2018 Workshop of the IUCr Commission on High Pressure

Honolulu, HI, July 29-August 2, 2018

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Schedule

Keynote Speakers

- Dr. John Eggert, Lawrence Livermore National Laboratory (U.S.A.)
- Dr. Yongjae Lee, Yonsei University (Korea)
- Dr. Shanti Deemyad, University of Utah, (U.S.A.)

Session 1: Emerging experimental techniques

Conveners: Nandini Garg and Madury Somayazulu
Chairs: Greg Finkelstein and Hannah Shelton

- Dr. Wendy Mao, Stanford University (U.S.A.)
- Dr. Dayne Fratanduono, Lawrence Livermore National Laboratory (U.S.A.)
- Dr. Thomas Meier, University of Bayreuth (Germany)
- Dr. Martin Meven, RWTH Aachen University (Germany)
- Dr. Camelia Stan, Lawrence Berkeley National Lab (USA)

Session 2: Advanced synchrotron and optical characterization of materials at extreme conditions

Chairs: Vitali Prakapenka and Dongzhou Zhang

- Dr. Viktor Struzhkin, Carnegie institution for Science, Washington D.C. (USA)
- Dr. Oliver Tschauner, University of Nevada, Las Vegas, NV (USA)
- Dr. Stanislav Sinogeikin, HPCAT, Argonne, IL (USA)
- Dr. Anna Pakhomova, DESY, Hamburg (Germany)
- Dr. Gaston Garbarino, ESRF, Grenoble (France)
- Dr. Yoshinori Tange, Spring-8 (Japan)
- Dr. Ross Howie, HPSTAR (China)
- Dr. Christopher A. Tulk, Oak Ridge National Laboratory (U.S.A.)
- Dr. Bin Chen, University of Hawaii, Honolulu, HI (USA)
- Dr. Przemyslaw Dera, University of Hawaii, Honolulu, HI (USA)
- Dr. Nicholas Holtgrewe, GSECARS, University of Chicago, Chicago, IL (U.S.A.)

Session 3: New frontiers in extreme conditions crystallography

Chairs: Amy Lazicki and David McGonagle

- Dr. Takeshi Sakai, Ehime University (Japan)
- Dr. Christopher Wehrenberg, Lawrence Livermore National Laboratory, (U.S.A.)
- Dr. Stewart McWilliams, University of Edinburgh, (U.K.)
- Dr. Earl O'Bannon, Lawrence Livermore National Laboratory, (U.S.A.)

Session 4: High pressure chemistry and synthesis

Chairs: Kamil Dziubek and Andrzej Katrusiak

- Dr. Christine Beavers, Advanced Light Sources, (U.S.A)
- Dr. David Allan, Diamond Light Source, (U.K.)
- Dr. Weizhao Cai, University of Utah, (U.S.A.)
- Dr. James Walsh, Northwestern University, (U.S.A.)
- Dr. Sebastian Vogel, University of Munich, (Germany)

Session 5: Materials science

Chair Haozhe Liu and Nenad Velisavljevic

- Dr. Siddhartha Pathak, University of Nevada, Reno (U.S.A.)
- Dr. Sheng-Yi Xie, Hunan University (China)
- Dr. Qiaoshi Zeng, HPSTAR (China)
- Dr. Zhidan Zeng, HPSTAR (China)
- Dr. Haozhe Liu, HPSTAR (China)

Session 6: Materials metastability under pressure

Chairs: Gouyin Shen and Peter Lazor

- Dr. Peter Lazor, Uppsala University (Sweden)
- Dr. Jodie Bradby, National University (Australia)
- Dr. Sung-kuen Lee, Seoul National University (Korea)
- Dr. Guoyin Shen, Carnegie Institution for Science, Argonne,IL (USA)
- Hannah Shelton, University of Hawaii at Manoa (U.S.A.)

Session 7: High-pressure crystallography in earth and planetary science

Chairs: Jiuhua Chen and Bin Chen

- Dr. Ho-kwang (David) Mao, HPSTAR (China)
- Dr. Yingwei Fei, Carnegie Institution (U.S.A.)
- Dr. Jonathan Z. Tischler, Argonne National Lab (U.S.A.)
- Dr. Jin Liu, Stanford University (U.S.A.)
- Dr. Li Zhang, HPSTAR (China)
- Dr. Ronald Miletich, University of Vienna (Austria)

Session 8: Electronic and magnetic materials at extreme conditions

Chairs: Narcizo Souza-Neto and Yang Ding

- Dr. Gilberto Fabbris, Advanced Photon Source, Argonne National Laboratory (U.S.A.)
- Dr. Mingliang Tian , Hefei Institutes of Physical Science Chinese Academy of Science (China)
- Dr. Ricardo Reis, Brazilian Synchrotron Light Laboratory (Brazil)
- Dr. Audrey Grockowiak, National High Magnetic Field Laboratory (U.S.A.)
- Dr. Xiancheng Wang, Institute of Physics, Chinese Academy of Science (China)
- Dr. Xiangang Wan, Nanjing University (China)
- Dr. Cheng-Chien Chen, University of Alabama at Birmingham,(U.S.A.)
- Dr. Weiwei Xie, Louisiana State University (U.S.A.)

Session 9: Computational approaches in extreme conditions science

Chairs: Zhongquing Wu and John Tse

- Dr. Koichiro Umemoto, Earth-Life Science Institute (ELSI), Tokyo Institute of Technology (Japan)
- Dr. Shuai Zhang, Lawrence Livermore National Laboratory (U.S.A.)
- Dr. Rajeev Ahuja, Uppsala University (Sweden)
- Dr. Zhongqing Wu, USTC (China)
- Dr. John Tse, University of Sasketchuan (Canada)

		Sunday 29-Jul	Monday 30-Jul	Tuesday 31-Jul	Wednesday 1-Aug	Thursday 2-Aug
8:00	8:30	Single-Crystal Training	Opening Remarks	Session 3	Session 6	Keynote 3
8:30	9:00		Session 1			
9:00	9:30					Session 8
9:30	10:00					
10:00	10:30			Session 4		
10:30	11:00		Coffee	Coffee	Coffee	Coffee
11:00	11:30				Keynote 2	
11:30	12:00		Session 2			
12:00	12:30				Session 7	
12:30	1:00					
1:00	1:30		Lunch	Lunch	Lunch	Lunch
1:30	2:00					
2:00	2:30					
2:30	3:00			Keynote 1		
3:00	3:30					Session 9
3:30	4:00		Coffee	Coffee	Coffee	Coffee
4:00	4:30			Session 5		
4:30	5:00					
5:00	5:30				Women Under Pressure	
5:30	6:00					
6:00	6:30	Welcome Reception			Poster Session	Closing Remarks
6:30	7:00					
7:00	7:30			Conference Dinner		
7:30	8:00					
8:00	8:30					
8:30	9:00					

Oral Presentations

Presenting author		Institution	Email	Presentation title	Session
Yongjae	Lee	Yonsei University/HPSTAR	yongjaelee@yonsei.ac.kr	Super-hydration from zeolites to clay	Keynote
Wendy	Mao	Stanford University	wmao@stanford.edu	Nanoscale x-ray imaging in a diamond anvil cell	Session 1: Emerging experimental techniques (Chairs: Greg Finkelstein and Hannah Shelton)
Dayne	Fratanduono	Lawrence Livermore National Laboratory	fratanduono1@llnl.gov	Phase transformation kinetics and the liquid structure factor of shock compressed Sn	Session 1: Emerging experimental techniques (Chairs: Greg Finkelstein and Hannah Shelton)
Thomas	Meier	Bayreuth University	thomas.meier@uni-bayreuth.de	On the way to NMR at Mega-bar Pressures: Observation of Nuclear Quantum Effects and Hydrogen Bond Symmetrization in High Pressure Ices	Session 1: Emerging experimental techniques (Chairs: Greg Finkelstein and Hannah Shelton)
Martin	Meven	RWTH Aachen University	martin.meven@frm2.tum.de	New High Pressure Cells for Single Crystal Diffraction with Hot Neutrons at the Heinz Maier-Leibnitz Zentrum (MLZ)	Session 1: Emerging experimental techniques (Chairs: Greg Finkelstein and Hannah Shelton)
Camelia	Stan	Lawrence Berkeley National Laboratory	cstan@lbl.gov	Tandem X-ray microdiffraction and microfluorescence for high-pressure materials characterization	Session 1: Emerging experimental techniques (Chairs: Greg Finkelstein and Hannah Shelton)
Viktor	Struzhkin	Carnegie Institution of Washington	vstruzhkin@carnegiescience.edu	Synthesis of new hydrides at high pressures	Session 2: Advanced synchrotron and optical characterization of materials at extreme conditions (Chairs: Vitali Prakapenka and Dongzhou Zhang)

Oliver	Tschauner	UNLV	olivert@physics.unlv.edu	Ice-VII and other natural mineral inclusions of former dense fluid components in diamonds from the deep mantle	Session 2: Advanced synchrotron and optical characterization of materials at extreme conditions (Chairs: Vitali Prakapenka and Dongzhou Zhang)
Stanislav	Sinogeikin	Carnegie Institution of Washington	ssinogeikin@carnegiescience.edu	Advanced synchrotron techniques for high-pressure high/low temperature research at HPCAT, Advanced Photon Source	Session 2: Advanced synchrotron and optical characterization of materials at extreme conditions (Chairs: Vitali Prakapenka and Dongzhou Zhang)
Anna	Pakhomova	Deutsches Elektronen-Synchrotron (DESY)	anna.pakhomova@desy.de	The Extreme Conditions Beamline (P02.2) at PETRA III (DESY): Recent advances and Outlook	Session 2: Advanced synchrotron and optical characterization of materials at extreme conditions (Chairs: Vitali Prakapenka and Dongzhou Zhang)
Gaston	Garbarino	European Synchrotron Radiation Facility (ESRF)	gaston.garbarino@esrf.fr	Extreme conditions studies at ID27 ESRF beamline: present and future status	Session 2: Advanced synchrotron and optical characterization of materials at extreme conditions (Chairs: Vitali Prakapenka and Dongzhou Zhang)
Yoshinori	Tange	Japan Synchrotron Radiation Research Institute	yoshinori.tange@spring8.or.jp	Time-resolved XFEL observation of shock-wave propagating material	Session 2: Advanced synchrotron and optical characterization of materials at extreme conditions (Chairs: Vitali Prakapenka and Dongzhou Zhang)
Ross	Howie	HPSTAR	ross.howie@hpstar.ac.cn	Synthesis and characterization of novel hydrides at high pressure and temperature	Session 2: Advanced synchrotron and optical characterization of materials at extreme conditions (Chairs: Vitali Prakapenka and Dongzhou Zhang)
Chris	Tulk	Oak Ridge National Laboratory	Tulkca@ornl.gov	An Update on Recent Developments and Research in High Pressure Neutron Scattering	Session 2: Advanced synchrotron and optical characterization of materials at extreme conditions (Chairs: Vitali Prakapenka and Dongzhou Zhang)
Bin	Chen	University of Hawaii at Manoa	binchen@hawaii.edu	Elasticity of single crystal ice VII up to 30 GPa	Session 2: Advanced synchrotron and optical characterization of materials at extreme conditions (Chairs: Vitali Prakapenka and Dongzhou Zhang)

Nicholas	Holtgrewe	University of Chicago	nicholas.holtgrewe@gmail.com	Advanced high-resolution integrated optical system for diamond anvil cell studies	Session 2: Advanced synchrotron and optical characterization of materials at extreme conditions (Chairs: Vitali Prakapenka and Dongzhou Zhang)
Przemyslaw	Dera	University of Hawaii at Manoa	pdera@hawaii.edu	Hypervalent penta-coordinated silicon and metastable phase transitions in chain silicates	Session 2: Advanced synchrotron and optical characterization of materials at extreme conditions (Chairs: Vitali Prakapenka and Dongzhou Zhang)
Takeshi	Sakai	Ehime University	sakai@ehime-u.ac.jp	Technical development of double-stage diamond anvil cell and equations of state at multi-megabar condition	Session 3: New frontiers in extreme conditions crystallography (Chairs: Amy Lazicki and David McGonegle)
Christopher	Wehrenberg	Lawrence Livermore National Laboratory	wehrenberg1@llnl.gov	Measuring twinning and slip during shock-compression of Ta from in-situ x-ray diffraction	Session 3: New frontiers in extreme conditions crystallography (Chairs: Amy Lazicki and David McGonegle)
Stewart	McWilliams	University of Edinburgh	rs.mcwilliams@ed.ac.uk	New advances in free electron laser x-ray diffraction under pressure: from complex structures to dynamic diamond cells	Session 3: New frontiers in extreme conditions crystallography (Chairs: Amy Lazicki and David McGonegle)
Earl	O'Bannon	Lawrence Livermore National Laboratory	obannon2@llnl.gov	Powder diffraction of simple metals at pressures greater than 5.0 Mbars	Session 3: New frontiers in extreme conditions crystallography (Chairs: Amy Lazicki and David McGonegle)
Christine	Beavers	UC Santa Cruz/LBNL	cmbeavers@lbl.gov	Coordination Chemistry & Porous Materials at High Pressure: What the Mineral Physicists Don’t Experience	Session 4: High pressure chemistry and synthesis (Chairs: Kamil Dziubek and Andrzej Katrusiak)
David	Allan	Diamond Light Source	david.allan@diamond.ac.uk	High-pressure structural chemistry studies on beamline I19 at Diamond Light Source	Session 4: High pressure chemistry and synthesis (Chairs: Kamil Dziubek and Andrzej Katrusiak)
Weizhao	Cai	University of Utah	wzhcai@gmail.com	High pressure behavior of hydrocarbons: case studies on benzene & benz[a]anthracene	Session 4: High pressure chemistry and synthesis (Chairs: Kamil Dziubek and Andrzej Katrusiak)

James	Walsh	Northwestern University	james.walsh@northwestern.edu	High-Pressure Synthesis of Novel Binary Intermetallics	Session 4: High pressure chemistry and synthesis (Chairs: Kamil Dziubek and Andrzej Katrusiak)
Sebastian	Vogel	University of Munich (LMU)	Sebastian.Vogel@cup.uni-muenchen.de	Phosphorus on the Brink of Six-fold Coordination in Nitride Compounds	Session 4: High pressure chemistry and synthesis (Chairs: Kamil Dziubek and Andrzej Katrusiak)
Sid	Pathak	University of Nevada, Reno	spathak@unr.edu	Structure and Properties of Pseudomorphically Transformed bcc Mg Synthesized Using Interface Strain Engineering	Session 5: Materials science (Chair: Haozhe Liu and Nenad Velisavljevic)
Sheng-Yi	Xie	Hunan University	shengyi_xie@hnu.edu.cn	Correlated High-Pressure Phase Sequence of Metal-dioxides under Strong Compression	Session 5: Materials science (Chair: Haozhe Liu and Nenad Velisavljevic)
Qiaoshi	Zeng	HPSTAR	zengqs@hpstar.ac.cn	Two-way tuning of order in a disordered metallic glass	Session 5: Materials science (Chair: Haozhe Liu and Nenad Velisavljevic)
Zhidan	Zeng	Center for High Pressure Science and Technology Advanced Research (HPSTAR)	zengzd@hpstar.ac.cn	Synthesis of quenchable amorphous diamond under high pressure and temperature	Session 5: Materials science (Chair: Haozhe Liu and Nenad Velisavljevic)
Peter	Lazor	Uppsala University	Peter.Lazor@geo.uu.se	Phase Transitions and Magnetovolume Anomaly in CoCrFeNixAl1-x (x = 0, 0.5, 0.75) High-Entropy Alloys	Session 6: Materials metastability under pressure (Chair: Guoyin Shen and Peter Lazor)
Jodie	Bradby	The Australian National University	jodie.bradby@anu.edu.au	Using both nanoindentation and diamond anvil cells to understand phase transformations in Si, Ge and Glassy Carbon	Session 6: Materials metastability under pressure (Chair: Guoyin Shen and Peter Lazor)
Sung Keun	Lee	Seoul National University	sungklee@snu.ac.kr	Nature of amorphous oxides under extreme compression via solid-state NMR and inelastic X-ray scattering	Session 6: Materials metastability under pressure (Chair: Guoyin Shen and Peter Lazor)

Guoyin	Shen	Carnegie Institution for Science	gshen@ciw.edu	Metastable melting under decompression	Session 6: Materials metastability under pressure (Chair: Guoyin Shen and Peter Lazor)
Hannah	Shelton	University of Hawaii at Manoa	sheltonh@hawaii.edu	The ideal crystal structure of cristobalite X-I: A bridge in SiO2 densification	Session 6: Materials metastability under pressure (Chair: Guoyin Shen and Peter Lazor)
Ho-Kwang	Mao	HPSTAR	maohk@hpstar.ac.cn	Crystal structures of high-pressure solid phases of hydrogen to 230 GPa based on x-ray diffraction	Session 7: High-pressure crystallography in earth and planetary science (Chairs: Jiuhua Chen and Bin Chen)
Yingwei	Fei	Carnegie Institution of Washington	yfei@carnegiescience.edu	Planetary core compositions constrained from density measurements and chemical differentiation	Session 7: High-pressure crystallography in earth and planetary science (Chairs: Jiuhua Chen and Bin Chen)
Jon	Tischler	Argonne National Laboratory	tischler@anl.gov	Application of sub-micron x-ray beams to diffraction from small high pressure samples.	Session 7: High-pressure crystallography in earth and planetary science (Chairs: Jiuhua Chen and Bin Chen)
Jin	Liu	Stanford University	jinliuyc@gmail.com	Oxygenated iron oxide at Earth's lower mantle conditions	Session 7: High-pressure crystallography in earth and planetary science (Chairs: Jiuhua Chen and Bin Chen)
Li	Zhang	Center for High Pressure Science and Technology Advanced Research (HPSTAR)	zhangli@hpstar.ac.cn	Interaction of major volatiles with the lower mantle: a multigrain approach	Session 7: High-pressure crystallography in earth and planetary science (Chairs: Jiuhua Chen and Bin Chen)
Ronald	Miletich	University of Vienna	ronald.miletich-pawliczek@univie.ac.at	Crystalline polymeric carbon dioxide is stable at megabar conditions	Session 7: High-pressure crystallography in earth and planetary science (Chairs: Jiuhua Chen and Bin Chen)
Gilberto	Fabbris	Argonne National Laboratory	gfabbris@anl.gov	Probing the electronic structure and magnetism of 5d materials using resonant x-ray techniques at high pressure	Session 8: Electronic and magnetic materials at extreme conditions (Chairs: Narcizo Souza-Neto and Yang Ding)

Mingliang	Tian	Hefei Institute of Physical Science，CAS， Hefei 230031， China	tianml@hmfl.ac.cn	Quantum transport property in trigonal layered PtBi2: a possible new triply degenerate point fermions and pressure-induced superconductivity	Session 8: Electronic and magnetic materials at extreme conditions (Chairs: Narcizo Souza-Neto and Yang Ding)
Ricardo	Dos Reis	Brazilian Center for Research in Energy and Materials (CNPEM)	ricardo.reis@lnls.br	Pressure tuning the Fermi surface topology of Weyl semimetals	Session 8: Electronic and magnetic materials at extreme conditions (Chairs: Narcizo Souza-Neto and Yang Ding)
Audrey	Grockowiak	Florida State University	grockowiak@magnet.fsu.edu	High pressure, high magnetic field Fermiology studies of YBCO	Session 8: Electronic and magnetic materials at extreme conditions (Chairs: Narcizo Souza-Neto and Yang Ding)
Xiancheng	Wang	Institute of Physics, Chinese Academy of Science	wangxiancheng@iphy.ac.cn	A New Quasi One-Dimensional Compound Ba3TiTe5 and Superconductivity Induced by Pressure	Session 8: Electronic and magnetic materials at extreme conditions (Chairs: Narcizo Souza-Neto and Yang Ding)
Xiangang	Wan	Nanjing University	xgwan@nju.edu.cn	Theoretical study of the magnetic anisotropy energy in bulk Na4IrO4	Session 8: Electronic and magnetic materials at extreme conditions (Chairs: Narcizo Souza-Neto and Yang Ding)
Cheng-Chien	Chen	University of Alabama at Birmingham	chencc@uab.edu	Computational Modeling of Mechanical and Electronic Properties of Superhard Boron-Carbon Materials	Session 8: Electronic and magnetic materials at extreme conditions (Chairs: Narcizo Souza-Neto and Yang Ding)
Weiwei	Xie	Louisiana State University	weiweix@lsu.edu	Dimorphic SrMn2P2 under variant pressures - Theory and experiment in harmony	Session 8: Electronic and magnetic materials at extreme conditions (Chairs: Narcizo Souza-Neto and Yang Ding)
Koichiro	Umemoto	Tokyo Institute of Technology	umeomto@elsi.jp	Post-post-perovskite transitions in MgSiO3 by first principles	Session 9: Computational approaches in extreme conditions science (Chairs: Zhongquing Wu and John Tse)

