111)/hcp (002), fcc (220)/hcp (110), and fcc (311)/hcp (112), continue to change to 115 GPa, suggesting conversion to hcp is not complete at this pressure. In Kr, stacking faults (SF) remain the only indicator of the hcp phase to 94 GPa.



Figure 22: Unrolled radial 2D diffraction patterns for Xe at 2.3 GPa (a) and 101 GPa (b) illustrating the appearance of stacking faults associated with hcp phase and the subsequent hcp peak development with pressure. The first appearance of diagonal features indicating stacking faults occurs at 2.2 GPa. By 101 GPa, stacking faults have transformed into hcp Xe (100) and hcp Xe (101) diffraction lines.

pressure (Figure 21a-b) illustrate more growth of the hcp phase at lower pressures in Xe relative to Kr. The hcp stacking fault peaks grow dramatically in Xe beginning at pressure ~30 GPa. Previous work on Kr (Rosa *et al.*, 2018) indicated a 20% volume fraction of hcp at 25-29 GPa, and complete transformation to hcp in Xe at ~75 GPa (Cynn *et al.*, 2001). Refined volume fractions from radial patterns indicate only ~4.8% hcp conversion at 22 GPa in Kr, due to the



Figure 23: Radial diffraction patterns for Kr at 10 GPa. Be, Be2, Be3, and BeO peaks are gasket material. Kr hcp peaks appear as stacking faults and increase in occurrence and intensity with pressure. Texture in fcc and hcp Kr peaks is interpreted primarily as crystallization texture. No evidence of significant non-hydrostatic strain in fcc or hcp Kr at 10 GPa.



Figure 24: Radial diffraction patterns for Kr at 94 GPa. Be, Be2, Be3, and BeO peaks are gasket material. Kr hcp peaks appear as stacking faults and increase in occurrence and intensity with pressure. Deformation texture is prevalent in both fcc and hcp Kr peaks and strain is evident as curvature in both fcc and hcp peaks.



Figure 25: Radial diffraction patterns for Xe at 12 GPa. Be, Be2, and BeO peaks are gasket material. Xe hcp peaks initially appear as stacking faults similar to onset of hcp Kr (Figure 23 and Figure 24) and increase in intensity with pressure. Texture at 12 GPa is interpreted as resulting from crystallization of fcc and hcp Xe. There is slight curvature in some diffraction lines, corresponding to qualitatively low non-hydrostatic strain in fcc and hcp Xe at 12 GPa.



Figure 26: Radial diffraction patterns for Xe at 101 GPa. Be and BeO peaks are gasket material. Stacking faults have completely transformed into hcp peaks, and significant strain is evident in hcp and shared fcc/hcp diffraction lines. The fcc 200 diffraction line is broad and highly textured, and strain cannot be reliably assessed for this plane.

lack of sharp hcp peaks and presence of diffuse stacking faults (Figure 26). We observe only ~77% conversion in Xe at 101 GPa and at 94 GPa, only about 18% of Kr is hcp (Figure 27). The



Figure 27: Volume % hcp in Kr and Xe with pressure. The transition proceeds more quickly in Xe than in Kr but is not complete in either phase at Mbar conditions. Rosa et al. (2018) report 20% conversion to hcp Kr at 20 GPa, which is not reached until 94 GPa in our radial analysis. Xe is not fully transformed to hcp at 101 GPa, 30 GPa greater than the estimate of full conversion to hcp at ~70 GPa (Cynn et al., 2001). Peaks from the low pressure fcc phase in Xe are seen at 101 GPa in Figure 26b.

continued presence of intensity from the fcc 200 peak indicates the transition remains incomplete in both phases at the maximum pressures (95-100 GPa). The fcc Xe 200 peak disappears in the axial orientation at ~70 GPa (Figure 21a), however radial data show persistence of fcc 200 peaks to at least 101 GPa. The transition is more sluggish in Kr, and weak peaks that develop at lower pressures remain the only evidence of hcp Kr above 90 GPa (Figure 22b) in axial patterns. Recent work has shown that the transition in Kr remains incomplete, with fcc peaks present up to 140 GPa (Rosa *et al.*, 2018). Our radial data indicate the pressure range observed for the fcc-hcp transition may be underestimated in previous studies due to preferred orientation and sampling bias of axial diffraction geometry. Axial geometry samples diffraction near the minimum stress direction (equivalent to the azimuthal wedge from radial diffraction containing the 90° angle). At this minimum stress orientation, our radial diffraction data for Kr and Xe indicate that intensity of hcp (100) is near a texture maximum, while fcc (111) is near a texture minimum (Figure 23-Figure 26). As a result, previous studies which applied diffraction in the axial geometry to Kr and Xe may be expected to overestimate the volume fraction of hcp and underestimate the pressures required to initiate and complete the phase transition.