Shuai	Zhang	Lawrence Livermore National Laboratory	zhang49@llnl.gov	Equations of state of carbon- and boron-materials by path integral Monte Carlo and density function theory simulations	Session 9: Computational approaches in extreme conditions science (Chairs: Zhongquing Wu and John Tse)
Rajeev	Ahuja	Uppsala University	rajeev.ahuja@physics.uu.se	Structural prediction of host-guest structure in Lithium at high pressure	Session 9: Computational approaches in extreme conditions science (Chairs: Zhongquing Wu and John Tse)
Zhongqing	Wu	USTC	wuzq10@ustc.edu.cn	Exploring the Earth's interior with the elasticity of minerals at high pressure and temperature	Session 9: Computational approaches in extreme conditions science (Chairs: Zhongquing Wu and John Tse)
John	Tse	University of Saskatchewan	john.tse@usask.ca	The Electronic Ground State of FeO_2	Session 9: Computational approaches in extreme conditions science (Chairs: Zhongquing Wu and John Tse)

Poster Presentations

Presenting author		Institution	Email	Presentation title
Abhishek	Chitnis	Bhabha Atomic Research Centre	abhishekchitnis87@gmail.com	The Effect of Electronegativity and Size of Divalent Metal Ion on Pressure Evolution of DmAMF
Amalia	Fernandez Panella	Lawrence Livermore National Laboratory	fernandezpan1@llnl.gov	X-ray diffraction of ramp-compressed copper up to 1.2 TPa
Amy	Lazicki	Lawrence Livermore National Laboratory	lazicki1@llnl.gov	Structure at Terapascal pressures from in-situ powder x-ray diffraction of laser ramp-compressed Magnesium
Anna	Pakhomova	Deutsches Elektronen-Synchrotron (DESY)	anna.pakhomova@desy.de	High-pressure phases of feldspars with five- and six-fold coordinated aluminium
Banele	Vatsha	University of Johannesburg	bvatsha@uj.ac.za	Ascertaining structural responses of porous soft crystals in comparatively moderate-high pressure environments
Christian	Plückthun	European X-ray Free_Electron Laser Facility GmbH (European XFEL)	christian.plueckthun@xfel.eu	The dynamic diamond anvil cell (dDAC) at the HED instrument of the European XFEL
Dongzhou	Zhang	University of Hawaii at Manoa	dzhang@hawaii.edu	High pressure single crystal diffraction at PX^2
Eleanor	Berryman	Princeton University	eb14@princeton.edu	High-pressure compressibility of synthetic tourmaline of near end-member compositions
Howard	Yanxon	University of Nevada Las Vegas and HiPSEC	yanxonh@unlv.nevada.edu	Structural Phase Transition of 1T-TiTe2
Jinfu	Shu	Center for High Pressure Science and Technology Advanced Research (HPSTAR)	jinfu.shu@hpstar.ac.cn	High-temperature and high-pressure shock causes thedecomposition of Ankerite to produce diamond and high-pressure iron magnesiumoxide（New mineral-Maohokite）

Jinlong	Zhu	HPSTAR	jinlong.zhu@hpstar.ac.cn	The Energy CH4 Gas Extraction by CO2 Substitution inClathrate Hydrate through Bimolecular Iteration
Kamil	Dziubek	LENS - European Laboratory for Non-Linear Spectroscopy	dziubek@lens.unifi.it	Pseudosymmetry in high pressure phosphorus and the phase relations in group 15 elements
Lijuan	Wang	HPSTAR	lijuan.wang@hpstar.ac.cn	10^9 -Fold conductivity enhancement of Li 2 C 2 : pressure-induced polymerization and disproportionation
Marcin	Sliwa	University of Oxford	marcin.sliwa@physics.ox.ac.uk	Femtosecond X-Ray Diffraction Studies of the Reversal of the Microstructural Effects of Plastic Deformation during Shock Release of Tantalum
Mary-Ellen	Donnelly	HPSTAR	mary-ellen.donnelly@hpstar.ac.cn	Metastable Synthesis of Gas Clathrates
Melissa	Sims	Stony Brook University	melissa.sims@stonybrook.edu	Deformation in olivine during rapid compression as an analogue for shock processes
Peng	Liu	Institute of High Energy Physics， Chinese Academy of Sciences	liup@iihep.ac.cn	High throughput experiment technology for synchrotron radiation high pressure diffraction
Sasithorn	Chornkrathok	University of Hawaii at Manoa	cs65@hawaii.edu	Structure and behavior of the Ni end-member schreibersite, (Ni3P), under deep Earth conditions
Shuhua	Yuan	Center for High Pressure Science and Technology Advanced Research	shuhua.yuan@hpstar.ac.cn	In situ XRD measurement for Se under pressure over 200 GPa
Takanori	Hattori	Japan Atomic Energy Agency	hattori.takanori@jaea.go.jp	Is there a liquid-liquid phase transition in Cs?
Takanori	Hattori	Japan Atomic Energy Agency	hattori.takanori@jaea.go.jp	Recent Developments of High-Pressure Neutron Experiments in J-PARC

Tommy	Yong	University of Hawaii at Manoa	tyong@hawaii.edu	Single-crystal X-ray diffraction of grunerite up to 25.6 GPa: A new high-pressure clinoamphibole polymorph
Vitali	Prakapenka	University of Chicago	prakapenka@cars.uchicago.edu	Cutting-edge synchrotron facilities for advanced sample characterization at extreme conditions
Weiwei	Dong	Institute of High Energy Physics， Chinese Academy of Sciences	dongww@ihep.ac.cn	Study the high pressure phase transition of ZnO with the wide-band synchrotron radiation
Xiaodong	Li	Institute of High Energy Physics， CAS	lixd@ihep.ac.cn	Design of high pressure beamline at HEPS
Xuejing	He	Peking University	xuejinghe@pku.edu.cn	High-pressure Equation of State of Schreibersite Fe2.15Ni0.85P
Yong-Hyun	Kim	Seoul National University	kyoh19@snu.ac.kr	Inelastic x-ray scattering of silica glasses beyond megabar pressure
Danae	Polsin	Laboratory for Laser Energetics	dpol@lle.rochester.edu	X-Ray Diffraction of Ramp-Compressed Sodium
Zachary	Fussell	University of Nevada Las Vegas	fussellz@unlv.nevada.edu	Shock Recovery of High-Pressure Bismuth-II

Nanoscale x-ray imaging in a diamond anvil cell

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Keywords: high pressure, x-ray imaging

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Coupling nanoscale x-ray transmission microscopy (nanoTXM) with a diamond anvil cell has exciting potential as a powerful 3D probe for non-destructive imaging at high spatial resolution of materials under extreme conditions. We discuss recent developments in conducting high pressure nanoTXM experiments at 3rd generation synchrotron sources including some of the technical considerations for successful measurements. We present results from recent in-situ high pressure measurements which illustrate the potential for this technique to address a wide range of research areas ranging from condensed matter physics and solid state chemistry to materials science and understanding planetary interiors. Future directions for this exciting technique are discussed.

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Phase transformation kinetics and the liquid structure factor of shock compressed Sn

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Keywords: synchrotron radiation, shock compression, liquid structures

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Over the past decade, laser drivers coupled to x-ray sources have been a fruitful area of science exploring the effects rapid pressure loading have on phase transitions. With recent improvements to x-ray sources, experimental techniques and diagnostics, probing the structure of dynamically compressed liquids at ultrafast timescales is within reach. In this work, using the Matter in Extreme Conditions (MEC) end station of the Linac Coherent Light Source (LCLS), we explore the solid phase and the liquid structure of shock-compressed tin.

Polycrystalline Sn foils of 99.95% purity and 20 µm thickness were shock compressed using the dual arm Nd:glass nanosecond drive laser at MEC. The LCLS x-ray probe beam is timed to probe the sample at peak compression and diffraction is collected in a transmission geometry. The ultra-high flux of the LCLS (~10^{12} photons in 50 fs) provides high quality x-ray diffraction of the crystalline and liquid states of shock-compressed materials.

Within the solid phase, we explored the Peierls distorted system (where the lattice lowers its symmetry to reach a lower energy state). These results show that there is a significant under-driving of the tetragonal → cubic phase transition as well as the solid → liquid transition, which contradicts our current understanding of material behavior under rapid pressure loading.

We also explored the pressure-temperature evolution of the liquid structure factor. In angle dispersive x-ray diffraction of crystalline materials, the long-range order of the crystal lattice is probed by the interference of monochromatic x rays and a crystalline sample. The interactions of the incident x rays with the crystalline sample produce constructive interferance when the conditions satisfy Bragg's law. This interference produces a diffraction pattern which can be used to determine the crystal structure. In a liquid, the long-range order of the system is lost. X-ray diffraction can be used to probe the medium range order by measuring the structure factor and extracting the radial-distribution function. The radial distribution function describes how the density of the system varies as a function of distance from a central particle. Using a monochromatic x-ray source, the intensity of x rays scattered through an angle 2θ from a liquid sample containing N atoms is $I(q) = N[f(q)]^2 S(q)$ where $q = 4\pi \sin(\theta)/\lambda$, λ is the x-ray wavelength, $f(q)$ is the scattering amplitude and $S(q)$ is the liquid structure factor. The measured structure factor can then be used to determinate the radial-distribution function by a Fourier transform: $g(r) = 1 + \frac{1}{2\pi^2 r\rho}\int_0^{qmax}[S(q) - 1]q\sin(qr)\,dq$.

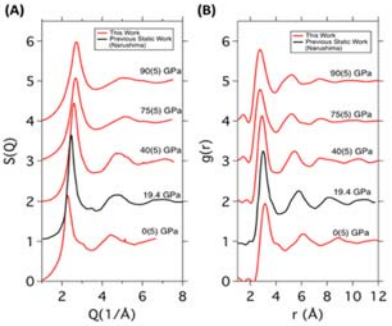

Figure 1: The liquid structure factor and the radial distribution function for tin are are shown in (A) and (B) respectively. Previous static work of Narushima [1] is shown in black can compares well to our dynamic work, shown in

Little is currently known regarding the liquid structure of materials at extreme conditions of high-pressure and high-temperature. The study of liquids under static high-pressure conditions has become a productive area of research over the past two decades. Due to recent advances, it is now possible to accurately determine liquid-liquid, changes in structural parameters, and liquid density through x-ray diffraction measurements. Using high energy x-rays that extend the Q-range to ~ 8 $Å^{-1}$, we are able to extract the liquid structure factor. The first results are presented here on shock compressed Sn up to ~ 100 GPa.

In his work, we obtained the liquid structure factor and the radial distribution function of shock compressed Sn, as shown in Figure 1. We find that Sn retains 8-10 fold coordination within the liquid. Further work is required to improve the experimental technique and optimization routine inorder to extract density measurements from the liquid XRD data.

[1] Narushima, T., et al. (2007). Physical Review B 76(10): 104204.

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On the way to NMR at mega-bar pressures: Observation of nuclear quantum effects and hydrogen bond symmetrization in high-pressure ices

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Keywords: nuclear magnetic mesonance, diamond anvil cells

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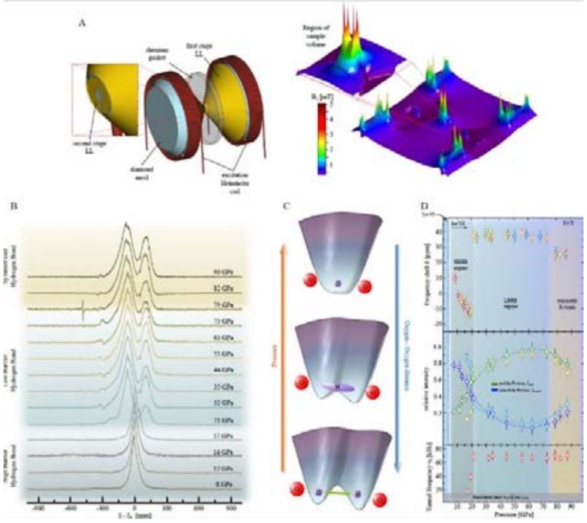
The last 15 years have seen an astonishing boost in NMR sensitivity and accessible pressure ranges [1] owing to developments in implementing NMR in diamond anvil cells (DACs) for high pressure experiments. Recently, with application of electro-magnetic lenses, so called Lenz lenses, in toroidal diamond indenter cells, pressures of up to 72 GPa with NMR spin sensitivites of about 10^{11} spins/$Hz^{1/2}$ could be realised [2]. In the first part of this contribution, a refined NMR resonator structure will be introduced. This structure employs a pair of double stage Lenz lenses driven by a Helmholtz coil within a standard DAC, with only 100 pl sample volume available prior to compression. With this set-up, pressures close to a mega-bar (1 Mbar = 100 GPa) could be achieved [3]. The second part focuses on the recently observed hydrogen bond symmetrisation in high pressure ices [4]. It is a long-standing paradigm that hydrogen bond symmetrisation in H-bonded systems is triggered by pressure induced nuclear quantum effects (NQEs). While theory clearly predicts that quantum-mechanical tunnelling of protons within hydrogen bonded systems is present for pressures between 20 GPa and the H-bond symmetrisation transition at about 70 to 80 GPa, clear experimental evidence is mostly absent. Here, first ^{1}H-NMR studies of high pressure ice in a range from 8 to 90 GPa demonstrate that NQEs govern the behaviour of the hydrogen bonded protons in ice VII already at significantly lower pressures than previously believed. A pronounced tunnelling mode was found to be stable up to the highest pressure, well into the stability field of ice X where NQEs are believed to be absent due to the unimodal probability distribution of the protons in a fully symmetrised H-bond network. Two distinct transitions in the shift data could be attributed to the stepwise symmetrisation of the H-bond network, i.e. High Barrier H-Bonds --> Low Barrier H-Bonds --> symmetric H-bond. This behaviour might be ubiquitous in other H-bonded systems, like hydrous minerals, which are also thought to exhibit pronounced proton conductivity.



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[1] T. Meier, Annual Reports on NMR Spectroscopy, 93rd ed., G. Webb, Ed. London: Elsevier, 2017, pp. 1–74.

[2] T. Meier, N. Wang, D. Mager, J. G. Korvink, S. Petitgirard, and L. Dubrovinsky, Sci. Adv., Dec. 2017.

[3] T. Meier, S. Petitgirard, S. Khandarkheava, T. Körber, E. Rössler and L. Dubrovinsky, J. Magn. Res., in press, arXiv: 1803.05472

[4] T. Meier, S. Petitgirard, S. Khandarkheava, and L. Dubrovinsky, Nature Comm., under review, arXiv: 1803.07019

New high-pressure cells for single-crystal diffraction with hot neutrons at the Heinz Maier-Leibnitz Zentrum (MLZ)

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Keywords: neutron radiation, single crystal diffraction

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X-ray and neutron single crystal diffraction are complementary methods both well established for detailed studies on crystalline structures (atom sites, bond lengths, mean square displacements and esp. in combination with neutron scattering magnetic scattering). In those cases, where X-ray diffraction cannot yield unambigous information neutron diffraction plays a major part. The hot single crystal diffractometer (scd) HEiDi [1, 2] at the Heinz Maier-Leibnitz Zentrum (MLZ) in Garching contributes for more than 10 years important scientific contributions to many scientific topics related to solid state matter, chemistry mineralogy and material sciences, e.g. energy or data storage related cmpounds for more thant ten years [3, 4]. Nevertheless, the neutron flux even of the most recent neutron sources lies orders of magnitude below the photon flux at synchrotrons and requires sample sizes >1 mm² which can be very difficult to grow. Efforts to overcome this problem fit perfectly to the growing request for experiments at non ambient pressure as they play an important role in detailed studies, for instance on various magnetic or superconducting compounds [e.g. 5, 6, 7, 8]. Therefore, measures were taken to extend the capabilities of the scd HEiDi for small samples/high pressure experiments by optimizing its optical components and developing suitable pressure cells of diamond anvil type with $P_{max}>5$ GPa in order to create a bridge to complementary synchrotron experiments. Focus of the later part was not maximum pressure but reliable collection of most complete Bragg data sets and the combination of high pressure and low temperature measurements down to T<10K using the benefits of short wavelengths. In this context various anvil cell designs (both panoramic and transmission type) were developed in order to maximize the acceptance angle to/from the cell body and to allow studies using the same pressure cell to collect both X-ray and neutron diffraction data as well as membrane cell for in-situ pressure change.

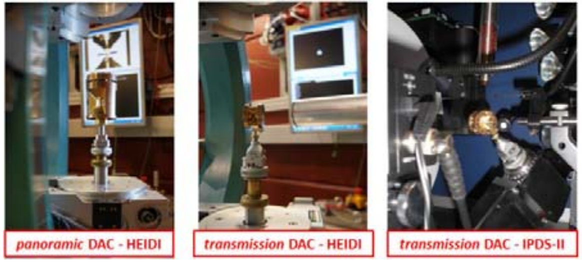

Figure 1. Newly designed high pressure cells [10]

This article presents the latest results of the pressure cell development for the single crystal diffractometer HEiDi at the MLZ as well as some other applications under extreme conditions.

Acknowledgments: This work was supported by the German Ministry for Education and Research (BMBF 05K16PA3). Neutron data were collected on the single crystal diffractometer HEiDi operated jointly by RWTH Aachen University and Forschungszentrum Jülich within the JARA (Jülich-Aachen Research Alliance) collaboration.

[2] M. Meven et al.; HEiDi: Single Crystal Diffractometer at the Hot Source of the FRM II; Neutron News 18, 19-21 (2007) [10.1080/10448630701328406].

[3] M. Meven et al.; HEiDi: Single crystal diffractometer at hot source; Journal of large-scale research facilities 1, A7 (2015) [DOI 10.17815/jlsrf-1-20].

[4] M. Ceretti et al.; Low temperature oxygen diffusion mechanisms in Nd_2NiO_{4+D} and Pr_2NiO_{4+d} via large anharmonic displacements, explored by single crystal neutron diffraction; J. Mater Chem A 3, 21140 (2015) [DOI 10.1039/C5TA05767A].

[5] Xiao, Y. et al; Magnetic structure of $EuFe_2As_2$ determined by single-crystal neutron diffraction; Phys. Rev. B 80, 174424 (2009) [DOI 10.1103/PhysRevB.80.174424].

[6] J.M. Posse et al.; Structural stability of $BaMF_4$ (M = Mg, Zn and Mn) at high pressures, J. Phys.: Condens. Matter 23(21), 215401 (2011) [DOI 10.1088/0953-8984/23/21/215401].

[7] H. Hegger et al.; Pressure-Induced Superconductivity in Quasi-2D CeRhIn5; Phys. Rev. Lett. 84,4986-4989 (2000) [DOI 10.1103/PhysRevLett.84.4986].

[8] K. Friese et al.; Refinement of high pressure single-crystal diffraction data using Jana2006, High Press. Res.33,196-201 (2013) [DOI 10.1080/08957959.2012.758723].

[9] P. Hering et al.;; Structure, Magnetism, and the Magnetocaloric Effect of $MnFe_4Si_3$ Single Crystals and Powder Samples; Chem. Mater. 27(20), 7128–7136 (2015) [DOI 10.1021/acs.chemmater.5b03123].

[10] K. Friese et al.; Structure–property relationships in magnetocaloric materials; Acta Cryst. A 73(a2), C1342-C1342 (2017) [DOI 10.1107/S205327331708233X].

[11] A. Grzechnik et al.; Single Crystal Neutron Diffraction in Diamond Anvil Cells with Hot Neutrons; Journal of Applied Crystallography 51(2), 351-358 (2018) [DOI 10.1107/S1600576718000997].

Tandem X-ray microdiffraction and microfluorescence for high-pressure materials characterization

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Keywords: synchrotron radiation, microdiffraction, x-ray fluorescence

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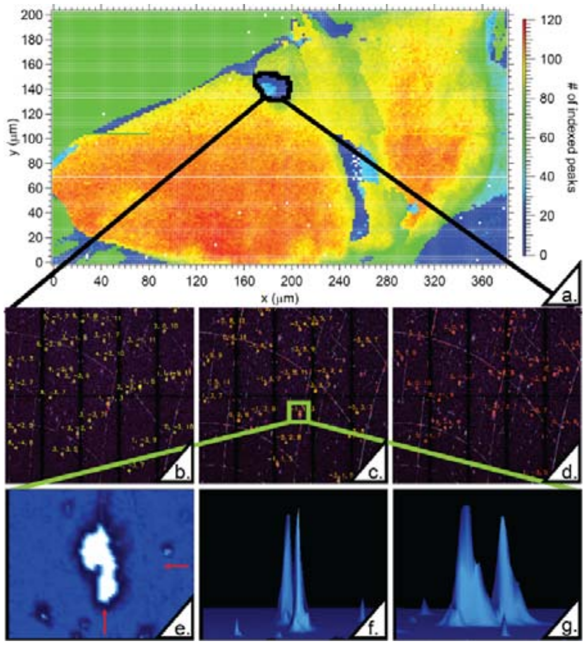
With the advent of higher and higher pressure measurements, as well as continued efforts in performing chemistry at high pressures, comes interest in not only basic high-pressure measurements such as compressibility, but also more challenging ones such as sample heterogeneity upon synthesis/decomposition, single crystal twinning at high pressure, and those of other such physical properties. As always, the main challenges with these experiments lie not only in the mechanisms for generation of pressure itself, but also in the limitations imposed by sample size and geometry. Many diffraction beamlines have spatial resolution between 3 - 40 µm, but high-pressure research sample dimensions are often > 100 µm, and many times > 10 µm, making spatially-resolved measurements challenging.