4.3.1.1 Texture in Kr and Xe due to phase transition and deformation

The radial diffraction geometry enables observations of preferred orientation developed at all orientations relative to the load axis and analysis of textures generated by phase transitions and plasticity. Representative radial diffraction patterns are presented in Figure 23-Figure 26. Azimuthal variation in intensity (texture) in Kr and Xe are determined with full-profile Rietveld refinement. Texture orientations are determined by analysis of inverse pole figures for Kr and Xe (Figure 28).



Figure 28: Texture evolution in Kr (left) and Xe (right). At low pressure, texture in fcc is probably due to crystallization. There is more initial texture in fcc Kr than in fcc Xe. Deformation texture becomes evident with increasing pressure as a texture maximum develops near (111) in both fcc Kr and fcc Xe. Initial texture in hcp Xe differs from hcp Kr, with initial Xe texture near (2112) in Xe and near (0001) in Kr. Deformation texture on (0001) increases with pressure in hcp Kr, but texture also develops near (2112). By the maximum pressure in both phases, texture in both hcp Kr and hcp Xe is concentrated around (0001).

At the lowest pressures, Kr and Xe crystallize as a few large fcc grains, observed as several diffraction spots. The initial grain size of fcc Xe is larger than the initial Kr grains (Figure 29), and compression rapidly decreases the fcc grain size for both as the weak RGS deform plastically. Significant (100) deformation texture develops by 10 GPa in fcc Kr (Figure 28). Texture in fcc Xe at 12 GPa is weak. At the highest pressures in Kr and Xe, the texture in



Figure 29: Crystallite size in Kr (squares) and Xe (circles) for fcc (main plot) and hcp (inset). Refined grain size decreases with pressure and is \sim 3 orders of magnitude larger in the fcc phase than in hcp phases. The crystallite size for fcc Xe is \sim 2x the size of fcc Kr, but hcp Xe crystallites size parameters refine to smaller values than hcp Kr. Crystallites in the hcp phase for both materials exhibit a slight increase before decreasing again, suggesting grain growth followed by compression.

the last remaining metastable fcc crystallites is (111), indicating this orientation is the most

resistant to transformation.

The hcp phase has also begun to crystallize by 10-12 GPa in both Kr and Xe. At 10 GPa

in hcp Kr, a (0001) texture is evident, which increases with pressure, but also develops near

 $(2\overline{11}2)$ as pressure increases and is then converted back to (0001). In hcp Xe, initial texture is

near $(2\overline{11}2)$, but is also converted to (0001) at higher pressures. We infer that texture evolution

occurs at lower pressures in hcp Xe, following the more complete transformation of fcc to hcp in

Xe.

4.3.2 Strength of Kr and Xe across the phase transition

Effects of the gradual transformation of fcc to hcp structure on the strength and stiffness of Kr and Xe can be evaluated indirectly through the stress transmitted by the Kr and Xe media to enclosed stress sensors and directly through strain in the Kr and Xe structures. Stress applied by the diamond anvil cell is nonhydrostatic, as opposed rigid anvils exert a ~uniaxial stress modified by resistance to flow from the gasket cylinder (Ruoff, 1975). The difference between stress parallel to the load axis σ_3 and radial stress in the gasket plane σ_1 is the differential stress, given by

$$t = (\sigma_3 - \sigma_1) \tag{15}$$

The differential stress sustained by a sample within the DAC is bounded from above by the yield strength or flow stress of the sample or surrounding pressure-transmitting medium (Ruoff, 1975; Singh, 1993). A purely hydrostatic medium supports no differential stress (t = 0) while a quasi-hydrostatic medium supports a low differential stress. A sample that is stronger than the surrounding weaker medium will exhibit elastic strain reflecting the differential stress transmitted by the medium; if the sample is weaker than the surrounding medium, the sample will fail and its strain will be a combination of elastic and plastic strains. In this study, differential stresses supported by Kr and Xe media through the transitions to hcp are assessed in ruby, Pt, and Ag stress sensors. Strain in Kr and Xe media are also examined through analysis of deviation of compression behavior from hydrostatic ideal, observed through diffraction.