Here we will discuss the microdiffraction and microfluorescence mapping beamline 12.3.2, at the Advanced Light Source, and its application to both *in situ* diamond anvil cell experiments and samples recovered from high pressure [1,2]. The beamline has x-ray focus down to 1 x 1 µm in white beam mode and 2 x 5 µm in monochromatic mode. The experimental hutch is designed for sample raster scanning, and is also equipped with a X-ray fluorescence detector capable of measuring elements with atomic number 15+. This makes the beamline particularly well-suited to generating 2D diffraction and elemental maps of crystal systems with good spatial resolution. In particular, it is easy to observe single crystal orientation/rotation (within 0.5°), plastic deformation, grain boundaries, and to directly measure differential as well as hydrostatic strain.

At 12.3.2, *in situ* Laue microdiffraction has been used on larger single crystals such as quartz in order to observe twin boundary formation with the application of pressure to several GPa. On smaller (but >1 µm) crystals, measurements have focused on the rotation of individual grains with the application of uniaxial pressure [3]. *Ex situ* measurements have been performed on silica samples recovered from large volume press deformation measurements, as well as from geological materials that formed at high PT and were either highly deformed or too small to identify and characterize with a conventional lab diffractometer.



From [2] a. Number of moissanite (SiC) diffraction peaks indexed as 6H-type, from a natural sample formed at high PT and then uplifted. b-d. Native Si grains embedded within the moissanite grain boundaries. e-g. enlarged (1,1,3) peak of Si, showing extensive plastic deformation and subgrain boundary formation.

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[1] Stan, C. V., Beavers, C. M., Kunz, M. & Tamura, N. X-Ray Diffraction under Extreme Conditions at the Advanced Light Source. *Quantum Beam Science* **2,** 4 (2018).
[2]Stan, C. V. & Tamura, N. Synchrotron X-ray Microdiffraction and Fluorescence Imaging of Mineral and Rock Samples. *JoVE* **in press,** (2018).
[3] Zhou, X. *et al.* Reversal in the Size Dependence of Grain Rotation. *Phys. Rev. Lett.* **118,** 096101 (2017).

Synthesis of new hydrides at high pressures

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Keywords: synchrotron radiation, hydrides, laser heating, high pressure

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We will describe experimental techniques for synthesis of hydrides of metals at the synchrotron facilities up to very high pressures (200 GPa), along with recent results for selected metals. The techniques at hand take advantage of the recently developed capabilities for laser heating in cryogenically cooled samples and also rely heavily on the pulsed laser heating techniques. The experimental results will be compared to theoretical predictions, usually demonstrating good agreement between theory and experiment. Some deficiencies and problems in theoretical approaches will be addressed and compared to experimental results. We will discuss a set of questions related to the equation of state approaches to the volume occupied by the interstitial hydrogen atoms in transition metal hydrides. Several techniques for detecting superconducting response of new poly-hydrides will be also presented.

Ice-VII and other natural mineral inclusions of former dense fluid components in diamonds from the deep mantle

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Keywords: synchrotron radiation, micro-diffraction, micro-mineralogy, diamond inclusions

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The combination of synchrotron micro-diffraction with micro-X ray fluorescence and IR-spectroscopy permits non-desctructive identification of micrometer-scale inclusions of minerals in diamonds. For the first time, record from optical spectroscopy can be linked to diffraction patterns of molecular species like H_2O, CH_4, and CO_2 which occur in diamonds but evade conventional analysis with SEM, TEM, and EPMA. This synchrotron-based approach opens a wide field for research on fluid phases, whose crystallized remnants we now find as inclusions in diamonds. Moreover, residual pressures of these inclusions are recorded along with structure-relevant information. Because of their small size these inclusions exert little stress on the surrounding host diamond and little or no annealing has occurred. Thus, the recorded remnant pressure is end point of a nearly isochoric path connecting this current pressure at 300 K to the pressure and temperature of entrapment.

This reconstruction of the conditions of entrapment in the diamond source region allows for the first time to directly link occurrence of mineral inclusions to the depth of their entrapment. Previous work had to rely on element distribution between inclusions phases, a method that carries large uncertainties from error propagation and only indirectly constrains pressure as a parameter.

We show that our method provides first direct evidence for the presence of aqueous and carbonaceous fluids in the transition zone and the shallow lower mantle of the Earth.

We discuss the new method and the relevance of its results for the geochemistry and petrology of the deep mantle.

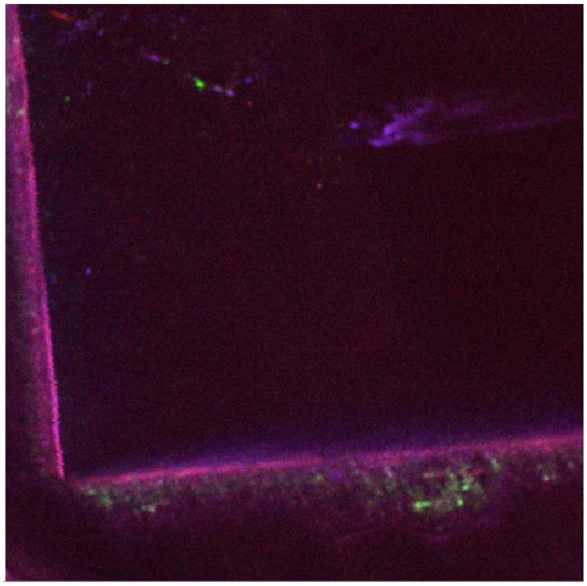

Figure 1. The Figure shows the relative distribution of K,Ca,Ti in a zoned diamond as RGB-colour-coded map. Spatial resolution was 2×3μm^2. Diffraction data are collected at the locations of inclusions.

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[1] O. Tschauner et al., *Science* 2018, **359,** 1136.

Advanced synchrotron techniques for high-pressure high/low temperature research at HPCAT, Advanced Photon Source

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Keywords: high pressure, synchrotron radiation, x-ray miro-diffraction, x-ray spectroscopy, HP sample environment

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High Pressure Collaborative Access Team (HPCAT) is dedicated to advancing cutting-edge, multidisciplinary, high-pressure science and technology using synchrotron radiation at Sector 16 of the Advanced Photon Source (APS) of Argonne National Laboratory. At HPCAT an array of novel x-ray diffraction and spectroscopic techniques has been integrated with high pressure and extreme temperature instrumentation for studies of structure and materials properties at extreme conditions.

HPCAT consists of four active independent beamlines performing a large range of synchrotron various experiments at extreme conditions – two bending magnet beamlines, 16BM (with x-ray fan split in space) and two insertion device (undulator) beamlines, 16ID. 16BM-B beamline is dedicated to energy dispersive (Paris-Edinburgh, PE, large volume press) and white Laue X-ray micro-diffraction. The experiments include amorphous and liquid structure measurement, white beam radiography, elastic sound wave velocity measurement of amorphous solid materials. The new developments include double-stage PE cell capable of reaching megabar pressures, and newly built micro-Laue setup with ~2x2μm focused beam and flexible area detector position with respect to the sample. 16BM-D is a monochromatic beamline optimized for powder and single crystal micro-diffraction at high pressure and high (resistive heating) / low (cryostats) temperature. The additional capabilities include high-resolution powder diffraction and x-ray absorption near edge structure (XANES) spectroscopy. The recent development of the beamline include an addition of a multilayer monochromator, which increases on-sample x-ray flux by ~50 times compared to a standard Si111 monochromator.

The insertion device beamline of HPCAT has two undulators in canted mode (operating independently) and LN cooled Si monochromators capable of providing a large range of energies. 16ID-B is a microdiffraction beamline mainly focusing on high-pressure powder and single crystal diffraction in DAC at high temperatures (double-sided laser heating and resistive heating) and low temperature (various cryostats). The modern instrumentation allows high-quality diffraction at megabar pressures from light element, fast experiments with pulsed/power modulated laser heating, fast dynamic experiments with piezo drives and Pilatus detector, and so on. The new developments include 1x2μm x-ray focusing systems, CO_2 laser heating capabilities, high-throughput multi-channel analyzer with 30x60 degrees opening suitable for single crystal diffraction, hexapod sample positioning control, and fly-scan capabilities with integrated multi-mode 2D scanning diffraction microscopy. 16ID-D beamline is dedicated to x-ray scattering and spectroscopy research of materials under high pressure in DAC. The available techniques include nuclear forward scattering, nuclear resonant inelastic scattering for determining phonon density of state and Mössbauer effect, x-ray inelastic scattering (X-ray Raman) for the study of charge dynamics and chemical bonding, x-ray spectroscopy for the study of electronic excitations, X-ray emission (including partial fluorescence yield, resonant emission) with 7-element spectrometer. Many of these measurements can be done at low temperature, with *in-situ* pressure measurement, or at high temperature with portable laser heating. The new developments include focusing of x-rays to 3x5μm or 1x10μm spots and use of polycapillary optics, which allows performing x-ray Raman experiments at megabar pressures.

Over the last several years a number of supporting facilities have been developed and implemented to expand the available P-T range of the experimental conditions, increase efficiency and productivity of the beamlines by automating pressure control, improve the quality of experimental data, and integrate additional methods of sample characterization with synchrotron investigations.

The supporting facilities include devices for remote and automatic pressure control and data collection in DACs during synchrotron experiments; devices for time-resolved synchrotron measurements (dynamic DAC); multiple DAC heaters and cryostats integrated with double-membrane and piezo pressure control systems for various synchrotron experiments; modular compact cryostats with stable sample position designed for use with stationary laser heating system; rotary and panoramic DACs for x-ray micro-tomography and 3D x-ray diffraction microscopy; portable online and stationary optical systems for ruby fluorescence pressure measurements and in-situ/ex-city Raman sample characterization; sample loading and preparation facilities and others.

All these advanced synchrotron techniques, as well as supporting facilities, employed at HPCAT, will be presented and discussed.

The Extreme Conditions Beamline (P02.2) at PETRA III (DESY): Recent advances and outlook

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Keywords: synchrotron radiation, extereme conditions

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3rd generation light sources continue to be an essential tool for conducting X-ray diffraction/scattering experiments simultaneously at high-pressures and high and low temperatures. While laboratory X-ray sources can provide some information at lower pressures because of lack of the flux and micrometer beam size, only the use of very brilliant hard X-ray sources enable multi-megabar expreriments at temperatures from the single didgits to several thousands of Kelvin. Here we present the capabilities, recent advances and an outlook on future upgrades plans for the Extreme Conditions Beamline (ECB, P02.2) at the synchrotron PETRA III, DESY, Hamburg.

In order to offer standart sample enviroments for extreme conditions research, the ECB was designed with two spatially separated setups: the general purpose (GP) experiment to support resistive heated (up to 2000 K) and cryogenically cooled (up to 5 K) experiments in diamond anvil cells (DAC) and laser heating (LH) experiment with permanent installations of near-infrared YAG (both on- and off-axis) and CO_2 lasers, optics for temperature measurements and ruby system for online pressure measurements. The two experimental setups possess identical X-ray focusing capabilities: Compound Refractive Lenses (CRLs) and KB mirror systems providing a miminum spot size of 8 (h) x 2 (v) μm^2 and 2 x 2 μm^2, respectively. Taken together with opportunity to operate at three different energies (25.6 keV, 42.7 keV and 60.0 keV), ECB is optimized for wide range of X-ray diffraction studies at extreme conditions of high pressure and simultaneous high and low temperatures: powder and single crystal diffraction at static pressure, dynamic powder diffraction, PDF studies on non-crystalline materials [1].

Several recent advances make the ECB an atractive high-pressure beamline. The fast compression in dynamically driven DACs [2] in conjunction with powder diffraction attracted much attention over the last decade as a powerful technique to explore phase transition kinetics as function of compression rates [3-6]. Combination of the fast and sensitive GaAs-based Lambda detector [7] and high flux provided by the beamline have made it possible to collect diffraction data during fast compression up to rates of the 100s of TPa/s acquiring diffraction images at kHz repetition. Another recent featured setup is a two-circle diffractometer with rotating laser heads to conducted *in situ* SCXRD experiments at simultaneously high temperatures and high pressures. The overcoming of the long-lasting limitation of SCXRD technique enables tracking of structural changes of geomaterials at real conditions of planetary bodies' interior conditions. In addition, the recent development of the CRL setup allowed to reach submicron X-ray focusing enabling XRD studies at multi megabar pressures.

Future upgrade plans focus on strengthening of the existing capabilities in order to continue to serve the high-pressure community to perform cutting edge experiments at extreme conditons.

[1] Liermann H.-P., Konopkova Z., Morgenroth W., Glazyrin K., Bednarcik J., McBride E., Petitgirard S., Delitz J. T., Wendt M., Bican Y., Ehnes A., Schwark I., Rothkirch A., Tischer M., Heuer J., Schulte-Schrepping H., Krachta T., Franza H., J. Synchrotron Rad. 22, 908–924 (2015).

[2] Konôpková Z., Rothkirch A., Singh A., Speziale S., Liermann H.-P., Phys. Rev. B., 91, 144101 (2015).

[3] Evans *et al.*, Rev. Sci. Instrum., 78, 073904 (2007).

[4] Chen J.-Y., Yoo C.-S., Kim M., Liermann H.-P., Cynn H., Jenei Z. and Evans W. J., Phys. Rev. B., 90, 144104 (2014).

[5] Chen J.-Y., Kim M., Yoo C.-S., Liermann H.-P., Evans W. J., J. Phy.: Conf. Ser. 500, 142006 (2014).

[6] Lin C., Smith J. S., Sinogeikin S. V., Park C., Kono Y., Kenney-Benson C., Rod E., Shen G., J. Appl. Phys., 119, 045902 (2016)

[7] Pennicard D., Lange S., Smoljanin S., Hirsemann H., Graafsma H., Epple M., Zuvic M., Lampert M.-O., Fritzsch T., Rothermund M.. J. Phys. Conf. Ser., 425, 062010 (2013)

Extreme conditions studies at ID27 ESRF beamline: present and future status

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Keywords: synchrotron radiation, extreme conditions, X-ray techniques

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In the last decades, we have witnessed an unprecedented surge in high-pressure research that has greatly improved our fundamental understanding of materials under high compression. The X-ray investigation of matter under extreme conditions has became one of the major activities at the ESRF and other 3rd generation synchrotron sources. The array of techniques, initially restricted to structural measurements using X-Ray diffraction, is now extended and includes many others such as Inelastic X-ray Scattering, Nuclear Inelastic Scattering, X ray absorption and emission spectroscopy, X ray magnetic circular dichroism, X-ray Compton scattering and X-ray magnetic scattering. As a direct consequence, many scientific breakthroughs have been achieved across fields ranging from Earth and planetary sciences to fundamental physics, chemistry and materials research, and extending into biophysics and biochemistry including questions concerning life and biological function under extreme conditions. The investigation of matter under extreme conditions is one of the natural issues addressed using X-ray diffraction. The very intense and highly focused X-ray beam available at the ESRF is a unique tool for probing microscopic samples at extreme pressures and temperature. In this presentation, we will introduce the beamline ID27 at the ESRF. This high-energy beamline is a multidisciplinary instrument that operates in user mode since 2006. It is fully optimized for monochromatic high pressure powder, single crystal, liquids and amorphous X-ray diffraction experiments. It is composed of two specialized experimental hutches (EH1 and EH2). EH1 hutch is dedicated to the large volume cell experiments using the Paris-Edinburgh (P-E) press and for diamond anvil cell (DAC) experiments at low, room and moderate high temperature using a helium flow cryostat and resistive heating, respectively. EH2 hutch is fully dedicated to DAC experiments at very high temperature using laser-heating systems (YAG and CO_2 systems). These unique characteristics make ID27 an excellent instrument to study matter at extreme conditions of pressure and temperature.

In view of the EBS ESRF program, an ambitious and innovative modernisation project to upgrade ID27 to a long beamline with unique photon flux and focusing, time resolution and coherence capabilities has been launched. The details of this project as well as the status of the high pressure activity at the ESRF with an overview of the possible X ray experiments available and the on-site high pressure preparation dedicated laboratories will be presented.

Finally, we will discuss a series of scientific examples opening the possibilities of collaborations and discussions on particular scientific problems.

Time-resolved XFEL observation of shock-wave propagating material

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Keywords: shock compression, free-electron laser, time-resolved observation

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An X-ray free electron laser (XFEL) facility, SACLA, was constructed in Hyogo prefecture, Japan, next to the third-generation synchrotron facility, SPring-8. Now in the SPring-8/SACLA, we have three experimental stations for extreme conditions sciences: BL04B1 for large volume press; BL10XU for laser heated diamond anvil cell; BL3EH5 for laser-driven shock experiment. We can conduct in situ high-pressure experiments at from less than 1 GPa to more than 1 TPa by using these high-pressure techniques with shychrotron X-rays and XFEL.

The BL3EH5 is in the SPring-8/SACLA interoperable experimental facility, and laser-driven shock compression experiments are available utilizing the ultra-short pulsed X-ray of SACLA as a probe. Laser-driven shock compression experiments are carried out using a Nd:YAG optical laser (532 nm, Hamamatsu Photonics K.K.) with ~3-ns pulse width. Total energy of the optical laser is currently 10 J and will be increased up to 100 J in future. The optical pump laser is introduced into a target vacume chamber and focused to ~200 μm on the target surface.

Time-resolved X-ray diffraction measurements were carried out using a quasi-monochromatic X-ray of 10 keV ($\Delta E/E \sim 0.5\%$) with <10 fs pulse duration containing $\sim 10^{12}$ photons. The X-ray was focused to 10 μm in vertical axis by a KB mirror and truncated to 100 μm in horizontal axis. 2D diffraction images were recorded by using a multi-port CCD detector (MPCCD) developed by Riken [1] and a flat panel detector (FPD). The MPCCD has ~50 × 50 mm^2 active area composed of 0.05 × 0.05 mm^2 pixels at a specific 2θ angle with a field of view of ±5°. For more wide-angle observation, the FPD is available (2θ = 10-120°). Here we show a result of the in situ observation of laser-driven shock compression experiments.

Laser-driven shock compression experiments were conducted for a polycrystalline Al_2O_3 (corundum, Cor). The grain size of corundum was 0.7(4) μm and less than 2 μm, which is sintered as pore-free and the density of corundum was identical with that of single crystal. The corundum sample was polished to be 20 μm in thickness and glued with a 40-μm thick aluminum (Al) light shield and a 30-μm thick polypropylene (PP) ablator using UV-cured resin. The composed targets (PP30-Al40-Cor20) were set on to the crosspoint of pump laser and XFEL probe inside the vacule sample chamber.

Pump-probe measurements were carried out varing delay times of FEL-probe exposure after flashing pump laser to generate shock wave on the surface of targets. After series of the pump-probe measurements, a peudo time-resolved profile was obtaind. Figure 1 shows a time-resolved XRD pofile of corundum in the timing delay of 6-14 ns. Three typical states were observed and the chenges occurred at 7, 10, and 11.5 ns in delay.

In the first shocked state in 7-10 ns, size of diffraction spots was identical to the starting material indicating the peak pressure was lower than the elastic limit of corundum. After 10 ns, smoky diffraction signal suddenly appeared and the shifted peaks showed increasing pressures up to ~50 GPa. Finally, after 12 ns, volume expansion was ovserved indicating the arrival of the strong shock wave at the free surface of corundum. In the presentation, we will show details of experimental setups and features of XRD profiles in the shock-compressed polycrystalline material.

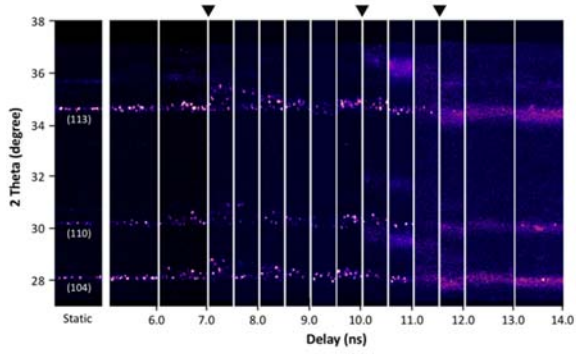

Figure 1. Time-resolved XRD profile of Cor.

Acknowledgments: The authors thank students in Kodama laboratory and engineering staffs of SACLA for their support in the experiments. This work was supported in part by JSPS KAKENHI grant numbers 25707041, 17K05714.

[1] T. Kameshima et al., *Rev.Sci. Instrum.* 2014, **85,** 033110.

Synthesis and characterization of novel hydrides at high pressure and temperature

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Keywords: x-ray diffraction, hydride

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Studies of hydrides systems are often driven by the pursuit to produce a material that has high volumetric hydrogen density and high gravimetric content. [1] High pressure, in combination with high-temperature, can facilitate compounds to adopt stoichiometries that would not be accessible at atmospheric conditions. Recent theoretical and experimental studies have shown that pressure can produce H_2 rich compounds with interesting geometrical arrangements and even exhibit novel properties, such as high Tc superconductivity. [2,3,4] In this presentation, I will discuss our recent experimental efforts in synthesising H_2-rich materials, which we characterized through both Raman spectroscopy and synchrotron x-ray diffraction analysis.

[1] W. L. Mao and H.-k. Mao, PNAS, **101**, 708 (2004).
[2] A. P. Drozdov et al., Nature, **525**, 73 (2015).
[3] C. M. Pepin, et al., Science **357**, 382 (2017).
[4] P. Murck, Z.M. Geballe. et al. Angew. Chem. Int. Ed. **57**, 688-692,(2018).