4.3.2.1 Non-hydrostatic stress measured by ruby fluorescence.

While the ruby R1 and R2 fluorescence peaks both shift to higher wavelengths with pressure, anisotropy of the ruby crystal results in different positions of the R1 and R2 peaks as non-hydrostatic stress increases. The R2 line is sensitive only to pressure, while the R1 line is

sensitive to both pressure and non-hydrostaticity of the applied stress (Chai and Brown, 1996; Syassen, 2008b). The difference between wavelengths of these peaks thus varies systematically with the stress conditions applied by the DAC and medium and orientation of the ruby crystal relative to the load axis. Non-hydrostatic stress in the DAC may then be determined in three ways; pressure gradients using standard deviation of the pressure of multiple ruby sensors, peak width ($\Delta\Gamma$) of the R1 lines, and the difference in the peak positions of R1-R2 (Forman *et al.*, 1972; Piermarini, 1973; Adams, Appleby and Sharma, 1976). To account for unknown crystallographic orientation of spherical ruby sensors, run-to-run differences in ruby position, spectral and spatial resolution of measurement instrumentation, and variation of stress state across a sample chamber under nonhydrostatic stress, we used the average wavelength difference R1-R2 for a population of rubies positioned across the cell chamber.

Ruby fluorescence was obtained from 8 rubies arranged across the sample chamber within Kr and Xe to 52 and 33 GPa respectively. Similar data have been reported for rubies surrounded by He, Ne and Ar media (Klotz *et al.*, 2009). Rubies compressed in He, Ne, and Ar media report approximately hydrostatic conditions below 15-20 GPa. The increase in the average of the difference R1-R2 for all rubies deviates from the ~hydrostatic trend followed by rubies in Ne and He media above this pressure (Figure 30), supporting stiffening of the media. Rubies compressed in Kr and Xe exhibit more non-hydrostatic stress than those in He, Ne, or Ar below 15-20 GPa, as well, suggesting they are stiffer in this pressure range as well. The R1-R2 values observed in Kr to 52 GPa appear to converge with the R1-R2 value reported in Ar (Klotz *et al.*, 2009), indicating differential stress supported by Kr may be comparable to that supported by Ar.



Figure 30: Difference in ruby R1-R2 peak positions vs pressure for rubies surrounded by RGS media, a measure of hydrostaticity of stress supported by the medium. Ruby peak splitting measured in He medium is inferred to represent ~hydrostatic stress applied to the ruby, and peak splitting values higher than this trend may be observed due to nonhydrostatic stress and anisotropy of the fluorescence behavior for these two fluorescence lines. Ruby peak splitting averaged from 8 or 9 rubies in Ar , Kr, and Xe exhibits an increase in slope indicative of stiffening above 15-20 GPa. The difference R1-R2 for both Kr and Xe is generally larger than for Ar, Ne, and He, indicating that Kr may become less hydrostatic than Ar at ~35 GPa, but Xe is less hydrostatic than all other RGS at all pressures studied.

4.3.2.2 Differential stress measured by lattice strain in Pt and Ag

Lattice strain theory describes the correspondence between crystal lattice spacings observed by way of diffraction and applied nonhydrostatic stress. Lattice spacings vary systematically with orientation, where ψ is the angle between the diffracting plane normal and the loading direction:

$$d_m(hkl) = d_p [1 + (1 - 3\cos^2\psi)Q(hkl)].$$
(16)

In this equation d_m is the measured spacing between lattice planes with Miller indices *hkl* at orientation ψ , and d_p is the lattice-spacing under hydrostatic stress (Singh, Balasingh, *et al.*, 1998). Strain is given by the strain Q(hkl). For purely elastic strain, Q is related to the differential stress *t*, the aggregate Voigt and Reuss shear moduli G_V and G_R , respectively, and α , a constant that describes the weight between isostress and isostrain conditions at grain boundaries (Singh, Balasingh, *et al.*, 1998; Singh and Takemura, 2001):

$$Q(hkl) = \frac{t}{3} \left[\frac{\alpha}{2G_R(hkl)} + \frac{1-\alpha}{2G_V} \right]$$
(17)

These equations can be simplified for the determination of stress and strain in cubic standards Pt and Ag to constrain the strength of the Kr and Xe media. For a cubic crystal structure, Q can be written (Singh, Balasingh, *et al.*, 1998):

$$Q(hkl) = -\frac{\alpha t}{3} (1 - 3\cos^2 \psi) \times \left([S_{11} - S_{12} - 3S\Gamma(hkl)] - (1 - \alpha^{-1}) \frac{5}{2} \frac{(S_{11} - S_{12})S_{44}}{[3(S_{11} - S_{12}) + S_{44}]} \right)$$
(18)

where *S* is the elastic anisotropy of a cubic material, given by $S = (S_{11} - S_{12} - S_{44})/2$, where the S_{ij} are elastic compliances (Singh, 1993), and crystal plane orientation is determined by $\Gamma(hkl) = \frac{(h^2k^2 + k^2l^2 + l^2h^2)}{(h^2 + k^2 + l^2)^2}$. In the axial diffraction geometry, equation (18) is a linear function, expressed in terms of the lattice parameter (Singh, 1993; Singh and Takemura, 2001):

$$a_d(hkl) = M_0 + M_1[3(1 - 3\cos^2\psi)]\Gamma(hkl),$$
(19)

where, $M_0 = Q(hkl)a_P$, and $M_1 = -a_P(\alpha St/3)$. Observed values of a(hkl) vs the orientation function in equation (19) are plotted at selected pressures for Pt compressed in Kr and Xe (Figure 31).