An Update on Recent Developments and Research in High Pressure Neutron Scattering at Oak Ridge National Laboratory

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Keywords: Neutron Scattering, High Pressure techniques

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Developments in high pressure neutron scattering at Oak Ridge National Laboratory continue apace, particularly at the purpose built high pressure neutron diffractometer known as SNAP. The aim of this presentation will be to provide an overview of the complementarity of neutron scattering with x-ray scattering, update the recent technical and scientific advances in high pressure neutron scattering, and explore the scientific prospects of high pressure neutron scattering at Oak Ridge National Laboratory overall. A comprehensive overview of the SNAP instrument current high-pressure capabilities will be given, including the available pressure cell suite and new developments in high pressure neutron techniques covering a reliably achieved range of P-T conditions. Instrument upgrades for 2018 and onward will be presented and the impact on scientific capabilities (i.e. enhanced background reduction, single crystal capabilities, and accommodation of smaller more complex structures) will be presented. Scientific examples will include recent studies of high pressure forms of glassy clathrate hydrates, recent studies of new forms of ultra-low-density ice, high pressure/high temperature phases of CO_2, and magnetic systems at high pressure. Finally, efforts to expand the high-pressure capabilities across the neutron instrument suite at ORNL, including single crystal and inelastic scattering, will be given.

Elasticity of single crystal ice VII up to 30 GPa

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Keywords: Brillouin scattering, ice, elastic constants

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H_2O water, consisting of two hydrogen atoms and one oxygen atom, exhibits a rich and intriguing phase diagram with more than 15 phases. It has been long found that H_2O water transforms to ice VI at 0.9 GPa and then to ice VII at 2.2-60 GPa. Numerous reports suggest a structural transition of ice VII at ~10-20 GPa [1]. We acquired Brillouin scattering data for ice VII using the time-domain thermoreflectance (TDTR) method [2,3], also indicating a structural transition of ice VII at 13-16 GPa at 300 K. Those data are, however, for the aggregates of ice VII crystals, instead of single crystals, impossible for us to determine the single crystal elasticity of ice VII.

In this study, we synthesized ice VII single crystals at high pressures and temperatures using externally-heated diamond anvil cells. Single crystal X-ray diffraction and Brillouin scattering measurements of single-crystal ice VII have been performed up to 30 GPa and at 300 K. The X-ray diffraction data provided the information on the orientation of the ice VII single crystal grown in the diamond anvil cell and its density at each pressure. The Brillouin scattering data then permitted the determination of single crystal elasticity of ice VII up to 30 GPa (**Fig. 1**). We found the similar Cauchy relation ($C_{12} \approx C_{44}$), with C_{12} slightly larger than C_{44} at all pressures. The single crystal elasticity results, concerted with Raman spectroscopy data and equation of state of ice VII at high pressures, help reveal the nature of the structural transition and its effects on the elastic properties of ice VII. The thermal equation of state and sound velocities of ice VII are essential physical properties for the modeling of icy satellites of giant planets or exoplanets.

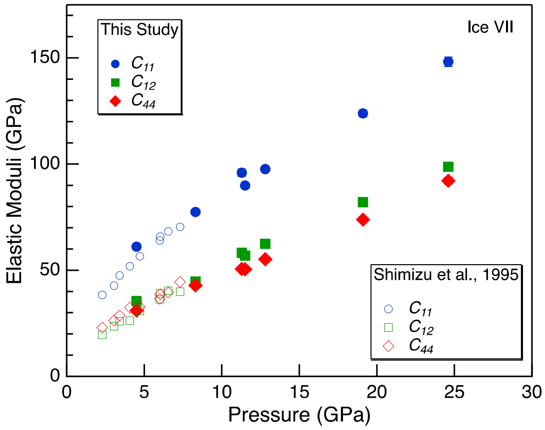

Figure 1. Single crystal elasticity of ice VII up to 30 GPa. Filled symbols: this study; open symbols: Shimizu et al. [4].

Acknowledgments: This work was performed at GeoSoilEnviroCARS (The University of Chicago, Sector 13), Advanced Photon Source, Argonne National Laboratory. GeoSoilEnviroCARS is supported by the National Science Foundation-Earth Sciences (EAR-1128799) and Department of Energy-GeoSciences (DE-FG02-94ER14466). This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. This work was supported by the NSF grant EAR-1555388 to BC.

References:

[1] Iitaka, T., Fukui, H., Li, Z., Hiraoka, N., Irifune, T., Pressure-induced dissociation of water molecules in ice VII. *Sci. Rep.* 2015, **5**, 12551.
[2] Hsieh, W.-P., Li, J., Keblinski, P., Cahill, D.G., Pressure tuning of the thermal conductivity of the layered muscovite crystal. *Phys. Rev. B* 2009, **80**, 180302.
[3] Chen, B., Hsieh, W.-P., Cahill, D.G., Trinkle, D.R., Li, J., Thermal conductivity of compressed H_2O to 22 GPa: A test of the Leibfried-Schlömann equation. *Phys. Rev. B* 2011, **83**, 132301.
[4] Shimizu, H., Ohnishi, M., Sasaki, S., Cauchy relations in dense H_2O ice VII. *Phys. Rev. Lett.* 1995, **74**(14), 2820-2823.

Advanced high-resolution integrated optical system for diamond anvil cell studies

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Keywords: raman spectroscopy, laser heating, diamond anvil cell

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Raman and optical spectroscopy in-situ at extreme high pressure and temperature conditions relevant to the planets' deep interior is a resourceful tool for characterization of a wide range of properties of minerals essential for understanding the structure, composition, and evolution of terrestrial and giant planets. The variety of different materials studied under such extreme conditions is therefore seemingly endless, calling for the need for such a versatile optical system.

The optical system consists of five Raman excitation lines (266, 473, 532, 660, and 946 nm) as well as Coherent Anti-Stokes Raman Spectroscopy (CARS)[1] and double sided IR laser heating capabilities[2]. Users can alternate between different configurations remotely, avoiding sample specific problems such as fluorescence by changing the excitation wavelength. In addition to excitation choice, samples can be mapped utilizing motorized control of the sample. The integrated system is mainly software controlled, making it user-friendly and safe.

Here we show the completed construction on a conceptually-new, user-friendly, integrated system for worldwide users at the Advanced Photon Source (APS) Sector 13 combining advanced Raman and optical spectroscopy tools adopted for studies of materials *in-situ* at static and dynamic extreme P-T conditions in the diamond anvil cell and newly synthesized materials at ambient conditions with a high spatial resolution.

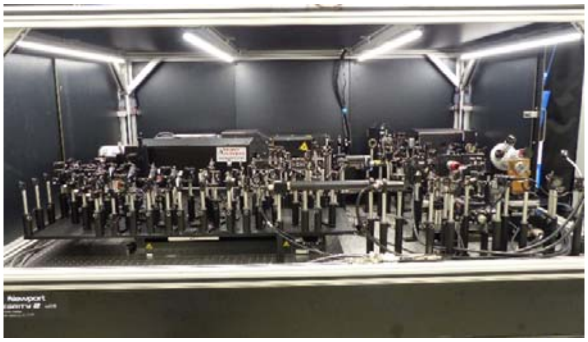

Figure 1. Photograph of the optical system at APS Sector 13.

Acknowledgments: This work was supported by NSF MRI proposal (EAR-1531583) and DOE – Geosciences (DE-FG02-94ER14466).

[1] C. L. Evans and X. S. Xie, *Annu. Rev. Anal. Chem.* 2008, **1**, 883.

[2] A. F. Goncharov *et al.*, *J. Synchrotron Radiat.* 2009, **16**, 769.

Technical development of double-stage diamond anvil cell and equations of state at multi-megabar condition

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Keywords: ds-DAC, equation of state, nano-polycrystalline diamond(NPD)

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Crystallography at a pressure above 500 GPa is necessary to understand a deep interior of big planets such as not only gas-giant planets but also exoplanets including super-Earths. Although diamond anvil cell is widely used as an experimental tool to generate very high pressure, its pressure is usually limited up to about 300 GPa. In order to beyond the limit of conventional diamond anvils, the double stage diamond anvil cell (ds-DAC) technique was invented by Dubrovinsky et al. [1], and it is thought as a promising technique to generate static ultra-high pressures. However, there are some technical difficulties and no other groups [2-3] have succeeded in generating pressures comparable to those by Dubrovinsky et al. [1], although this same group has reported generation of even higher pressures reaching the TPa regime [4].

For reproducible pressure generation, we have developed a ds-DAC technique by precisely fabricating 2nd stage anvils using a focused ion beam system [2,5]. We used 2nd stage micro-anvils made of ultra-fine (< 10 nm) nano-polycrystalline diamond, which synthesized from glassy carbon at high pressure and temperature, with various shapes and dimensions. One example of the micro-anvils is shown in *Figure 1*. Powder XRD experiments were performed at BL10XU, SPring-8. Pressure was determined from the unit-cell volume of rhenium using the equation of state (EoS) reported by Anzellini et al. [6].

The X-ray diffraction patterns from the rhenium sample always showed very broad peaks due to large pressure gradients in the culet of the micro-anvils. Deconvolution of the broad 101 diffraction peak results in compression of rhenium to $V/V_0 = 0.633$ for the smallest d-spacing. This volume corresponds to about 430 GPa based on the Re-EoS proposed by Anzellini et al. [6], while it is about 630 GPa according to the Re-EoS reported in Dubrovinsky et al. [1].

In order to explore the consistency of the EoSs of rhenium and those of platinum, we performed an additional experiment using a conventional DAC with a 40 µm double beveled culet. Rhenium and platinum samples were compressed up to 280 GPa with a silica glass as a pressure medium using a tungsten gasket.

The compression curves of rhenium based on platinum pressure scales reported by Dewaele et al. [7] is consistent with the Re-EoS curve by Anzellini et al. [6], while the pressures based on Yokoo et al.'s platinum scale [8] are slightly higher pressures at above 200 GPa. In contrast, there is a large difference between the present results and the Dubrovinsky et al.'s Re-EoS [1] curve.

We conclude that the most likely pressure achieved for the minimum volume of rhenium is in a range of 430–460 GPa based on a calibration using the platinum pressure scale to 280 GPa and the latter value of 630 GPa is unreasonably high, suggesting that the pressures in an earlier study for the equation of state of rhenium would have been significantly overestimated. This result clearly indicates a difficulty of ds-DAC experiments and also an importance to confirm a concistency between various pressure scales at multi-megabar conditions by further "static" ultra-high pressure experiments.

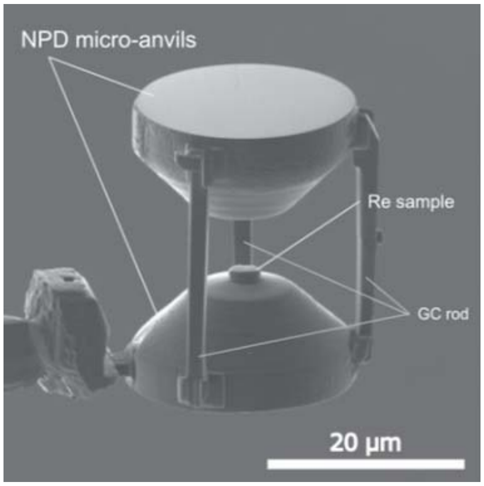

Figure 1. Scanning ion microscopic image of the micro-anvils. The size of rhenium sample is $^{\varphi}3$ µm and $^{t}1$ µm. NPD, the ultra-fine NPD. GC, glassy carbon.

Acknowledgments: This work was supported by Japan Society for the Promotion of Science [JSPS] KAKENHI [grant numbers JP15K13594, JP17H02985, JP25220712, JP15H05829 and JP16K05530].

[1] L. Dubrovinsky, et al., *Nat Commun.* 2012, **3**, 9114. DOI:10. 1038/ncomms2160

[2] T. Sakai, et al., *Rev Sci Inst.* 2015, **86**, 033905. DOI:10.1063/1.4914844

[3] SS. Lobanov, et al., *J Appl Phys.* 2015, **118**, 035905. DOI:10.1063/1.4927213

[4] N. Dubrovinskaia, et al., *Sci Adv.* 2016, **2**, DOI:10.1126/sciadv.1600341

[5] T. Sakai, et al., *High Press Res.* 2018, 38, 107-119. DOI:10.1080/08957959.2018.1448082

[6] S. Anzellini, et al., J Appl Phys. 2014, **115**, 043511. DOI:10.1063/1.4863300

[7] A. Dewaele, et al., *Phys Rev B.* 2004, **70**, 1–8.

[8] M. Yokoo, et al., *Phys Rev B.* 2009, **80**, 614.

X-ray diffraction of ramp-compressed sodium

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Keywords: x-ray diffraction, laser-driven compression

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Sodium is quasi-isentropically compressed into the terapascal regime to test theoretical predictions that sodium transforms to a transparent, electride phase. Experiments are performed to investigate the crystal structure, optical properties, and melting behavior of sodium at pressures over 200 GPa. Sodium samples, sandwiched between diamond plates and lithium-fluoride windows, are ramp compressed by a gradual increase in the drive-laser intensity on the OMEGA EP Laser System. Powder x-ray diffraction is used to constrain the structure of sodium at these high pressures. We show preliminary data that reveal a solid phase above 300 GPa.

This material is based upon work supported by the Department of Energy National Nuclear Security Administration under Award Number DE-NA0001944, the University of Rochester, and the New York State Energy Research and Development Authority. The support of the DOE does not constitute an endorsement by the DOE of the views expressed in this abstract.

New advances in free electron laser x-ray diffraction under pressure: From complex structures to dynamic diamond cells

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Keywords: free-electron laser

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X-ray free electron lasers have provided unprecedented access to the structural and phase behavior of extreme states of matter under dynamic extreme conditions. Studies using laser dynamic compression at facilities such as LCLS have reached maturation, while new facilities such as European XFEL are providing new capabilities, driving rapid improvement and innovation in experimental approaches.

Here I will discuss new work by several large teams engaged in cutting edge experimental studies at LCLS and European XFEL. I will discuss the use of x-ray diffraction measurements on multiphase solids under dynamic compression and release, revealing the detailed and often surprising structural evolution of these materials. This includes direct observations on the formation of complex incommensurate structures under dynamic high pressures, characterizing sluggish transformation dynamics, partial disordering, and the nature of intermediate metastable states in metals Sc, Bi and Sb. These measurements reveal new dynamic structural phenomena ranging from transient recovery to ambient pressures of high pressure structures on nanosecond timescales, to occurance of high pressure phase transitions at lower pressure than at equilibrium through novel kinetic-energetic mechanisms.

I will also discuss the promise and challenge of implementing high pressure structural studies in the time domain using diamond anvil cell techniques at free electron lasers, as soon to be soon implemented at the European XFEL 'High Energy Density' beamline. These include serial structural measurements during compression at tunable strain rates and pulsed heating to extreme temperatures, using MHz diffraction exposure and readout.

Powder diffraction of simple metals at pressures greater than 5.0 Mbars

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Keywords: ultra-high-pressure diffraction, toroidal diamond anvils

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Static compression experiments over 4.0 Mbars using beveled or double beveled diamond anvils are rare. Typically diamond anvils that have 20 µm culets, a bevel angle of ~8.5°, and a B/C ratio between 14-18 (B = bevel diameter and C= culet diameter) are used to reach these pressures. Studies that utilize beveled anvils with culets that are ≤15 µm in diameter are incredibly scarce [1,2], and the pressures reported unsing these anvils are lower than pressures reported from experiments using beveled anvils with 20 µm culets.

Here we utilize a toroidal diamond anvil design first reported by Deweale et al.[3]. We used focused ion beam techniques to craft the toroidal surface onto a standard beveled diamond anvil. Our toroidal diamond anvils have ~9.0 µm culets can produce pressures over 5.0 Mbars. The toroidal anvil is well established in the large volume press community, and the toroidal design serves two purposes (1) it sharply reduces the extrusion of the central portion of the gasket and (2) decreases the magnitude of the shear stresses in the anvils themselves. Moreover, the toroidal configuration provides a confining pressure to the central culet which increases the yield strength of the central culet allowing for higher maximum achievable pressures.

We studied simple metals (V, Al) as well as Re to pressures as high as 6.15 Mbars using angle-dispersive powder diffraction techniques. Pressure was determined *in-situ* using current community accepted standards. Notably, these pressures are typically only accessed by double-stage diamond anvils and dynamic compression platforms. Optimizing single-crystal diamond anvil design is key for extending the pressure range over which x-ray and optical studies can be routinely performed in the DAC.

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[1] Akahama, Y., Kawamura, H. *J. of Phys: Con Series*. 2009, 215, 1.

[2] Dalladay-Simpson, P., Howie, R.T., Gregoryanz, E. *Nature*. 2016, 529, 63.

[3] Dewaele, A., Loubeyre, P., Occelli, F. *ESRF Experimental report*. 2014.

Coordination chemistry & porous materials at high pressure: What the mineral physicists don't experience

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Keywords: high pressure, synchrotron radiation, crystallography

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Crystallographic studies of molecular and chemical compounds at high pressure have become more common in the recent literature[1]. This trend has certainly been encouraged by improved X-ray sources, from microfocus silver Ka sealed tubes to high brightness synchrotron beamlines[2],[3]. Further improvements can be traced to advanced 2-D X-ray detectors, which allow the experimenter to collect data on larger unit cell compounds in a timely manner, within dynamic range[4]. Diamond anvil cell improvements have also played a part- miniature DACs[5] and those with a wide opening angle, like the BX90 design[6], and Boehler-Almax cut diamonds[7] have enabled higher completeness high pressure data collections, allowing for improved structural precision and more reliable structure solution.

The challenges facing a chemist doing a high pressure experiment are similar to those faced by a mineral physicist, but with additional challenges, for example, it is rare that a mineral dissolves in the methanol: ethanol pressure medium. The symmetry of the average molecular material is much lower than the average mineral, and this can have devastating effects in the subsequent structure solution and refinement. There are further considerations when dealing with porous materials- is the observed behavior impacted by uptake of pressure medium or pore desolvation? There are many aspects to examining chemical compounds under pressure that are exotic to the other branches of the high pressure community; these considerations will be discussed, and relevant examples will be provided.

Acknowledgments: This work was supported by COMPRES, the Consortium for Materials Properties Research in Earth Science, under NSF Cooperative Agreement EAR-1606856. This research used resources of the Advanced Light Source, which is a DOE Office of Science User Facility under contract no. DE-AC02-05CH11231

1. Katrusiak, A., High-pressure crystallography. *Acta Crystallographica Section A* **2008,** *64* (1), 135-148.
2. McCormick, L.; Giordano, N.; Teat, S.; Beavers, C., Chemical Crystallography at the Advanced Light Source. *Crystals* **2017,** *7* (12), 382.
3. Stan, C.; Beavers, C.; Kunz, M.; Tamura, N., X-Ray Diffraction under Extreme Conditions at the Advanced Light Source. *Quantum Beam Science* **2018,** *2* (1), 4.
4. Dawson, A.; Allan, D. R.; Parsons, S.; Ruf, M., Use of a CCD diffractometer in crystal structure determinations at high pressure. *Journal of Applied Crystallography* **2004,** *37*, 410-416.
5. Moggach, S. A.; Allan, D. R.; Parsons, S.; Warren, J. E., Incorporation of a new design of backing seat and anvil in a Merrill-Bassett diamond anvil cell. *Journal of Applied Crystallography* **2008,** *41*, 249-251.
6. Kantor, I.; Prakapenka, V.; Kantor, A.; Dera, P.; Kurnosov, A.; Sinogeikin, S.; Dubrovinskaia, N.; Dubrovinsky, L., BX90: A new diamond anvil cell design for X-ray diffraction and optical measurements. *Review of Scientific Instruments* **2012,** *83* (12), 125102.
7. Boehler, R.; De Hantsetters, K., New anvil designs in diamond-cells. *High Pressure Research* **2004,** *24* (3), 391-396.

High-pressure structural chemistry studies on beamline I19 at Diamond Light Source

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Keywords: synchrotron radiation, single-crystal diffraction, high-pressure

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Beamline I19, at Diamond Light Source, provides a facility for the study of the crystal structures of small-molecule materials using single-crystal X-ray diffraction techniques. As well as supporting a core user base in chemical crystallography, the beamline also offers users a range of techniques for studying crystalline materials under a variety of conditions such as variable temperature and pressure and, for porous materials, under the influence of various exchange gases. High-pressure single-crystal diffraction has proved to be one of the more popular techniques that the beamline offers and, as the beamline provides all of the equipment required for these experiments, including a stock of diamond-anvil cells, we have encouraged users new to this technique to apply the variable of high-pressure to their own research. This approach has proved to be extremely successful and has developed new research areas.

In this presentation, the current status of the beamline for high-pressure studies will be described with the techniques to allow pressure studies in the tens of bars through to kilobars outlined. A number of recent results will be described to illustrate the capabilities of the beamline for high-pressure structural chemistry studies.

High pressure behavior of hydrocarbons: Case studies on benzene and benz[*a*]anthracene

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Keywords: hydrocarbons, high pressure, polymerization

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Hydrocarbons are considered as one of the most abundant carbon materials in the solar system. The simplest aromatic hydrocarbon benzene (C_6H_6), has been extensively studied on its structural phase diagram and polymerization reaction mechanism under extreme conditions.[1-3] The current tentative *P-T* phase diagram of C_6H_6 includes up to seven polymorphs, out of which only two (phases *Pbca* and $P2_1/c$) are unanimously agreed upon.[4-6] Recently, Fitzgibbons *et al.* observed benzene forming a new type of ordered nanothread when slowly decompressed from 20 GPa to ambient pressure, which differs from previously reported products of hydrogenated amorphous carbon. It is proposed that the two-dimensional (2-D) crystalline material has an intermediate structure between tube (3,0) and polymer I.[7] C_6H_6 and its isotopologue perdeuterobenzene (C_6D_6) have relatively large difference in its molecular masses (~7.5%). Therefore, large kinetic isotope effect may be in place resulting variations in their reaction progression under extreme conditions. Herein, we used synchrotron X-ray diffraction and micro-Raman techniques to perform comparative high pressure study of C_6H_6 and C_6D_6 at room temperature (RT).[8] We found both isotopologues show negligible effect in the first-order structural phase transition (at ~2.2 GPa) and onset of chemical reaction (~16.5 GPa). The Raman spectra of polymeric products recovered from different pressures show a prominent kinetic isotope effect: C_6D_6 polymerization reaction proceeds considerably slower than C_6H_6, leading to substantially lower fractions of sp^3 bonding in C_6D_6 polymers recovered from comparable pressures.

Then I will present another high pressure study of a polycyclic aromatic hydrocarbon (PAH) benz[*a*]anthracene (BaA, $C_{18}H_{12}$) which contains four fused aromatic rings (Figure 1).[9] It is widely found in coal combustion emissions and diesel exhaust. The structure of BaA adopts the common herringbone-type motif, with a herringbone angle of 49.8°. From synchrotron powder X-ray diffraction data at RT, we found the ambient-pressure molecular solid phase of BaA stabilizes up to ∼15.0 GPa. Increasing the external pressure within this region would induce a reversible piezochromic color change in the sample, from yellow-green to light brown. Further compression beyond 15 GPa leads to polymerization of the sample and forms an amorphous hydrogenated carbon. The low pressure crystalline phase is not recoverable when the sample is decompressed from pressure above 15 GPa. DFT calculations of the structures at 0 K suggests that the formation of a crystalline polymeric phase can take place between 30 and 117 GPa, however the kinetic barriers hinder the process at low pressure regions. The phase transition is therefore suggested to proceed along a gradual transition path to an amorphous phase at a lower reaction threshold, activated by finite temperature effects. Optical absorption measurements reveal that the band gap of BaA decreases at high pressure, from 2.4 eV at 0.5 GPa to 1.0 eV at 50.6 GPa, which is consistent with the prominent piezochromism. DFT calculations further suggest that the band gap of BaA in the molecular phase could reduce to ∼0.1 eV at 117 GPa.

Based on the results of these two different hydrocarbons, their similarities and differences under high pressure will be presented and discussed.

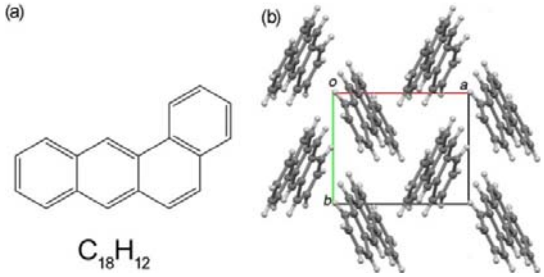

Figure 1. (a) Molecular structure of BaA. (b) Herringbone-type crystal structure of BaA viewed along the *c* axis.

Acknowledgments: This work was supported by American Chemical Society grant PRF#55176-ND10.

[1] M. M. Thiéry, J. M. Leger, *J. Chem. Phys.* 1988, **89**, 4255.
[2] P. Pruzan, *et al*., *J. Chem. Phys.* 1990, **92**, 6910.
[3] L. Ciabini, M. Santoro, R. Bini, V. Schettino, *J. Chem. Phys.* 2002, **116**, 2928.
[4] P. Raiteri, R. Martoňák, M. Parrinello, *Angew. Chem. Int. Ed.* 2005, **44**, 3769.
[5] X.-D. Wen, R. Hoffmann, N. W. Ashcroft, *J. Am. Chem. Soc.* 2011, **133**, 9023.
[6] A. Budzianowski, A. Katrusiak, *Acta Crystallogr. Sect. B.* 2006, **62**, 94.
[7] T. C. Fitzgibbons, *et al*., *Nature Mater.* 2015, **14**, 43.
[8] W. Cai, *et al*., *J. Phys. Chem. Lett* 2017, **8**, 1856.
[9] W. Cai, R. Zhang, Y. Yao, S. Deemyad, *Phys. Chem. Chem. Phys.* 2017, **19**, 6216.

High-pressure synthesis of novel binary intermetallics

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Keywords: solid-state, synthesis, laser heating

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The pressure scale of the universe spans roughly fifty orders of magnitude, and yet most chemistry is carried out under atmospheric pressures. We already know that under the colossal pressures found in the center of stars, chemistry as we know it makes way for nuclear fusion—but what happens at intermediate pressures? Do chemical syntheses follow the same rules under planetary core pressures that they do under standard pressures? And in what ways do electronic and magnetic structure respond as atoms are forced closer to each other? We can begin to answer such questions using handheld devices known as diamond anvil cells (DACs), which are able to provide access to static pressures on the order of millions of atmospheres—the same pressures found deep within our planet.

This talk will discuss the use of the DAC as a reaction vessel for the synthesis of novel binary intermetallic compounds that are unattainable under ambient pressures, with a focus on *in situ* XRD experiments performed at the HPCAT beamlines at the Advanced Photon Source. The combination of laser heating methods with highly focused and high-brilliance radiation is ideal for the real-time detection of new intermetallic phases forming under extreme conditions of temperature and pressure, and has led to the discovery and characterization of a number of new compounds that cannot be synthesized by traditional solid-state techniques [1-5]. The unprecedented bonding and structure exhibited by the compounds we have synthesized hint at the enormous potential of high-pressure synthesis as a route toward materials with exotic emergent properties.

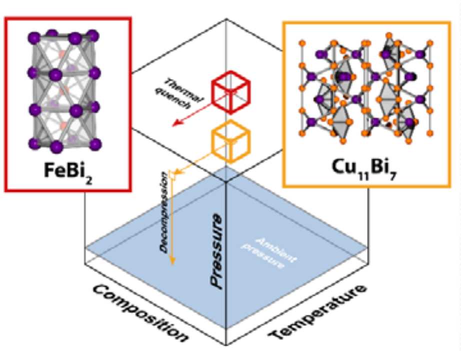

Figure 1. Schematic representation of the synthetic phase space opened up by the use of high pressure as an additional thermodynamic variable, allowing for the discovery of novel intermetallic compounds such as $FeBi_2$ and $Cu_{11}Bi_7$.

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[1] Clarke, S. M., Walsh, J. P. S., Amsler, M., Malliakas, C. D., Yu, T.; Goedecker, S., Wang, Y., Wolverton, C., Freedman, D. E., *Angew. Chem. Int. Ed.* **2016**, *55*, 13446–13449.

[2] Clarke, S. M., Amsler, M., Walsh, J. P. S., Yu, T., Wang, Y., Meng, Y., Jacobsen, S. D., Wolverton, C., Freedman, D. E., *Chem. Mater.* **2017**, *29*, 5276–5285.

[3] Powderly, K. M., Clarke, S. M., Amsler, M., Wolverton C., Malliakas, C. D., Meng, Y., Jacobsen, S. D., Freedman, D. E., *Chem. Commun.* **2017**, *53*, 11241–11244.

[4] Walsh, J. P. S., Clarke, S. M.; Meng, Y.; Jacobsen, S. D.; Freedman, D. E. *ACS Cent. Sci.* **2016**, *2*, 867–871.

[5] Walsh, J. P. S., Freedman, D. E., *Acc. Chem. Res.* **2018**.

Phosphorus on the brink of sixfold coordination in nitride compounds

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Keywords: nitride materials, synchrotron radiation, diamond anvil cell

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High-pressure polymorphs featuring increased coordination numbers have already been reported for fundamental main-group oxides and nitrides. Concerning phosphorus, which is predominantly found in four-fold coordination at ambient conditions, five- and six-fold coordination by O has been observed in high-pressure forms of $TiPO_4$ and $AlPO_4$, respectively.[1,2] In nitride materials only five-fold coordination has been proven so far, while a six-fold coordination has been predicted for spinel-type BeP_2N_4 and □-P_3N_5 from theoretical investigations.[3–6] Silica-analog phosphorus oxonitride PON, however, turned out to be a promising candidate, as well. Among others, PON forms cristobalite-, quartz- and coesite-type structures, which are isotypic with the eponymous SiO_2 polymorphs.[7–9] A stishovite-type form of PON, however, has not been reported so far and would be the first example of six-fold coordinated P in a nitride compound. Thus, a stishovite-type form of PON is considered the missing link in fundamental structural chemistry of phosphorus oxonitrides. Utilizing the a hydraulic 1000 t press and the multianvil technique we recently synthesized a post-coesite (pc) form of PON at 20 GPa exhibiting a stishovite-related structure ($P4_2/mnm$ (no. 136), $a = 4.6184(2)$, $c = 2.45536(9)$ Å, $Z = 2$, $R_{\mathrm{Bragg}} = 0.021$), which was refined from powder X-ray diffraction data.[10] In contrast to Si in the stishovite structure, herein P is situated at a split position within the octahedral coordination polyhedra, leading to a (5+1) coordination (Figure 1a). This is, in turn, a unique feature in fundamental structural research of phosphorus (oxo)nitrides. Using DACs and synchrotron radiation pc-PON was further investigated at pressures up to almost 40 GPa. Its isothermal bulk modulus has been determined to 163(2) GPa and the pc-PON structure was verified by in situ single-crystal X-ray diffraction at high-pressure conditions. At pressures exceeding 20 GPa we observed a displacive phase transition into an orthorhombic (o) form, which was described by a *translationengleiche* symmetry reduction (*t*2) to the orthorhombic crystal system ($P4_2/mnm$ (no. 136) → $Pnnm$ (no. 58); Figure 1b). The recovered sample, however, showed tetragnonal symmetry again, when re-measured at ambient conditions. Thus, the o-PON may be the initial product of the multianvil synthesis and the tetragonal pc-PON might form upon pressure quenching. Additional GGA-based DFT calculations are in line with the experimental findings and corroborate o-PON the stable modification at pressures exceeding 17 GPa.

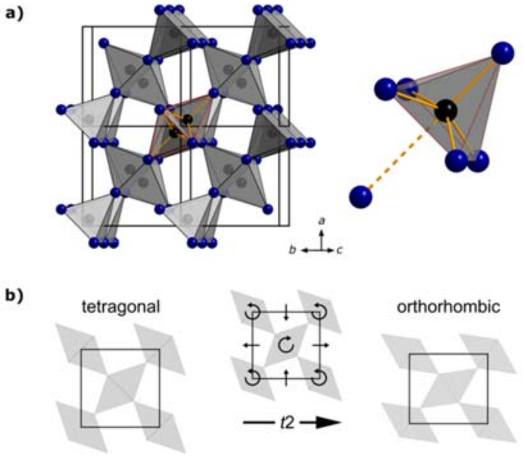

Figure 1: Crystal structure of pc-PON with a split position of P leading to a (5+1) coordination by O and N (a) and assumed phase transition from pc- to o-PON (b).

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[1] M. Bykov, E. Bykova, M. Hanfland, H.-P. Liermann, R. K. Kremer, R. Glaum, L. S. Dubrovinsky, S. van Smaalen, *Angew. Chem. Int. Ed.* 2016, **55**, 15053.
[2] J. Pellicer-Porres, A. M. Saitta, A. Polian, J. P. Itie, M. Hanfland, *Nat. Mater.* 2007, **6**, 698.
[3] D. Baumann, W. Schnick, *Angew. Chem. Int. Ed.* 2014, **53**, 14490.
[4] K. Landskron, H. Huppertz, J. Senker, W. Schnick, *Angew. Chem. Int. Ed.* 2001, **40**, 2643.
[5] P. Kroll, W. Schnick, *Chem. – Eur. J.* 2002, **8**, 3530.
[6] F. J. Pucher, S. R. Römer, F. W. Karau, W. Schnick, *Chem. – Eur. J.* 2010, **16**, 7208.
[7] L. Boukbir, R. Marchand, Y. Laurent, P. Bacher, G. Roult, *Ann. Chim. (Cachan, Fr.)* 1989, **14**, 475.
[8] J.-M. Léger, J. Haines, L. S. de Oliveira, C. Chateau, A. Le Sauze, R. Marchand, S. Hull, *J. Phys. Chem. Solids* 1999, **60**, 145.
[9] D. Baumann, R. Niklaus, W. Schnick, *Angew. Chem. Int. Ed.* 2015, **54**, 4388.
[10] S. Vogel, D. Baumann, R. Niklaus, E. Bykova, M. Bykov, N. A. Dubrovinskaia, L. S. Dubrovinsky, W. Schnick, *Angew. Chem. Int. Ed.* DOI: 10.1002/anie.201803610.

Structure and properties of pseudomorphically transformed bcc Mg synthesized using interface strain engineering

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Keywords: interface strain engineering, pseudomorphic phase transformation, multilayered Mg/Nb nanocomposite

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In recent years two-phase nanolayered composites with individual layer thicknesses varying from 200-300nm down to 1-2 nm have been the subject of intensive study because of their unusual physical, chemical and mechanical properties. For example, with decreasing layer thicknesses (down to nanometer length scales) the mechanical response of these nanocomposites becomes increasingly interface dominated, and they exhibit ultrahigh strengths approaching the theoretical limit for ideal crystals. Moreover, if the constituent phases present large differences in strength, elastic modulus and ductility, these multilayers give rise to new possibilities for the deformation mechanisms and properties of the composite as a whole. In this work, we explore the possibility of synthesizing multilayered composites where one constituent phase has a low ductility, with a final goal of enhancing both the strength and ductility of the system.

Using physical vapor deposition (PVD) techniques we synthesized a hexagonal close-packed (HCP) – body-centered cubic (BCC) Mg-Nb system (where twinning in Mg leads to its lack of ductility), over a range of layer thicknesses ranging from 5 nm to 200 nm [1, 2]. Testing of such miniaturized poses significant challenges. We utilize a combination of nanoindentation, in-situ SEM compression testing of micro-pillars, and in-situ SEM fracture toughness testing of 3 point bend micro-beams containing these multilayered nano-composites to evaluate their deformation mechanisms. Micropillar testing for three different orientations, with the interfaces oriented normal, parallel and oblique (45°) to the compression axis, enable us to explore the anisotropy in the mechanical response of the multilayer system, while the fracture toughness of the specimens are measured using the notched 3-point bend tests [2]. These results are compared for varying layer thicknesses as well as under varying ambient temperatures.

Additionally we utilized high pressure X-ray diffraction studies using synchrotron radiation to show that at low enough layer thicknesses the crystal structure of Mg can be transformed and stabilized from simple hexagonal (hcp) to body center cubic (bcc) at ambient pressures through interface strains [1]. Use of interface strains is the only technique through which pure Mg can be made to exist in the bcc phase at ambient temperature and pressures [3]. Although alloying is known to stabilize Mg in cubic (both bcc and face centered cubic, fcc) structures, pure Mg can exist in the bcc structure only under enormously high pressures (50±6 GPa) [4]. A balance of strain energy in the Mg and the energy of the interface formed with the neighboring dissimilar material drives the phase transformation, and hence the bcc Mg in the nanolayer is intrinsically different from the bcc (bulk) Mg that forms as a high-pressure phase [5].We show that when introduced into a nanocomposite bcc Mg is far more ductile, 50% stronger, and retains its strength after extended exposure to 200 C, which is 0.5 times its homologous temperature. These findings reveal an alternative solution to obtaining lightweight metals critical needed for future energy efficiency and fuel savings.

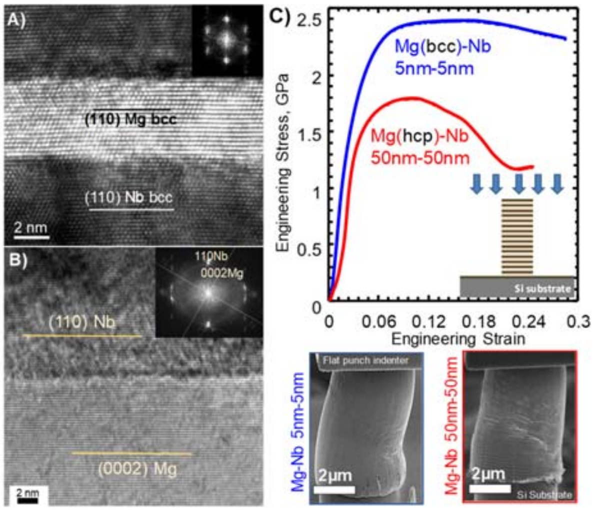

Figure 1. (A) TEM of the 5nm/5nm bcc/bcc pseudomorphic phase, (B) the 50nm/50nm hcp/bcc Mg/Nb nanocomposite. (C) Comparison of the compressive response of 5nm/5nm bcc/bcc vs. 50nm /50nm hcp/bcc Mg/Nb nanocomposites.

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[1] S. Pathak, N. Velisavljevic, J.K. Baldwin, M. Jain, S. Zheng, N.A. Mara, I.J. Beyerlein, Strong, Ductile, and Thermally Stable bcc-Mg Nanolaminates, Scientific Reports 7(1) (2017) 8264.
[2] M. Ardeljan, M. Knezevic, M. Jain, S. Pathak, A. Kumar, N. Li, N.A. Mara, J.K. Baldwin, I.J. Beyerlein, Room temperature deformation mechanisms of Mg/Nb nanolayered composites, Journal of Materials Research 33(10) (2018) 1311-1332.
[3] B. Ham, X. Zhang, High strength Mg/Nb nanolayer composites, Materials Science and Engineering: A 528(4–5) (2011) 2028-2033.
[4] H. Olijnyk, W.B. Holzapfel, High-pressure structural phase transition in Mg, Physical Review B 31(7) (1985) 4682-4683.
[5] A. Junkaew, B. Ham, X. Zhang, A. Talapatra, R. Arróyave, Stabilization of bcc Mg in Thin Films at Ambient Pressure: Experimental Evidence and ab initio Calculations, Materials Research Letters 1(3) (2013) 161-167.

Correlated high-pressure phase sequence of metal dioxides

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Keywords: phase transformation, metal-dioxides, structure evolution

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Like a temperature or external field, pressure can profoundly alter the physical behavior of a substance. For instance, applying high-pressure can cause a phase transition, which is often accompanied by a structural change with atomic re-arrangement due to the compressed volume and increased coordination number (CN), and subsequently a change in the materials' physical properties. Such a change can be vital for material science, geological and mineral physics. A lot has been done in the past to characterize such changes, as in principle they can be measured by various experiments such as XRD and Raman, or infrared techniques. How the applied pressure affects the bonding network, whose change serves as the prerequisite for the structural change and phase transition, is more important but much less known. Taking ambient metal dioxides (MO_2) as an example, where M is a metal cation, the typical structure comprises M-centered octahedrons that may be viewed as having a square basal plane, consisting of four corner oxygen atoms and the M atom, capped by two oxygen apexes. A series of TiO_2 phase transitions were confirmed through the distortion of the octahedrons at CN = 6 and the formation of post-octahedrons at CN > 6. A structural transformation of VO_2 was also found under pressure and accompanied by an insulator-to-metal transition. So far, little is known about the relationship between these compressed phases, except for the change in coordination number.

The situation may originate from the understanding of crystal. Traditionally, a crystal is considered as the stacking of a unit cell with special symmetry, which is usually characterized by space group. This definition of crystal has gained a great success to analyze some physical properties centered on symmetry, such as band structure, phonon vibration or optical transition. Yet this definition of crystal limits the understanding for the high-pressure phase transformations, which is based on the change of local bonding and coordination, instead of symmetry, as the firsthand effect of compression.

Here using VO_2 as an example, we suggest an alternative way to describe the crystal as the stacking of the coordination polyhedra under strong compression [1]. Following this description, we illustrate how the crystal structure evolves with pressure from CN = 6 at ambient conditions to CN = 10 (theory) and 9 (experiment; pressure ≤ 214 GPa). The increase in CN is realized by the formation of post-octahedrons (CN > 6), which can be characterized by a sequential oxygen insertion from 1 to 3 at one of the two apexes of the octahedron, forming a second basal plane. Conversely, the other apex and the original basal plane are topologically unchanged. To obtain CN = 10, the last inserted oxygen caps the second basal plane to form a bicapped cube. Accordingly, the oxygen sharing pattern also changes from corner to edge, and eventually to a mix between the edge and face to maintain the VO_2 formula. Our literature analysis suggests that similar transition also applies to other MO_2s such as TiO_2 and SiO_2. Thus, our new description of crystal provides a general way to clarify the relationship between the structures driven by compression.

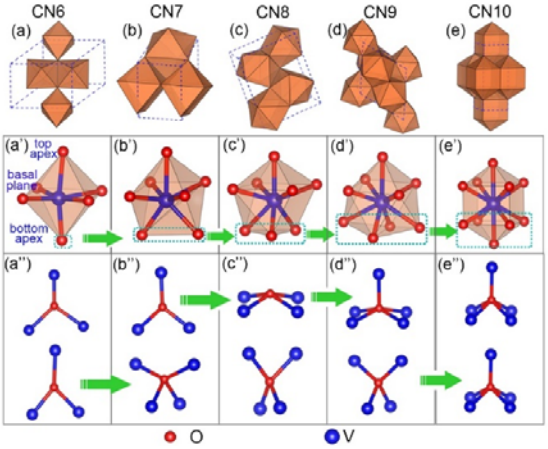

Figure 1. Crystal structures and related V-centered coordination polyhedra as the building blocks of VO_2.