If the elastic anisotropy *S* is known as a function of pressure, differential stress *t* can be determined based on observed cubic lattice spacings. Elasticity of Pt obtained as a function of *P* has previously been calculated by first principles (Menéndez-Proupin and Singh, 2007). Elasticity of Ag at high pressure was extrapolated according to finite strain (Birch, 1978) incorporating ultrasonic EOS data (Holzapfel, Hartwig and Sievers, 2001), ultrasonic measurements of elastic constants $c_{ij}(0)$ (Neighbours and Alers, 1958), and ultrasonic measurements of their derivatives $c_{ij}'(0)$ (Daniels and Smith, 1958).

Differential stress observed in Pt compressed in Kr and Xe increases steadily up to 40 GPa, consistent with significant differential stress sustained in the media, but less differential stress than would be observed with no medium for grain sizes ranging from 70-300 nm (Figure 32a). While Pt with similar grain size would exhibit ~4 GPa differential stress at 10 GPa (Dorfman, Shieh and Duffy, 2015), ~1 GPa differential stress is observed at 10 GPa in Pt within Kr and Xe. At ~40 GPa, the trend of differential stress with pressure in Pt changes slope, consistent with yielding and the onset of plastic deformation in Pt. Above this pressure, the measured *t* in Pt is 5-7 GPa (Figure 32a), similar to flow stress in Pt in no medium (Kavner and Duffy, 2003; Dorfman, Shieh and Duffy, 2015). These conditions correspond to rapid growth of hcp Kr and Xe peaks.

Ag is a softer metal than Pt (particularly the ~nano-grained Pt used in these experiments), and thus yields at lower differential stresses. For Ag compressed in Xe, differential stress remains below 2 GPa to 115 GPa pressure. The strength of Ag determined from lattice strain in



Figure 31: Plots of a(hkl) from axial diffraction lines vs $3 \times (1-3\cos^2 \varphi) \Gamma(hkl)$ for Pt compressed in Kr (top) and Xe (bottom). The slope and intercept of the gamma plots are used with elastic anisotropy to calculate differential stress. A slope of zero corresponds to hydrostatic conditions, and for materials with positive elastic anisotropy such as Pt, the slope becomes increasingly negative as differential stress on the sample increases.

this work is in good agreement with previous work on the strength of silver (Liermann *et al.*, 2010) with grain size ~300 nm up to 40 GPa (Figure 32b). This indicates that the yield strength of Ag is exceeded throughout the experimental pressure range, and thus Ag and cannot be used to determine the strength of Xe. The formation of a connected network of hcp within the fcc matrix may result in stiffening of the heavy RGS, which become stronger than Pt and Ag and induce plastic deformation in the metals.

4.3.2.3 Strain in Kr and Xe

Strain and differential stress can also theoretically be assessed directly in Kr and Xe using axial and radial diffraction data through lattice strain theory, but the broad phase transition and overlapping diffraction peaks between these related structures (Figure 21) and background from the gasket impede separation of the strain of the fcc and hcp structures in the analysis. The lattice strain analysis used above to constrain stress and strain in Pt and Ag based on axial diffraction data depends on relative differences in lattice parameters determined by multiple different diffraction lines e.g. (111) and (200). However, once hcp Kr and Xe begins to form, the fcc (111) line overlaps with the analogous close-packed plane in hcp, 002, and similarly all fcc diffraction peaks except fcc 200 are overlapped with corresponding hcp peaks. With radial diffraction data, observation of lattice spacings at a range of orientations relative to the load axis allows measurement of strain and potentially stress based on a single line, if it does not overlap with diffraction from the gasket.