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[1] Sheng-Yi Xie, et al, J. Phys. Chem. Lett., **9** 2388 (2018).

Two-way tuning of order in a disordered metallic glass

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Keywords: Ordering, disordering, high pressure, glass

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Metallic glasses (MGs) [1-3] are "disordered" systems that lack identifiable symmetry in their atomic arrangement. Therefore, MGs are expected to have quite flexible and tunable structures, without the strict constraints of a well-defined crystalline symmetry and large energy barriers separating different states in crystals. Over the last few decades, intense efforts have been made to modulate the structures of MGs to obtain desired properties, primarily focusing on different synthesis routes or post-fabrication treatments. However, effectively modulating the structure of metallic glasses has shown to be rather difficult.

Here, combining high temperature and high pressure with complementary in situ synchrotron X-ray techniques, we reveal thermal-driven structural ordering in a Ce-based metallic glass, and a reverse disordering process via a pressure-induced rejuvenation between two polyamorphous states with distinct structural order characteristics. Our findings demonstrate the feasibility of two-way structural tuning amorphous states in terms of their dramatic ordering and disordering far beyond the nearest-neighbor shells (Figure 1). We extend accessible metallic glass states to unexplored phase regions, introducing new avenues for the development of novel metallic glasses.

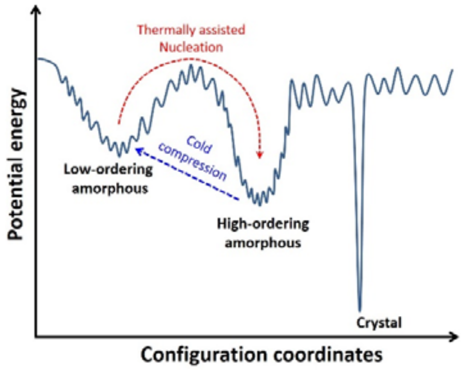

Figure 1. Diagram of the potential energy landscape (PEL) evolution

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1. Johnson, W. L.. MRS Bull. 24, 42–56 (1999).
2. Greer, A. L. & Ma, E., MRS Bull. 32, 611–619 (2007).
3. Sheng, H. W., Luo, W. K., Alamgir, F. M., Bai, J. M. & Ma, E., Nature 439, 419–425 (2006).

Synthesis of quenchable amorphous diamond under high pressure and temperature

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Keywords: high pressure, diamond, amorphous, synchrotron radiation

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Diamond has many unparalleled properties due to its extremely strong sp^3 C-C bonding. The search for the same sp^3-bonded tetrahedral amorphous carbon which would have properties complementary to diamond has been a long-sought after yet elusive goal.

By combining high pressure with *in situ* laser heating at 50 GPa and around 1800 K, we successfully synthesized a completely sp^3-bonded tetrahedral amorphous carbon, i.e., "amorphous diamond", for the first time.[1] Moreover, this amorphous diamond obtained under high pressure can be recovered to ambient conditions. We preformed comprehensive studies including x-ray diffraction (see Fig.1), high-resolution transmission electron microscopy, electron energy-loss spectroscopy experiments and *ab initio* molecular dynamics simulations on the amorphous diamond. The results suggest the amorphous diamond has a three dimensional sp3-bonded network structure similar to crystalline diamond, except no long-range order. In our *in situ* high pressure x-ray diffraction experiment, this amorphous diamond showed ultrahigh incompressibility (bulk modulus) comparable to diamond.

The three important Group-14 elements C, Si and Ge all have sp^3-bonded crystalline phases with the same diamond-cubic structure. Si and Ge also have well-known sp^3-bonded tetrahedral amorphous forms which have widespread applications. However, the counterpart in C, an amorphous form of diamond, was conspicuously missing and remained a puzzle, until now. Our high pressure study finds this missing member of the carbon allotrope family, and demonstrates that it can be maintained at ambient conditions. These results enhance our fundamental understanding of carbon materials and will trigger follow-up studies on the mechanical, thermal, optical, electrical, and chemical properties of amorphous diamond for potential applications.

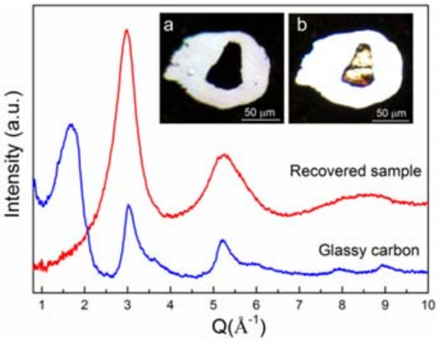

Figure 1. XRD patterns of the starting material glassy carbon (blue) and the sample recovered from high pressure and temperature (red). Optical microscope image of the sample in the DAC at 49.6 GPa before (inset a) and after (inset b) laser heating.

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[1] Z. Zeng, L. Yang, Q. Zeng, H. Lou, H. Sheng, J. Wen, D. Miller, Y. Meng, W. Yang, W. Mao, and H. Mao, *Nat. Commun.*,2017, **8**,322,DOI: 10.1038/s41467-017-00395-w.

Phase transitions and magnetovolume anomaly in $\mathrm{CoCrFeNi_xAl_{1-x}}$ (x = 0, 0.5, 0.75) high-entropy alloys at high pressure

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Keywords: High-entropy alloys, phase transition, high pressure, synchrotron x-ray diffraction, magnetovolume effect

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High-entropy alloys (HEAs) attract a growing interest in material science and engineering due to their revolutionary metallurgical concepts and remarkable properties. Comparing to conventional alloys containing only one or two principal elements, HEAs include at least five principal elements whose concentrations range between 5-35 *at.*% [1]. In the present study, HEAs of $\mathrm{CoCrFeNi_xAl_{1-x}}$ (x = 0, 0.5 and 0.75) were compressed at room temperature to high pressures using diamond anvil cells in order to investigate the severe lattice distortion effect on their phase stability.

Using technique of synchrotron x-ray diffraction, it has been discovered that both bcc $\mathrm{CoCrFeNi_{0.5}Al_{0.5}}$ (see Fig. 1) and fcc $\mathrm{CoCrFeNi_{0.75}Al_{0.25}}$ alloys transform to the hcp structure at high pressures, following a process of gradual phase transition, which has not been completed even at the highest experimental pressures (~41 and ~48 GPa, respectively). The sluggish character of these transitions originates from the local energy fluctuations caused by the chemical disorder, which represents an intrinsic feature of HEAs. We thus infer that the observed sluggish nature of the pressure-induced crystallographic phase transitions is universal for HEAs. The phase transitions in both studied compounds commenced when their intrinsic lattice strain had reached the maximum value, indicating that the lattice distortion effect plays a key role in these crystal-structure transforming processes. These results provide a fundamental information on the phase selection rules of HEAs, which are important for physical metallurgy theories and HEAs design in the future [2].

X-ray diffraction patterns obtained on the CoCrFeAl under hydrostatic and non-hydrostatic conditions show that HEA of this composition retains its bcc symmetry up to the maximum pressure applied (~61 GPa). Analysis of the compressional p-V data, supported by the *ab initio* calculations, reveals pressure-induced magnetovolume effect (the characteristic of Invar alloys) coupled with magnetic phase transitions from ferromagnetic to paramagnetic, and to non-magnetic states, originating from the successive collapse of local magnetic moments of Co and Fe. These results provide new insights into the longstanding controversy over the mechanism of the Invar effect [3], and a possible route to synthesize HEAs displaying Invar-like thermal attributes.

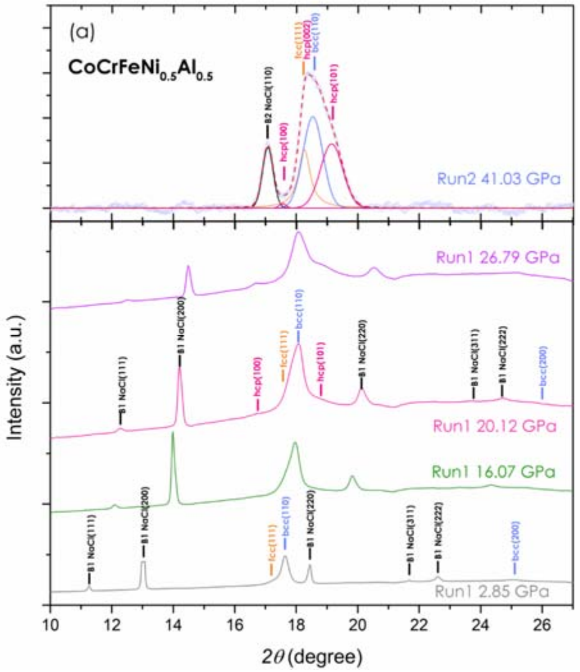

Figure 1. Typical x-ray diffraction patterns observed on compression of $\mathrm{CoCrFeNi_{0.5}Al_{0.5}}$

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[1] Y.F Ye, Q. Wang, J. Liu, C.T. Liu, Y. Yang, *Mater. Today* 2016, **19,** 349.

[2] D. Ma, B. Grabowski, F. Körmann, J. Neugebauer, D. Raabe, *Acta Mater.* **100,** 90.

[3] J. P. Rueff, A. Shukla, A. Kaprolat, M. Krisch, M. Lorenzen, F. Sette, R. Verbeni, *Phys. Rev. B* **63** 132409

Using nanoindentation and diamond anvil cells to understand phase transformations in Si, Ge and Glassy Carbon

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Pressure-induced phase transformations have been studied using both diamond-anvil cells (DAC) and uniaxial loading via nanoindentation. The respective strengths of both techniques are exploited to gain a more complete understanding of phase transformations pathways in Si, Ge and glassy carbon.

DACs were prepared to either create a quasihydrostatic environment by placing only a small volume of sample in the cell and an higher shear environment by using a larger volume of sample. In situ powder x-ray diffraction was performed at High Pressure Collaborative Access Team (HPCAT), Advanced Photon Source, Argonne National Laboratory. Neon gas was used as the pressure medium in most cases. Pressure was applied and released using HPCAT's membrane pressure control system with some cells heated in-situ using external resistive heaters.

Nanoindentation studies were done using a Hysitron TI-950 system fitted with a heating and cooling stage. After nanoindentation residual indents were characterised using a variety of techniques including focussed ion-beam milling (FIB), transmission electron microscopy (TEM), and Raman micro-spectroscopy. Three example where this combination of approaches have resulted in a deeper understanding the phase-transformation pathways in Ge, Si and Carbon, and, in particular on the importance of shear, will be covered in this presentation.

Firstly, a new rhombohedral phase of Ge with 8 atoms per unit cell (r8-Ge) which had not been widely reported to form after decompression in a DAC was observed after nanoindentation of Ge. To understand these puzzling results, Ge was loaded up to ~18 GPa using a membrane system to control the loading and unloading rates. Unexpectedly, in quasihydrostatic conditions, a transition from (β-Sn)-Ge to the rhombohedral r8-Ge phase was clearly observed, independent of unloading rates. In contrast, a DAC with a sample bridging the anvils resulting in a non-hydrostatic environment, yielded the more commonly observed tetragonal st12-Ge structure. Thus shear is thought to play a major role in determining the phase transformation pathway of Ge.[1]

The second example concerns Si. Ex-situ heating of phase-transformed residual indents in Si strongly suggests the formation of a new metastable phase arising from either the rhombohedral r8-Si or the cubic bc8-Si phase. The new phase was named 'Si-13' due to a lack of information about its structure. A series of in-situ annealing DAC experiments were conducted to attempt to form Si-13 in a DAC and measure its structure.[2] However, in the DAC, bc8-Si transformed to the hexagonal-diamond structure at elevated pressure, consistent with previous studies at ambient pressure. In contrast, r8-Si transformed directly to diamond-cubic Si at a temperature of 255°C. These data were used to construct diagrams of the metastability regimes of the polymorphs formed in a DAC however, in contrast to the indentation -induced regions, no clear formation of Si-13 was observed. The current hypothesis is that the residual stress within the nanoindentation assists in preserving small regions of the metastable phase.[2]

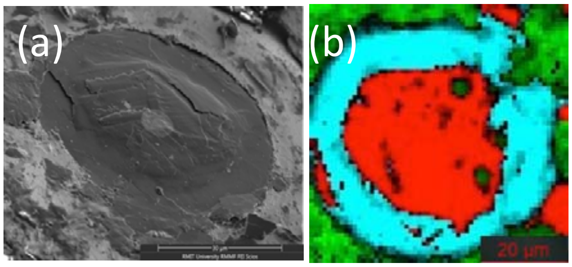

Figure 1. Scanning electron microscopy image (a) and *Raman map (b) of a recovered carbon sample showing a blue annular region consisting of Lonsdaleite surrounding a red inner region of sp2-bonded graphic carbon. The precursor material used was glassy carbon. The sample was loaded to ~100 GPa and heated to ~400°C in a DAC.*

In the last example, glassy carbon was loaded to ~100 GPa and the whole DAC annealed at ~400°C. A series of TEM, X-ray diffraction and Raman micro-spectroscopy results showed that a transformation to a nano-crystalline hexagonal diamond (Lonsdaleite) structure occurred in the outer annular region of the recovered (still in the gasket) sample. This is shown in Fig. 1. It is proposed that the combination of the initial cross-linked glassy-carbon precursor with a high-pressure, high-shear environment promote the formation of the sp3-bonded Lonsdaleite structure.[3] Transformations in glassy carbon via nanoindentation were not observed at all as the hardness of the material is not sufficient to support the a high uniaxial load.

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[1] B. Haberl, M. Guthrie, B. D. Malone, J. S. Smith, S. V. Sinogeikin, M. L. Cohen, J. S. Williams, G. Shen, and J. E. Bradby Physical Review B, 89, 144111 (2014)

[2] B. Haberl, M. Guthrie, S. V. Sinogeikin, G. Shen, J. S. Williams and J. E. Bradby High Pressure Research, 35:2, 99-116, (2015).

[3] T. B. Shiell, D. G. McCulloch, J. E. Bradby, B. Haberl, R. Boehler and D. R. McKenzie Scientific Reports 37232, (2016)

Nature of amorphous oxides under extreme compression via solid-state NMR and inelastic X-ray scattering

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Keywords: amorphous oxides under extreme compression, NMR, IXS

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Identifying the atomistic origin of the *anomalous* elastic and thermodynamic properties of oxide glasses at high pressure is one of the fundamental unsolved problems in modern physical sciences. The unique configurational properties of glass-forming liquids at high pressure may be inferred from the presence of high-energy clusters that are not known to exist at ambient pressure. Despite its importance, the formation of *highly* coordinated oxygens ($^{[3,4]}$O) and framework cations (e.g., $^{[4,5]}$B) as well as bridging carbonates in the oxide glasses remain to be explained due most to lack of suitable experimental probes.

Progress in element-specific experimental probes, such as nuclear magnetic resonance spectroscopy and inelastic x-ray scattering (IXS) allowed us to reveal the detailed structural transitions around oxygen, boron, and carbon under extreme compression. Here, we provide an overview of the recent progress that we have made into the element-specific bonding transitions in amorphous oxide at high pressure [1,2,3], revealing the presence of these high-energy clusters.

We report the ^{17}O NMR and IXS spectra for oxide glasses and reveal the presence of $^{[3,4]}$O in the archetypal amorphous oxides. We also report the first megabar boron and oxygen K-edge IXS spectra for prototypical B_2O_3 and SiO_2 glasses at high pressure up to ~125 GPa, where it is found that only four-coordinated boron ($^{[4]}$B) is prevalent, indicating the extended stability of *sp*^{3}-bonded $^{[4]}$B. Together with earlier results with other archetypal oxide glasses, such as SiO_2 and GeO_2, the current results confirm that the transition pressure of the formation of highly coordinated framework cations systematically increases with the decreasing atomic radius of the cations. Finally, C-13 NMR spectra for carbon-bearing silicate glasses revealed the preferential formation of bridging carbonate in the glassy network under compression up to 10 GPa, implying a substantial increase in melt viscosity upon densification [4].

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[1] S. K. Lee, S. B. Ryu, *J. Phys. Chem. Letts*, 2018, **9**, 150.

[2] S. K. Lee, R. Han, E. J. Kim, G. Y. Jeong, H. Khim, T. Hirose, 2017, *Nat. Geoscience,* **10**, 436.

[3] S. K. Lee, Y.-H, Kim, P. Chow, Y. Xiao, C. Ji, G. Shen, 2018, *Proc. Nation. Aca. Sci.,* https://doi.org/10.1073/pnas.1800777115.

[4] E. J. Kim, Y. Fei, S. K. Lee, 2018, *Geochimica et Cosmochimica Acta,* **224**, 327.

Metastable melting under decompression

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Liquid can exist under conditions where the stable state is either a solid or a vaper, a widely studied subject in temperature domain such as in supercooled and superheated liquids, respectively. When we consider pressure, one interesting feature of some materials is their vitrification below the glass transition temperature Tg, through either heating a metastable high pressure phase at ambient pressure, or compression (decompression) of a low (high) pressure phase to a pressure domain outside its stability field, with the latter commonly referred as pressure induced amorphization. It is found that vitrification generally occurs when the trajectory of the representative point in P-T space crosses the extrapolated melting curve. Hence, such vitrification is often viewed as a phenomenon of metastable melting. However, little attention seems to have been paid on metastable melting at temperatures above Tg. Given the wide existence of supercooled liquids, it could be possible for a metastable liquid to exist when pressure pathways cross the extrapolated melting curve above Tg. I will discuss two examples: (1) a transient liquid of bismuth appeared in a solid-solid transition under decompression; (2) observation of a low density liquid water in the water's no man's land via rapid decompression.

The ideal crystal structure of cristobalite X-I: A bridge in SiO_2 densification

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Keywords: SiO_2, metastable, cristobalite
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SiO_2 is one of the most common, yet important, compounds found on Earth. Despite its compositional simplicity, and because of its crystal chemical characteristics, SiO_2 exhibits a complex phase diagram featuring a variety of thermodynamically stable crystalline phases, as well as numerous metastable crystalline polymorphs and glasses. This includes phase transition sequences and resulting polymorphs that are strongly path-dependent. In the solid state silicon strongly prefers four-coordinated tetrahedral crystallographic sites. This low coordination number results in pronounced structural flexibility, with a tendency to form extended silicate chains, sheets, and framework polyhedral motifs, and accounts for a majority of the mineral diversity observed in shallow-depth terrestrial rocks and commonly utilized SiO_2-derived materials. In response to pressurization, silicon can assume five- and six- coordinated states; carbon, although similar in chemistry, achieves these hypervalent states only rarely [1]. Densification of silicates involving a change of the coordination number of the Si^{4+} cation is one of the sources of stratification of the Earth's mantle, and is responsible for the major seismic discontinuities that are observed as a function of depth [2, 3]. The pressure-dependent behavior of SiO_2 also plays a role in mechanochemical reactions with industrial applications, such as zeolite-facilitated polymerization of organic molecules [4, 5]. The interactions of SiO_2 polymorphs with other fundamental systems, CO_2 in particular, create complex host-guest structures and solid solutions with properties relevant to both planetary and materials science [6-8].

Compression mechanisms of tetrahedral silicate frameworks typically proceed via rigid unit modes [9], which enable structural distortions resulting in small symmetry changes, but do not allow for easy coordination changes of the central Si^{4+} cations. More significant polymorphic transformations involved in silica densification have long been thought to occur through first order reconstructive phase transitions, which typically require thermal activation, and do not easily proceed at ambient temperature. A number of intermediate metastable silica phases have been reported, but their crystal structures have not been reliably determined, despite decades of research. Computational efforts employing density functional theory (DFT) and molecular dynamics identified a number of candidate structure models; however, extensive metastability results in a Gibbs free energy hyper-surface pitted with abundant local minima, and selecting the structures that are actually realized in nature has proven challenging [10-12]. Knowledge about the structural and chemical properties of these more elusive polymorphs may provide a better understanding of the factors controlling silica densification.

One of these little-understood phases is cristobalite X-I, which forms on compression of α-cristobalite at ambient temperature above about 12.9 GPa [13-17]. Cristobalite, found typically in nature as the α-polymorph, is a high-temperature, four-coordinated form of SiO_2 with well-documented occurrences in a variety of different geologic environments, including terrestrial igneous rocks, protoplanetary disks around young stars [18], and meteorites that were shocked beyond 10 GPa [19]. α-cristobalite was also the starting material for the first successful high-pressure synthesis of quenchable octahedral seifertite-SiO_2 [11], found in heavily shocked meteorites such as Shergotty and Zagami [20, 21], where it is considered a possible proxy of the peak pressure during shock metamorphism.

Most of the earlier experimental studies involving cristobalite X-I were limited either in terms of the sample quality or by the shortcomings of high-pressure powder diffraction, and thus did not provide definitive answers or solid platforms for computationally generated structure models. Here, we report the results of single-crystal synchrotron x-ray diffraction experiments with α-cristobalite, using a diamond anvil cell, in which a well-diffracting specimen of the X-I phase was formed via a single-crystal to single-crystal transformation at ambient temperature. We solved the structure using both direct methods [22] and simulated annealing [23, 24], which both independently arrived at the same model. Our X-I structure model features only two symmetry independent Si sites, which are sufficient to produce the ideal SiO_2 stoichiometry. All Si atoms reside in octahedral sites, which are arranged in an edge-sharing zigzag chain pattern. The $P2_1/n$ space group in which SiO_2 X-I crystallizes is equivalent, in a different setting, with the $P2_1/c$ space group of post-quartz [21, 25, 26].

The crystal structure of this phase was shown to be nearly defect-free, with ideal SiO_2 stoichiometry. Our experimental results are compared with those of previously proposed structures [27], and are supplemented with density functional theory calculations that compare the enthalpy of various silica polymorphs on compression, and examine the dynamic stability of the X-I structure. These calculations show that cristobalite X-I's enthalpy and stability sits between between other tetrahedrally and octahedrally coordinated SiO_2 phases above 5 GPa. Additional phonon density of states calculations do not predict any imaginary frequencies, confirming the dynamic stability of the structure determined from our X-ray diffraction experiment.

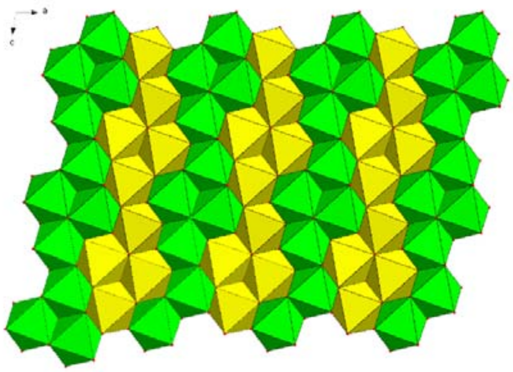

Figure 2: Octahedral chain geometry of the cristobalite X-I phase. Yellow and green octahedra represent chains in alternating layers, with void space between layers of like color.

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[1] C. McKee William, *et al.*, Covalent Hypercoordination: Can Carbon Bind Five Methyl Ligands?, Angewandte Chemie International Edition 53(30) (2014) 7875-7878.

[2] J.K. Wicks, T.S. Duffy, Crystal Structures of Minerals in the Lower Mantle, Deep Earth: Physics and Chemistry of the Lower Mantle and Core, 1, John Wiley & Sons, Inc2016, pp. 69-87.

[3] R.J. Angel, *et al.*, A silica-rich sodium pyroxene phase with six-coordinated silicon, Nature 335 (1988) 156.

[4] M. Santoro, *et al.*, Synthesis of 1D Polymer/Zeolite Nanocomposites under High Pressure, Chemistry of Materials 28(11) (2016) 4065-4071.

[5] D. Scelta, *et al.*, High Pressure Polymerization in a Confined Space: Conjugated Chain/Zeolite Nanocomposites, Chemistry of Materials 26(7) (2014) 2249-2255.

[6] D. Santamaría-Pérez, *et al.*, Structural Evolution of CO2-Filled Pure Silica LTA Zeolite under High-Pressure High-Temperature Conditions, Chemistry of Materials 29(10) (2017) 4502-4510.

[7] M. Santoro, *et al.*, Carbon enters silica forming a cristobalite-type CO_2–SiO_2 solid solution, Nature Communications 5 (2014) 3761.

[8] M. Santoro, *et al.*, Partially collapsed cristobalite structure in the non molecular phase V in CO_2, Proceedings of the National Academy of Sciences 109(14) (2012) 5176-5179.

[9] K.D. Hammonds, *et al.*, Rigid-unit phonon modes and structural phase transitions in framework silicates, American Mineralogist 81(9-10) (1996) 1057-1079.

[10] C. Campana, *et al.*, Irreversibility of the pressure-induced phase transition of quartz and the relation between three hypothetical post-quartz phases., Physical Review B 70 (2004) 224101.

[11] D. Donadio, *et al.*, Influence of temperature and anisotropic pressure on the phase transition in a-cristobalite., Physical Review Letters 100 (2008) 165502.

[12] N. Garg, S.M. Sharma, Classical molecular dynamical simulations of high-pressure behavior of alpha cristobalite (SiO_2). Journal of Physics: Condensed Matter 19 (2007) 456201.

[13] Y. Tsuchida, T. Yagi, New pressure-induced transformations of silica at room temperature, Nature 347(6290) (1990) 267-269.

[14] L.S. Dubrovinsky, *et al.*, A class of new high-pressure silica polymorphs., Physics of the Earth and Planetary Interiors 143-144 (2004) 231-240.

[15] L.S. Dubrovinsky, *et al.*, Pressure-induced transformations of cristobalite., Chemical Physics Letters 333 (2001) 264-270.

[16] V.P. Prakapenka, *et al.*, High pressure induced phase transformation of SiO_2 and GeO_2: difference and similarity., Journal of Physics and Chemistry of Solids 65 (2004) 1537-1545.

[17] P. Dera, *et al.*, New insights into the high-pressure polymorphism of SiO_2 cristobalite, Physics and Chemistry of Minerals 38(7) (2011) 517-529.

[18] C. Koike, *et al.*, Infrared Spectra of Silica Polymorphs and the Conditions of Their Formation, The Astrophysical Journal 778(1) (2013) 60.

[19] U.W. Bläß, Shock-induced formation mechanism of seifertite in shergottites, Physics and Chemistry of Minerals 40(5) (2013) 425-437.

[20] A. El Goresy, *et al.*, Seifertite, a dense orthorhombic polymorph of silica from the Martian meteorites Shergotty and Zagami., European Journal of Mineralogy 20 (2008) 532-528.

[21] P. Dera, *et al.*, Characterization of a high-pressure phase of silica from the Martian meteorite Shergotty, American Mineralogist 87(7) (2002) 1018.

[22] A. Altomare, *et al.*, SIR92 - a program for automatic solution of crystal structures by direct methods, Journal of Applied Crystallography 27(3) (1994) 435.

[23] K. Brandenburg, H. Putz, Endeavour, Crystal Impact GbR, Bonn, 2009.

[24] H. Putz, *et al.*, Combined Method for 'Ab Initio' Structure Solution from Powder Diffraction Data., Journal of Applied Crystallography 32 (1999) 864-870.

[25] J. Haines, *et al.*, Crystalline post-quartz phase in silica at high-pressure., Physical Review Letters 87 (2001) 155503.

[26] D.M. Teter, *et al.*, High Pressure Polymorphism in Silica, Physical Review Letters 80(10) (1998) 2145-2148.

[27] A. Černok, *et al.*, Compressional pathways of α-cristobalite, structure of cristobalite X-I, and towards the understanding of seifertite formation, Nature Communications 8 (2017) 15647.

Crystal structures of high-pressure solid phases of hydrogen to 230 GPa based on x-ray diffraction

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Keywords: hydrogen, crystal structure, synchrotron x-ray diffraction

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Hydrogen is the most abundant element of planets in the solar system. Under the pressures of planetary interiors, hydrogen goes through many phase transitions to reach the metallic state. At least seven high-pressure solid phases of hydrogen, i.e., phases I, II, III, IV, IV', V and VI, have been reported experimentally up to 388 GPa based on optical spectroscopy evidences. Direct X-ray diffraction (XRD) measurements which provide the basic understanding of their crystal structures under strong compression, however, remaining a formidable technical challenge due to the extremely low x-ray scattering power of hydrogen and the extremely small sample size at megabar pressures. Here we present the first XRD measurement of hydrogen phase IV above 230 GPa at room temperature by developing the synchrotron nano-scale X-ray diffraction techniques. Our data suggest that hydrogen molecules in the phase IV remains in an HCP-like lattice. The predicted partially order HCP phase, with weakly coupled H_2 molecular layer and strongly coupled graphene-like layer, qualitatively explains both the XRD and Raman results.

Planetary core compositions constrained from density measurements and chemical differentiation

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Keywords: core composition, equation of state, high-pressure

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Silicate-metal differentiation naturally leads to iron-dominant metallic cores of the Earth and other terrestrial planets. The amounts of light elements, such as S, Si, and O, incorporated in the core are controlled by accretion process and conditions of the silicate-metal separation. Direct constraint on composition of the Earth's core comes from seismic observations that provide measurements of the densities and sound velocities of Earth's liquid outer core and solid inner core. To develop a core composition model that meets the geophysical constraints, it is essential to have full knowledge of thermal equations of state of core materials and density-velocity relationships over a wide pressure-temperature range. We have been systematically determining the effect of S, Si, and O on the density and sound velocity of iron alloys and map out the possible composition space that can explain the observed density and sound velocity of the liquid outer core and solid inner core. Here I present new compression data on Fe-9wt%Si alloy up to 200 GPa using FIB-modified stepped diamond anvils. The data are integrated with static P-V-T data up to 100 GPa and 2000 K and shockwave Hugoniot data to develop an accurate thermal equation of state that is used to evaluate the Si content in the inner core. Additional data on compressional velocity obtained by IXS technique and shockwave method are used to further constrain the composition difference between the inner and outer cores. The geophysically constrained possible core compositions are further evaluated by Si and S partitioning between liquid and solid metals at high pressure and temperature.

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Application of sub-micron x-ray beams to diffraction from small high-pressure samples

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Keywords: synchrotron radiation, micro-diffraction

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Due to the intrinsic limits of materials that can be used to compress samples, higher sample pressures naturally lead to smaller sample volumes. Thus, probing the atomic structure of these smaller sample volumes requires ever smaller x-ray beams. As the sample size shrinks, the same x-ray flux must be completely focused onto the smaller sample to maintain the diffracted intensity as much as possible. Also, the wings of the focused x-ray beam must remain low to prevent parasitic scattering from any nearby gasket material. With the advent of planned new high emittance synchrotron sources, the brightness of the focused x-ray beams should increase by a factor of ~100, making it easier to measure smaller sample volumes and samples composed of weakly scattering elements. We will discuss the expected improvements and limitations that will be provided by these new x-ray sources, and how they are likely to affect x-ray scattering from high-pressure samples.

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Oxygenated iron oxide at Earth's lower-mantle conditions

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Keywords: synchrotron radiation, free-electron laser

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Oxygen and iron are Earth's most abundant elements by number of atoms and by mass, respectively. They form compounds dictating major chemistry of our planet [1]. The generally accepted view believed that O_2 dimer only existed on Earth's highly oxidized surface, and that oxygen anion existed in the invariable 2- valence state in minerals throughout the deep interior, where the redox states were controlled by the 3*d* transition element Fe which could vary between two valance states, ferric Fe^{3+} and ferrous Fe^{2+}. The oxygen fugacity decreases with increasing depth as defined by a series of iron oxides with O/Fe stoichiometry from the end-member $Fe^{3+}{}_2O_3$, through Fe_5O_7 [2], Fe_3O_4, Fe_4O_5 [3], Fe_5O_6 [4] to the other end-members $Fe^{2+}O$ at the highly reducing core-mantle boundary (CMB). High pressures in the deep lower mantle could overcome the Pauli's exclusive energy and cause 3*d* electrons with opposite magnetic spins to pair, and the spin-pairing transition drastically impacts the geochemical, geophysical, and geodynamic processes.

High pressure drastically alters chemical bonding, valence states, electron spin, and other generally accepted chemistry "rules" at zero pressures, but these changes are difficulties to measure under pressures and are poorly understood. Here we studied pressure-induced changes on O, Fe, and H and their interactions in a recently discovered iron superoxide (FeO_2H_x with x = 0 to 1) which was proposed to be an important component in the deep Earth. Their altered behaviors in the middle Earth certain have major impacts to this planet.

Integrating a battery of synchrotron X-ray techniques to probe the Mössbauer effect and pre-K-edge spectroscopy in situ at high pressures, here we found many unexpected chemical behaviors. Iron remains in the reduced, spin-paired ferrous state in spite of its unprecedentedly high O/Fe ratio. The valence state of oxygen is not constant at 2- as commonly known in other oxides, but varying around 1-. It forms interactive dimer with an O–O bond length ~30% longer than commonly considered as interactive dimer, but still shorter than non-interactive dimer. Hydrogen becomes weakly bonded in the structure, and its amount does not affect the valence of iron. Considering other exotic pressure-induced phenomena previously reported in similar high-pressure region, such as the redox paradox of ferric iron, formation of O_8 molecular clusters, and the symmetrical hydrogen bonds and superionic hydrogen in ice, our study indicates a broad chemical paradigm change in the middle Earth.

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[1] V. Stagno, *et al.*, *Nature* 2013, **493,** 84.
[2] E. Bykova, *et al.*, *Nature Comm.* 2014, **7,** 10661.
[3] B. Lavina, *et al.*, *PNAS* 2011, **108,** 17281.
[4] B. Lavian and Y. Meng, *Sci. Adv.* 2015, **1**, e1400260.

Interaction of major volatiles with the lower mantle: A multigrain approach

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Keywords: lower mantle, multigrain

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The distribution and behavior of major volatiles (water, carbon dioxide, and chlorine) in the deep Earth remain an open question, largely due to our lack of knowledge on the deep geological processes. Through high *P-T* experiments in a laser heated diamond anvil cell (DAC), we are able to simulate the lower mantle processes on how the major volatiles interact with the lower mantle system. A reaction between volatile(s) with the lower mantle system under the high-pressure–temperature (P-T) conditions produces a multiphase system which often includes new phases. Identification of an unknown phase in an environment of multiple crystals and multiple phases under high *P-T* conditions remains a great challenge. Fortunately the high degree of spottiness in our high *P-T* experiments allowed the multigrain indexation [1], which could provide single-crystal–like information for each individual crystal in the multiphase assemblage [2].

Recent discoveries found hydrous phases AlOOH (Z = 2) with a $CaCl_2$-type structure [3] and FeOOH (Z =4) with a cubic pyrite-type structure (Py phase) [4,5] stable under high *P-T* conditions of the DLM. Our experiments at 107–136 GPa and 2,400 K have further demonstrated that (Fe,Al)OOH is stabilized in a hexagonal lattice. By combining powder X-ray diffraction techniques with multigrain indexation, we are able to determine this hexagonal hydrous (HH) phase with a = 10.5803(6) Å and c = 2.5897(3) Å at 110 GPa [6]. Hexagonal (Fe,Al)OOH can transform to the cubic pyrite structure at low T with the same density, as shown in Figure 1. The Py phase can repeatedly transform to the nearly pure HH phase after reheating at 2000 K (Figure 1A), an indication of the Py phase being a low-T polymorph of the HH phase.

Water and chlorine (Cl) cycles are closely related through subduction into the Earth's mantle. We discovered, the Py phase FeOOH will readily form up to 1700 K near 100 GPa, and it further reacts with NaCl at elevated temperature, producing a previously unknown cubic phase of $FeCl_2$. The $FeCl_2$ phase adopts a cubic structure with with the $Pa\overline{3}$ space group. This study suggests that the recycling Cl can be partially carried down to a greater depth than previously thought.

Carbon dioxide is another major volatile component and recent study by Boulard et al. found that a high-T-induced chemical reaction in the Fe-C-O-H system, producing a tetrahedral carbonate phase $Fe_4C_3O_{12}$ at the expense of the Py-phase FeOOH [7]. In summary, interactions of volatile-bearing minerals with the lower mantle may largely alter the fate of volatiles in the mantle and fundamentally change the deep volatile cycles.

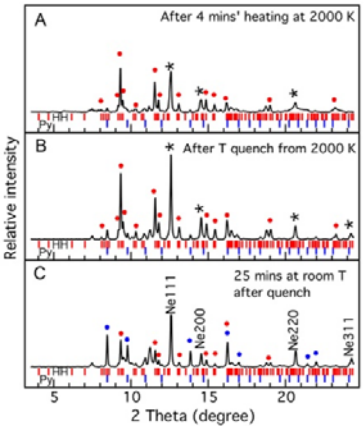

Figure 1. Powder XRD patterns of the coexisting Py phase and HH phase in $(Fe_{0.8}Al_{0.2})OOH$. The conversion between the Py phase and the HH phase upon reheating at 107.8 GPa (P measured after T quench): (A) the nearly pure HH phase (marked with red dots) after reheating at 2,000 K for 4 min; (B) after T quench; (C) gradual conversion from the HH phase to the Py phase (marked with blue dots) after 25 min at room temperature after quench (X-ray wavelength:0.3738 Å).

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[1] H. O. Sørensen, et al., *Zeitschrift fur Krist.* 2012*,* **227,** 63.
[2] L. Zhang et al., *Am. Mineral.* 2016, **101**, 231.
[3] I. Ohira, et al., *Earth Planet. Sci. Lett.* 2014, **401**, 12.
[4] Q. Hu, et al., *Proc. Natl. Acad. Sci.* 2017, **114,** 201620644.
[5] M. Nishi, Y. Kuwayama, J .Tsuchiya & T. Tsuchiya, *Nature* 2017, **547,** 205.
[6] L. Zhang, H. Yuan, Y. Meng & H.-k. Mao, *Proc. Natl. Acad. Sci.* 2018, **115,** 2908.
[7] E. Boulard, et al., *Natl. Sci. Rev.* 2018, nwy032.

Crystalline polymeric carbon dioxide is stable at megabar conditions

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Keywords: carbond dioxide, megabar, laser heating

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Static high-pressure experiments at megabar pressures give evidence for a stable extended form of crystalline carbon dioxide [1]. Synchrotron X-ray diffraction and Raman studies of laser-heated carbon dioxide in a diamond-anvil cell (DAC) suggest the polymeric phase V (space-group symmetry I-42d) [2] to be the thermodynamically stable crystalline structure at conditions relevant to the Earth's lowermost mantle.

By using a carbonate crystal as a potential laser absorber, a CO_2 sample compressed to about 120 gigapascals was successfully heated up to 2700 Kelvin. Contrary to earlier experimental findings, but in agreement with reported theoretical calculations [3-5], neither dissociation into diamond and ε-oxygen nor ionization was observed. Even amorphization can be definitely ruled out from the experimental findings.

The observation of ß-ReO_2 occurring at the interface to the Re-gasket suggests that earlier findings on the CO_2 breakdown most likely originate from a simple redox reaction between hot CO_2 and the Re gasket used in the DAC [6].

The experimental equation of state and a negative linear compressibility along the tetragonal *c* axis are confirmed. Additional features in the diffraction pattern demonstrate the existence of severe deviatoric stress and lattice deformation along with preferred orientation. Their disappearance on progressive annealing suggest CO_2-V being the stable structure also above one megabar.

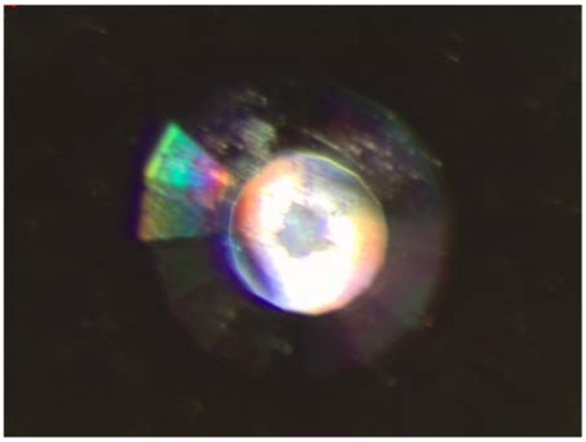

Figure 1. Sample chamber of DAC with CO_2 at 18 GPa, recrystallized after heating to 2700 K at 120 GPa.

[1] F. Dziubek et al., *Nat. Communications* 2018, (in press)
[2] M. Santoro et al., *PNAS* 2012, **109,** 5176
[3] K.D. Litasov et al.., *EPSL* 2011, **309,** 318-323
[4] F. Maeda et al., *Sci Rep.* 2017 **7,** 40602
[5] C-S Yoo, *PRL* 2013, **83,** 5527
[6] D. Santamaria-Perez, *Inorg. Chem.* 2016, **55,** 10793

Probing the electronic structure and magnetism of 5*d* materials using resonant x-ray techniques at high pressure

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Keywords: x-ray spectroscopy, magnetism, strongly correlated electron systems, iridates

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The strongly correlated *d* orbitals of transition metal oxides host a myriad of emergent phenomena, which are highly sensitivity to the structural motif surrounding the transition metal ions, thus making high pressure a prime tool to probe their behavior and drive new phenomena. However, directly accessing electronic and magnetic properties at high pressure has been proven to be quite difficult since many of the standard techniques used at ambient pressure are often incompatible with diamond anvil cells. In this talk, I will use our work on the archetypical iridate Sr_2IrO_4 [1,2,3] as an example on the power of resonant x-ray techniques to investigate strongly correlated electron systems at high pressure, with particular focus to the techniques available at the 4-ID-D beamline of the Advanced Photon Source, Argonne National Laboratory.

The substantial attention devoted to iridates derives from their large spin-orbit coupling that, contrary to most 3*d* transition metal oxides, largely affect their 5*d* orbital. In fact, the magnetic and electronic properties of Sr_2IrO_4 closely resemble that of the La_2CuO_4 family of high-T_c superconductors, raising the prospect that, much like in cuprates, emergent phenomena might arise in Sr_2IrO_4 when magnetic order is suppressed [1,3]. We combine high pressure with x-ray magnetic circular dichroism and resonant x-ray magnetic diffraction techniques to show that in fact the magnetic ordering is suppressed in Sr_2IrO_4 above 20 GPa. X-ray absorption near edge structure data show that such magnetic phase transition is not accompanied by a collapse of spin-orbit effect in the 5*d* orbital. These results imply that above 20 GPa Sr_2IrO_4 features a phase with no long-range magnetic order, but with persistent, strongly coupled, local magnetic moments, which leads to the tantalizing possibilities of quantum paramagnetic or spin liquid states. Finally, I will discuss our plans for high-pressure techniques development at 4-ID-D, with particular focus on the opportunities that will be enabled by the Advanced Photon Source upgrade.