Deviatoric strain Q(hkl) is observed as curvature in diffraction lines in radial 2D patterns. Q(hkl) was refined or fixed manually for (111), (200), (220), and (311) in fcc and (100_ for hcp Kr and Xe. Due to overlapping diffraction lines between multiple related structures and the Be



Figure 32: Differential stress *t* of metals within RGS media compared to strength of metals, i.e. maximum *t* observed with no medium. a) Pt in Xe (green circles, this study) and Kr (blue and gray squares, this study) media, and no media: red, gold, pink, and black triangles (Dorfman, Shieh and Duffy, 2015), and b) Ag in Xe (green and gray circles, this study), and no media: red and gold triangles (Liermann et al., 2010). Under hydrostatic conditions, *t* is 0. The differential stress supported by Pt in both media remains lower than the strength of Pt below 20 GPa, but then increases rapidly above 20 GPa to match the strength of Pt by ~40 GPa. Ag has been observed to be weaker, and stress supported by Ag in Xe is consistent with the flow stress in Ag throughout the studied pressure range. A change in the EOS of Kr at 20 GPa in previous work (Rosa et al., 2018) was attributed to stiffening induced by the fcc-hcp phase transition.

gasket, some constraints were needed to successfully refine strain for additional *hkl*. For both Kr and Xe, strain in the shared fcc/hcp planes was fixed equal, allowing refinement of hcp (002) with fcc (111), hcp (110) with fcc (220), and hcp (112) with fcc (311). Higher order planes parallel to lower order planes were fixed equal to the corresponding lower order plane, allowing refinement of fcc (222) with fcc (111), hcp (200) with hcp (100), and hcp (004) with hcp (002). Only the *hkl* values for which strain was fit at all pressures were used in the calculation of flow stress. Because of overlap in peaks from shared planes, as well as stacking faults, broadening, and high texture in non-overlapped diffraction lines, we conclude that calculation of flow stress from radial patterns is not quantitatively reliable. Qualitative trends in Q(hkl) which may prove meaningful for comparison to observations of stress markers are discussed below.

Strain in fcc and hcp Kr and Xe is plotted in Figure 33a-d. In both Kr and Xe strain in fcc (111)/hcp (002) and fcc (311)/hcp (112) increases and then levels off or decreases. In fcc (220)/hcp (110) strain increases monotonically above ~20 GPa. Strain in hcp 100 in both Kr and Xe rises at low pressure and then decreases at ~20 GPa to values similar to other *hkl*. Strain in hcp (101) is poorly fit in both Kr and Xe due to intensity and peak width variation arising from stacking faults. The fcc (200) line in Kr and Xe is highly textured, and in Xe it broadens substantially with pressure. It is affected by deviation from the ideal d-spacing ratio in both Kr and Xe, and trades intensity with the adjacent hcp (101) peak. As a result, fitting Q for this line is not reliable.

The strength of fcc Kr and Xe generally increases with pressure. Stiffening in the EOS of Kr is observed at 20 GPa (Rosa *et al.*, 2018) and predicted in Xe at 20 GPa, though the effect in Xe is attributed to a transition to a face-centered orthorhombic (fco) structure (Kim *et al.*, 2006).



Figure 33: Refined strain *Q* for *hkl* from fcc (top, A and B) and hcp (bottom, C and D) Kr (left, A and C) and Xe (right, B and D). Strain in peaks from planes shared between the fcc and hcp structure fcc (111)/hcp (002), fcc (220)/hcp (110), fcc (311)/hcp (112) generally increases with pressure, with some non-monotonic behavior. For hcp 100 in both Kr and Xe, strain is refined successfully, but does not increase systematically with P.

We compared the compression curves and F-f plots (Figure 34) from our axial Kr data to those of Rosa *et al.* (2018), and observe a similar deviation from the normal compression behavior at ~20 GPa. Our radial data suggest only about 7% hcp conversion at this pressure however, and we infer the stiffening is probably not caused by a substantial volume of hcp phase. While strain generally appears to increase in fcc Kr and Xe in our radial data, there is no notable qualitative change in slope at 20 GPa. Non-hydrostaticity at 20 GPa is observed in Kr and Xe by an



Figure 34: Compression curve (a) for Kr (blue circles and yellow circles, this study) with EOS (red line, (Rosa et al., 2018)), and F-f plot (b) with Kr data from this study and red triangles and gray triangles from (Rosa et al., 2018). Red triangles represent F-f values below observed stiffening at $f_E = 0.4$ (corresponding to ~20 GPa pressure), and gray triangles above stiffening. Their assessment of deviation from normal behavior at 20 GPa is supported by our data, though the change in slope at $f_E = 0.4$ is less pronounced in our data. The change at 40 GPa may be attributed to plastic flow in the Pt pressure standard.

increase in ruby R1-R2 separation however (Figure 30). A deviation in ideal ratios of fcc (111)-(200) peak positions in Xe, which could indicate lattice strain due to strengthening of the Xe, which becomes prominent above 20 GPa is also observed in (Jephcoat *et al.*, 1987) and attributed to texture, however our radial data demonstrate that while preferred orientation is present in both fcc and hcp Xe, it does not explain the shift in peak position.

4.4 Conclusions

Phase equilibria, strength, and texture of heavy RGS Kr and Xe have been studied in the diamond anvil cell and have been evaluated in the context of the systematics of the RGS. The onset of the fcc-hcp phase transition is observed at 2.2 and 2.3 GPa in Kr and Xe respectively. Above 15-20 GPa, the d-spacing ratio (111)/(200) deviates from the ideal fcc structure. Overall, the transition proceeds to a larger phase fraction of hcp at lower pressures in Xe than in Kr, but is not complete in Xe to 101 GPa, and progresses over a wider pressure range in Kr than previously reported. Flow stress determined from lattice strain was not accurately determined in the axial geometry, however it must exceed 5 GPa in order to explain deformation observed in Pt compressed in Kr and Xe. This suggests Kr and Xe are similar in strength below 40 GPa and that both are stronger than Ar within this pressure range. This suggests that Kr and Xe are not ideal pressure-transmitting media, as they are remarkably stronger than the lower-Z RGS He and Ne. Strain in fcc diffraction lines remains lower than for fcc Ar, however.

The strength of the hcp phase in Xe appears low indicating the strength calculated from these lines is not capturing the overall strength of the two-phase mixture. This is possibly due to difficulty fitting the fcc (200) line to the non-ideal d-spacing conditions and/or stacking faults confounding accurate fitting of the hcp (100)/(101) lines. There is no significant difference in the overall non-hydrostatic stress supported by Kr or Xe, based on Pt and ruby standards within the medium. Differences in stress reported by R1-R2 ruby fluorescence peaks indicate that non-hydrostaticity in Kr and Xe is higher than other RGS below 52 GPa, with Xe exerting more non-hydrostatic stress than Kr, and both exhibiting stiffening above 15-20 GPa.

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CHAPTER 5: Conclusions and implications of this work

WC, Kr, and Xe exhibit simple crystal structures and cover a range of important physical behavior, including elastic compression, failure, and plastic deformation. In this dissertation, I have used multiple complementary experimental methods in the diamond anvil cell to determine their strength and deformation behavior. In this final chapter, I discuss the conclusions and implications of chapters 2-4 for Earth and materials science. I begin with best practices in the setup of high-pressure experiments. I then discuss the implications of grain size, strength anisotropy, plasticity-modified strength calculations, and the impact of deformation mechanisms and phase transitions on material properties. Understanding the properties of simple materials at high-pressure provides a foundation for work on more complex materials and can guide discovery of similar properties in materials found in the interiors Earth and other planets.

5.1 Some reflections and recommended best practices for experimental

measurements of physical properties at high pressure

Technique is important for obtaining the best results from experiments at high pressure. This includes appropriate experimental setup, DAC preparation, and loading conditions. Careful consideration of diffraction geometry, gasket dimensions, and choice of pressure medium can improve results dramatically. Experiments on Kr and Xe in the radial diffraction geometry clearly show the fcc-hcp phase transition occurs over a much wider pressure range than was detected in the axial geometry. Because experiments in the axial geometry sample minimum strain, calculated unit cell volume may be too high in highly strained materials. Texture minima oriented in the direction of minimum strain could make diffraction peaks invisible in the axial geometry and will affect peak intensity ratios used to calculate phase fraction.
The effects of non-hydrostatic stress on EOS measurements discussed in Chapter 3 is important for measurements of EOS in the DAC. For pressures below ~12 GPa, liquid media may be used, and this will generate truly hydrostatic stresses. For pressures above 12 GPa, Ne remains the ideal candidate for quasi-hydrostatic pressure generation. Ne retains its low strength to upwards of 2.5 Mbar (Dorfman *et al.*, 2012). Ne atoms are larger than He and are less likely to diffuse into samples and affect measurements (e.g. Sato, Funamori and Yagi, 2011; Shen *et al.*, 2011), or diffuse into the anvils and weaken the DAC (Dewaele *et al.*, 2006).

Kr and Xe have not been compressed hydrostatically in any DAC experiments. Compression under quasi-hydrostatic conditions might improve the EOS of both materials. It has also been suggested that hydrostatic compression of Xe could eliminate the extra peak (Belonoshko, Ahuja and Johansson, 2001). Better EOS measurements would improve our understanding of the behavior of heavy RGS in planetary interiors and might help reconcile important differences between experiments and theoretical predcitions (e.g. Sasaki *et al.*, 2008; Troitskaya, V. V. Chabanenko, *et al.*, 2012).

Kr and Xe become sufficiently non-hydrostatic to induce yielding in the Pt marker at ~40 GPa, above which pressure differential stress supported by Pt in Kr and Xe is at least 5-7 GPa. The high strength and additional diffraction intensity from stacking faults and peaks from the onset of the fcc-hcp phase transition occurring below 3 GPa make Kr and Xe poor candidates for pressure transmitting media in DAC experiments unless non-hydrostatic stress is desirable, and the presence of diffraction peaks is not a concern (for example in experiments using Raman or ruby to characterize the sample).

5.2 Grain size effects on elastic deformation behavior

The mineral physics community is actively addressing effects of grain size on plasticity of the crust and mantle (e.g. Karato, 1984; Dannberg *et al.*, 2017; Maierová *et al.*, 2017; Mohiuddin, Karato and Girard, 2020), but the possibility of grain size effects on elasticity is not commonly addressed and thus not well understood. The effects of grain size in Earth science deal with size differences on the order of μ m-mm in the mantle (Solomatov, El-Khozondar and Tikare, 2002; Dannberg *et al.*, 2017) μ m-km in the inner core (Bergman, 1998). The behavior of nano-grain materials may be very different than that of microcrystalline or larger materials, as has been observed in the Hall-Petch effect (Hall, 1951; Petch, 1953; and e.g. Schiøtz, 2001), yet inferences about planet-scale dynamics are routinely made from experiments on materials with ~100 nm grain sizes.

We observe a difference of ~20 GPa in the bulk modulus between nano-crystalline (~50 nm particles) and bulk (micron-scale particles) WC determined under quasi-hydrostatic loading conditions. Similar differences in elasticity have been observed in other materials, but effects of grain size are not systematic. Nano-crystalline WC is less incompressible than its bulk counterpart, similar to many other ceramics (Chen *et al.*, 2002; Al-Khatatbeh, Lee and Kiefer, 2012; Le Godec *et al.*, 2012), but differing from many other materials, including ceramics and metals (Chen *et al.*, 2001; Q F Gu *et al.*, 2008; Q. F. Gu *et al.*, 2008; Mikheykin *et al.*, 2012; Wang *et al.*, 2014; Hong *et al.*, 2015). Changes in the EOS resulting from nano-crystalline grain size may be important to industry for tailored composites (Lin *et al.*, 2011) and the manufacture of hard components. More work is needed to understand these effects in ceramics and other materials. Grain size is also known to affect material hardness (e.g. Hall, 1954; Rice, Wu and

Boichelt, 1994). The effects of size on the bulk modulus (as a parameter of hardness) may be important for better understanding both the incompressibility and the hardness of materials.

Grain size effects include the Hall-Petch relationship for strength and changes in deformation mechanisms (e.g. Yamakov *et al.*, 2003; Cheng *et al.*, 2013). Future work analyzing the effects of nano-crystalline grain size on strength and slip system activities in WC might yield a bigger picture of the interplay between grain size, elasticity, yield strength, and rheological properties in WC, which can guide similar lines of inquiry on other materials. A thorough understanding of the relationships between these properties would allow for optimization of materials in industrial applications, and perhaps help constrain the dynamics of planetary interiors.

5.3 Effects of anisotropy and plasticity on material strength

Very few strength measurements obtained in the DAC provide information on individual lattice planes. In WC the (0001) plane supports remarkably higher differential stress than other *hkil*, consistent with the absence of basal slip predicted by the EVPSC simulation. This could be quite important for understanding mantle dynamics in the Earth and for the production of oriented components which take advantage of this property.

Oriented anvils which take advantage of strength anisotropy may be useful in extending the pressure range of large-volume presses. Multi-anvil devices allow compression of substantially larger volumes of material and generate homogeneous P-T distributions in the sample material (Ishii *et al.*, 2017). This is useful for the production of materials. The use of sintered diamond anvils has greatly improved the pressure regime attainable, but these anvils are much more expensive than WC anvils (Ishii, Liu and Katsura, 2019). Oriented (0001) cubes should be used to maximize pressure in opposed anvil devices using WC anvils. Anisotropic strength has also been observed in a few boride materials, WB (Lei *et al.*, 2018), ZrB₁₂ and YB₁₂ (Lei *et al.*, 2019). Differences in the strength of various *hkil* in WB are attributed to differences in the W-B bond structure. Likewise, our assessment for WC is that covalent W-C bonds and positioning of C-atoms block basal slip and dislocation propagation (Bolton and Redington, 1980). Anisotropic strength is related to elastic anisotropy, which is common in Earth materials. Carbides and borides are probably most similar to alloys or intermetallic compounds in the Earth's core. Experiments to determine the anisotropic strength of Fe and FeNi alloys, as well as compounds such as Fe₃C and Fe₇C₃ would provide information on important materials and could help illuminate seismic anisotropy in the core.

In WC, pyramidal slip activation on $\{10\overline{1}1\}\langle\overline{2}113\rangle$ at 40-50 GPa was needed to induce any yielding of (0001) in the EVPSC simulation. Development of secondary slip systems with pressure have been observed in olivine (Raterron *et al.*, 2011), and are important for accurately describing rheology and viscosity in the mantle. Further work using radial diffraction to isolate strength values for individual *hkil* could provide similar information on other materials, including prominent mineral phases in the deep Earth, and industrial materials used in the manufacture of strong components.

In Chapter 3, EVPSC simulations are used to obtain a more complete assessment the strength of WC calculated from the mean of all *hkil* by including the effects of plasticity. Strength determined from elasticity theory from all planes is the standard reported by most studies on strength in the DAC. It is known that plastic deformation affects strength calculations obtained in this way (Weidner *et al.*, 2004; Raterron and Merkel, 2009). For WC, strength as determined from lattice strain is an overestimate when compared with strength derived from EVPSC simulation. More studies using EVPSC simulations are needed to better constrain the

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strength of other materials in which lattice strain is used to determine strength. This may lead to an improved understanding of slip and strength in industrial materials but is equally relevant to materials in the interiors of planets. Strength determined from EVPSC simulations for MgO at ~5 GPa is higher than all previous experimental measurements (Lin *et al.*, 2017), though still in good agreement with work by Merkel *et al.* (2002), so assumptions that strength is systematically overestimated may not be accurate for all materials. However, these comparisons support the importance of modeling plasticity to support accurate measurement of the yield stress.

5.4 Impact of sluggish phase transitions on physical properties

Gradual phase transitions from element partitioning or metastability are important to plasticity and convection of the mantle over a range of P-T conditions. Partitioning of Al from garnet to bridgmanite (Weidner and Wang, 1998) and of Fe between bridgmanite and pPv (Hernlund, Thomas and Tackley, 2005) near the D'' region at the base of the mantle result in transition gradients composed of two-phase regimes with different bulk properties than either single phase. Metastable, lower-density minerals which persist in the transition zone may increase mantle viscosity and contribute to stagnation of sinking slabs (Faccenda and Dal Zilio, 2017), while the kinetics of the forsterite-wadsleyite-ringwoodite phase transition, which are notably also associated with grain size, may weaken the slabs and alter convection properties (Mohiuddin, Karato and Girard, 2020). Plasticity is associated with the sluggish fcc-hcp transition in Kr and Xe as well. Texture orientations for Kr and Xe vary with pressure in both the fcc and hcp structures.

In the fcc-phase, low-pressure textures are inferred to be associated with crystallization of the fcc phase and high-pressure textures are associated with deformation. For hcp, texture development is more complicated and the LPO changes from the initial crystallization texture on

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(0001), proceeds through texture near (2112) and converts back to (0001). This change in the LPO may be important for understanding the development of LPOs in planetary interiors, and whether they are associated with nucleation or deformation of the minerals involved. It may also be significant for deformation in the interiors of gas planets, where large regions of the planetary interior could exist in a two-phase mixture, potentially weaker than either pure phase because the ongoing transition could accommodate strain. More work is needed to determine strain in the individual phases during the transition, and to separate strength in individual phases and relate them to strength in the two-phase bulk.

Determination of the thermodynamic conditions of phase transformations is important for understanding the effects of pressure on bonding within the material. Changes in bonding can lead to changes in elasticity and conductivity (e.g. metallization). Elasticity affects the transport and storage (Rosa *et al.*, 2020) of Kr and other volatiles in the deep Earth. Conductivity and metallization are important for reactions leading to intermetallic Fe-Xe and Ni-compounds (Dewaele *et al.*, 2017) which are controversial proposed mechanisms for Xe storage in the deep Earth (Caldwell, 1997; Lee and Steinle-Neumann, 2006; Zhu *et al.*, 2014; Dewaele *et al.*, 2017; Stavrou *et al.*, 2018). Future work on the phase diagram of Xe should also include temperature effects. Theoretical P-T behavior of Xe indicates a triple-point with a bcc phase phase at ~2700-4000 K and 25-50 GPa (Belonoshko, Ahuja and Johansson, 2001; Belonoshko *et al.*, 2002; Lukinov *et al.*, 2015). Understanding the phase equilibria of Kr and Xe is important for determining their physical properties at high pressure and their reactions with other materials in the deep Earth.

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