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[1] B. J. Kim et al., *Science* 2009, **323**, 1329.
[2] D. Haskel *et al.*, *Phys. Rev. Lett.* 2012, **109**, 027204.
[3] Y. K. Kim *et al.*, *Science* 2014, **345**, 187.

Quantum transport property in trigonal layered PtBi$_2$: A possible new triply degenerate point fermions and pressure-induced superconductivity

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Keywords: PtBi2, quantum transport,topological semimetals

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Triply degenerate point (TP) fermions in tungsten-carbide-type materials (e.g., MoP), which represent new topological states of quantum matter, have generated immense interest recently. However, the TPs in these materials are found to be far below the Fermi level, leading to the TP fermions having less contribution to low-energy quasiparticle excitations. Here, we theoretically predict the existence of TP fermions with TP points close to the Fermi level in a new system, i.e., trigonal layered PtBi$_2$, by *ab initio* calculations, and experimentally verify the predicted band topology by magnetotransport measurements under high magnetic fields up to 40 T. Analyses of both the pronounced Shubnikov–de Haas and de Haas–van Alphen oscillations reveal the existence of six principal Fermi pockets. Our experimental results, together those from *ab initio* calculations, reveal the interplay between transport behaviors and unique electronic structures, and support the existence of TP fermions in trigonal layered PtBi$_2$.

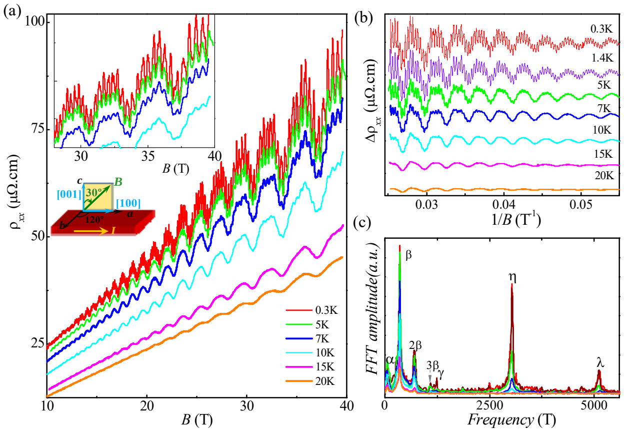

Figure 1. (a) Magnetic field dependence of resistivity at different temperatures when the field is applied along $\theta=30°$. (b) SdH oscillatory components as a function of $1/B$ after subtracting a smooth background. (c) Corresponding FFT spectra of oscillations.

Pressure tuning the Fermi surface topology of Weyl semimetals

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Keywords: Weyl semimetals, quantum oscillations, chiral anomaly, anomalous Hall effect

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Recently enormous attention has been given to a class of material called Weyl semimetal (WSM) due to the prediction of many exotic phenomena, in particular exceptional transport properties, making these systems not only interesting for fundamental research, but also promising materials for novel applications. WSM can be viewed as the hybrid of “3D graphene” and topological insulators. The band crossing point, the so-called Weyl point, acts as a magnetic monopole (a singular point of Berry curvature) in momentum space, which always comes in a pairs. If the time-reversal and inversion symmetries are respected, a pair of Weyl points is degenerate in energy, forming another topological phase called Dirac semimetal. Owing this complex band structure the details of the electronic structure can play a significant role in the electrical transport properties of these materials. In this context, external pressure is an important control parameter to effectively tune lattice structures and the corresponding electronic states in a systematic fashion, avoiding the complexity brought by chemical doping. Since surface-sensitive probes such as ARPES cannot be used for detecting the topological states under pressure, quantum oscillation studies become an ideal tool to determine the effects of pressure on the Fermi-surface topology. In this talk, I will present the effects of pressure on the fermi surface topology of two Weyl semimetal compounds, NbP and Mn_3Ge.

In the former compound, NbP, I will show the pressure evolution of the Fermi surface topology of the Weyl semimetal NbP, probed by Shubnikov-de Haas oscillations in the magnetoresistance combined with *ab-initio* calculations of the band-structure [1]. Although we observe a drastic effect on the amplitudes of the quantum oscillations, the frequencies only exhibit a weak pressure dependence up to 2.8 GPa. The pressure-induce variations in the oscillation frequencies are consistent with our band-structure calculations. Furthermore, we can relate the changes in the amplitudes to small modifications in the shape of the Fermi surface. Our findings evidenced the stability of the electronic band structure of NbP and demonstrate the power of combining quantum-oscillation studies and band-structure calculations to investigate pressure effects on the Fermi-surface topology in Weyl semimetals.

For the Mn_3Ge compound, the external pressure was used to tune the Berry curvature of this chiral antiferromagnetic compound and to investigate the effect of this change on the transport properties of the material. Our results demonstrate that the giant anomalous hall effect (AHE) observed in the Mn_3Ge can be easily tuned by application of the external pressure. We observed that at 100 K, where the Hall conductivity is of about of 100 $ohm^{-1}.cm^{-1}$, the AHE is continues suppressed by application of external pressure and vanish for p=2 GPa. For higher pressure, the AHE change the signal and starts increase again, reaching a maximum of hall conductivity 40 $ohm^{-1}.cm^{-1}$ for p=2.8 GPa. A similar behavior was observed in the range of temperatures from 5 to 300 K. The pressure-induced variations in the AHE amplitudes are consistent with our observation from powder neutron diffraction experiments [2], where we verify that the application of pressure up to 5 GPa causes the gradual change from the non-collinear triangular structure to a uniformly canted non-collinear triangular structure and a successive change to the collinear FM structure. Our findings evidenced the tunability of the electronic structure of the chiral antiferromagnetic Mn_3Ge what might expand significantly the potential of application for this family of compounds.

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[1] R. D. dos Reis et al, *Phys Rev. B. v. 93, p. 205102, 2016* .
[2] A. S. Sukhanov et al, http://arxiv.org/abs/1805.09372

High-pressure, high-magnetic field Fermiology studies of YBCO

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Keywords: Fermiology, YBCO, high pressure, high magnetic fields

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The pnictide, cuprate and molecular conductor families exhibit similar phase diagrams, leading to a great deal of interest in a common mechanism for a “universal phase diagram”. The typical ingredients for such phase diagrams include an antiferromagnetic phase, a superconducting dome, and possibly one, or several quantum critical points (QCP). Chemical doping is one traditional way to look at such materials, however thermodynamic variables such as magnetic field or hydrostatic pressure have proven to be powerful tools to explore this phase diagram, with very strong magnetic fields being used to suppress the superconducting dome, allowing one to investigate the QCP.

YBCO’s temperature-oxygen doping phase diagram exhibits a small antiferromagnetic region at lowest doping and charge and spin orders around p=0.1 that compete with or induce superconductivity, as well as a pseudogap region and a QCP under the SC dome [1]. Over this range of doping, the Fermi surface changes from small pockets to arcs and finally a large pocket beyond the superconducting dome. Both rhe QCP and this change in FS are critical to our understanding of the cuprates and the universal phase diagram. Ramshaw, et al. [2] have found a divergence of the effective mass in the region of the CDW that hints at a QCP around p=0.19. Ideally, strong fields could also be used to suppress Hc2, allowing for the observation of quantum oscillations (QOs) in the region around the QCP, but this would require fields of approximately 150 T, well above the 100 T limit currently available. Instead doping has been used to suppress the dome to about 30 K [3], but doping at this level precludes the observation of QOs.

Our group performed high pressure SdH studies of YBCO6.5 (p=0.1) at He-3 temperatures in pulsed fields to 70 T and 7 GPa at HLD and dc fields of 45 T and pressures of 24.7 GPa at NHMFL using plastic and metal diamond anvil cells (DACs), respectively, that are coupled with an LC tank circuit based on a tunnel diode oscillator. The small coil that makes up the inductor of this LC circuit and resides in the high pressure volume of the DAC senses changes in sample resistivity due to variations in temperature, pressure or magnetic field.

Our Fermiology studies clearly show a strongly diverging effective mass at 4.5 GPa that is associated with a local maximum in frequency and Tc. The high Hc2 in this material limits our study in the low pressure range to pressures below 7 GPa. However,, at P> 24.7 GPa we are able to once again see quantum oscillations and find that the orbital frequency has increased from 550 T at ambient pressure to 690 T monotonically. Pulsed field high pressure studies are currently planned to shed light on the region between 7 and 24 GPa. This now allows us to use pressure to develop a B-P-T phase diagram that will permit a more complete picture of HTS to be pursued, perhaps answering how CDWs and the pseudogap play a role in superconductivity and allowing for the investigation of the QCP.

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[1] S. Badoux, et al., Nature, 531, 210 (2016).
[2] B. Ramshaw, et al., Science, 348, 317 (2015).
[3] J.L. Tallon, et al., Phys. Rev. Lett., 79, 5294 (1997).
[4] S. Sadewasser, et al., Phys. Rev. B, 56, 14168 (1997).

A new quasi one-dimensional compound Ba_3TiTe_5 and superconductivity induced by pressure

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Keywords: Quasi 1D conducting chains, Superconductivity

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The one-dimension (1D) system has attracted many attentions because its novel physical phenomena are dramatically different from higher dimensions (2D/3D) systems[1,2]. We report the discovery of quasi one-dimensional compound Ba_3TiTe_5 and the superconductivity induced by pressure. Ba_3TiTe_5 was synthesized at high pressure and high temperature. It crystallizes into a hexagonal structure (*P*6₃*/mcm*) with the lattice constants a=b=10.1529 Å and c=6.7217 Å, which consists of infinite face-sharing octahedron $TiTe_6$ chains as well as Te chains (shown in Fig. 1). Ba_3TiTe_5 presents a semiconductor behavior under ambient pressure due to the Umklapp scattering effect in one dimensional conducting system. The superconductivity emerges above 16GPa and reaches the maximum T_c ~6 K at about 36 GPa, where the spin/charge density wave (SDW/CDW) state is completely suppressed. When pressure further increases, the system develops towards Fermi Liquid state. At the same time, T_c monotonously decreases. Pressure reduces the adjacent distance between the conducting paths and then enhances the interchain hopping, which should play a key role in the pressure dependence of superconductivity and SDW/CDW. It is hinted that the superconductivity associates with the fluctuation of SDW/CDW.

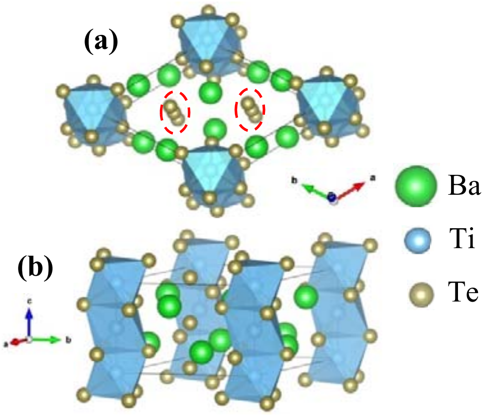

Figure 1. the sketch of the crystal structure of Ba_3TiTe_5 with the view of projection along c axis and perpendicular to c axis, respectively.

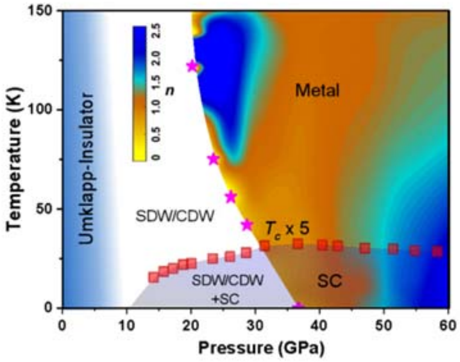

Figure 2. The schematic temperature-pressure phase diagram of Ba_3TiTe_5.

Acknowledgments: This work was financially supported by NSFC, National Basic Research Program of China.

[1] J. Zhang, R. Su, X. C. Wang, W. M. Li, J. F. Zhao, Z. Deng, S. J. Zhang, S. M. Feng, Q. Q. Liu, H. Z. Zhao, P. F. Guan and C. Q. Jin, Inorg. Che. Front. 2017, **4**, 1337

[2] J. Zhang, M. Liu, X. C. Wang, K. Zhao, L. Duan, W. M. Li, J. F. Zhao, L. P. Cao, G. Y. Dai, Z. Deng, S. M. Feng, S. J. Zhang, Q. Q. Liu, Y. F. Yang and C. Q. Jin, J. Phys.: Condens. Matter, 2018, 30, 214001

Theoretical study of the magnetic anisotropy energy in bulk Na4IrO4

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Keywords: Theoretical calculation, Magnetic properties

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In 5d transition-metal oxides, novel properties arise from the interplay of electron correlations and spin-orbit interactions. Na_4IrO_4, where the 5d transition-metal Ir atom occupies the center of the square-planar coordination environment, has attracted research interest. Based on density functional theory, we present a comprehensive investigation of electronic and magnetic properties of Na_4IrO_4. We propose the magnetic ground-state configuration, and find that the magnetic easy axis is perpendicular to the IrO_4 plane. The magnetic anisotropy energy (MAE) of Na_4IrO_4 is found to be giant. We estimate the magnetic parameters in the generalized symmetry-allowed spin model, and find that the next-nearest-neighbor exchange interaction J(2) is much larger than other intersite exchange interactions and results in the magnetic ground-state configuration. The numerical results reveal that the anisotropy of interatomic spin-exchange interaction is quite small and the huge MAE comes from the single-ion anisotropy. This compound has a large spin gap but very narrow spin-wave dispersion, due to the large single-ion anisotropy and quite small intersite exchange couplings. We clarify that these remarkable magnetic features are originated from its highly isolated and low-symmetry IrO_4 moiety. We also explore the possibility to further enhance the MAE.

Computational Modeling of Mechanical and Electronic Properties of Superhard Boron-Carbon Materials

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Keywords: crystal structure prediction, evolutionary algorithm, boron-carbon composites, superhard materials

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Superhard materials with a Vickers hardness larger than ~30 GPa have a wide range of industrial applications such as protective coatings. Superhard boron-carbon composites are especially important because of their superior high-temperature performance as compared to diamond and their low reactivity with ferrous metals. Here we employ the powerful evolutionary algorithm as implemented efficiently in the USPEX software [1,2] to predict the crystal structures of superhard boron-carbon composites, including the elusive BC_5 compound. The mechanical properties, electronic structures, phonon and Raman spectra of these predicted structures are computed accordingly also from first principles using density functional theory. The simulation results are discussed together with previous high-temperature high-pressure synthesis of BC_5 [3], and with more recent large-area synthesis based on microwave plasma chemical vapor deposition methods.

Acknowledgments: This work is supported in part by the NSF EPSCoR RII-Track-1 Cooperative Agreement OIA-1655280.

[1] C. W. Glass, A. R. Oganov, and N. Hansen, *Comp. Phys. Commun.* 2006, **175,** 713.

[2] A. O. Lyakhov, A. R. Oganov, H. T. stokes, and Q. Zhu, *Comp. Phys. Commun.* 2013, **184,** 1172.

[3] V. L. Solozhenko, O. O. Kurakevych, D. Andrault, Y. L. Godec, and M. Mezouar, *Phys. Rev. Lett.* 2009, **102**, 4.

Dimorphic $SrMn_2P_2$ under variant pressures: Theory and experiment in harmony

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Keywords: high-pressure synthesis, layered compounds

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It is well known that materials can show intriguing properties under pressure. Magnetic materials are extremely useful and strategically important to many major economies. The studies of atomic and magnetic structures under pressure have important implications for revealing previously unknown information about the structure of these materials, expanding the number of properties and uses that they potentially could have. Intermetallic compounds with the formula AM_2X_2, where A is an electropositive element from columns I, II or rare-earth elements, M is a transition metal, and X is a main group element, are relatively common. Materials in the body centered tetragonal $ThCr_2Si_2$ structure type are well studied for their usual magnetic and superconducting properties. In contrast with variety of $ThCr_2Si_2$-type AM_2X_2 compounds, fewer trigonal anti-anti-La_2O_3 type AM_2X_2 systems were reported. Although both structure types contain MX_4 tetrahedral framework, only d^0, d^5, and d^{10} electron configurations on the M atoms can yield trigonal anti-La_2O_3-type structures AM_2X_2. MX_4 tetrahedral appears in both $ThCr_2Si_2$-type and anti-La_2O_3-type AM_2X_2 compounds with M atom occupying the center of X_4 tetrahedron. Unlike the 4-fold M-X bond in the tetragonal structure, two different M-X bonds are observed in the trigonal structure. Based on Hoffmann's interpretation, one can be regarded as 1-fold "handle" bonds along c-axis; the other is 3-fold umbrella-like "rib" bonds. Although all of the d^0, d^5, and d^{10} electron configurations on the M atom can form a trigonal 122-structure, the half-filled d^5 configuration is anomalous because the bond length between the "handle" and "rib" types is much smaller, which is unexpected because half-filled d^5 can be seen as a mixture of d^0 and d^{10} configurations. Moreover, the d electrons will contribute dispersed band and unique magnetic phenomena may emerge from them.

$SrMn_2P_2$ crystalizes in the trigonal La_2O_3-type at ambient pressure. For the high pressure experiments performed in a Rockland Research cubic anvil cell, the single phase $SrMn_2P_2$ powder (~200mg in mass) was sealed in a BN crucible and heated in a compressed pyrophylite cell at 900ºC for 30 minutes. The pressure was maintained at 5 GPa during the heating. The cell was quenched to ambient temperature by switching off the electrical current. The final product was a dense pellet; part of it was ground and characterized by powder X-ray diffraction.

As predicted, $SrMn_2P_2$ forms in a previously unreported structure, the tetragonal $ThCr_2Si_2$-type structure under high pressure.

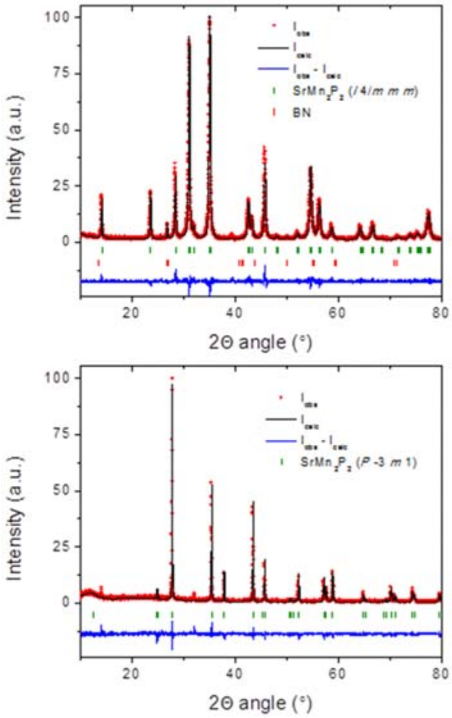

Figure 1. (Upper): Powder X-ray diffraction (PXRD) pattern for $SrMn_2P_2$ synthesized under high pressure (red points). The black line shows the Rietveld fit to the experimental data. Green ticks mark are the positions of the tetragonal $SrMn_2P_2$ reflections. Peaks marked by purple ticks originate from a minor contamination of the sample with hexagonal boron nitride from the high-pressure crucible. (Lower) Powder diffraction pattern from the previously known, ambient pressure stable trigonal phase, with the fit performed by the LeBail method.

Acknowledgments: This work was supported by by the Gordon and Betty Moore Foundation, EPiQS initiative, grant GBMF-4412.

[1] Zheng, C.; Hoffmann, R. *J. Am. Chem. Soc.* 1986, **108**, 3078

[2] Xie, W.; Winiarski, M.; Klimczuk, T.; Cava, R.J. *Dalton Trans.* **2017**, *46*(21), 6835.

Post-post-perovskite transitions in $MgSiO_3$ by first principles

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Keywords: synchrotron radiation, free-electron laser

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$MgSiO_3$ (bridgmanite) is the major constituent of the lower mantle of the Earth. It transforms to the post-perovskite (ppv) structure at pressure and temperature conditions near the core-mantle boundary. The ppv is the final form of $MgSiO_3$ in the Earth. Under higher pressures, what will happen? In other words, what are post-ppv transitions? This question becomes important when we consider big terrestrial exoplanets, i.e., super-Earths, in which pressure and temperature are much higher than those of the Earth's lower mantle. Understanding of fate of $MgSiO_3$ ppv under ultrahigh pressures is crucial for nature of interiors of super-Earths. Here we discuss the post-ppv transitions in ternary system of Mg-Si-O, based on results of first-principles calculations.

For pure $MgSiO_3$, the recent studies agree that $MgSiO_3$ ppv undergoes three-stage dissociations, involving MgO, SiO_2, Mg_2SiO_4 and MgSi2O5 under ultrahigh pressures [1,2]. The predicted crystal structures of Mg_2SiO_4 and $MgSi_2O_5$ have not occurred in any substance so far, as far as we know. It should be noted that the crystal structure of Mg_2SiO_4 relevant for the post-ppv transition is completely different from those of Mg_2SiO_4 which exist in the upper mantle of the Earth (forsterite, wadsleyite, and ringwoodite).

In the lower mantle of the Earth, $MgSiO_3$ coexist with a small amount of MgO. Therefore, also in super-Earths whose chemical compositions are similar to those of the Earths, $MgSiO_3$ and small amount of MgO are expect to coexist. In this case, combination of $MgSiO_3$ and MgO into Mg_2SiO_4 is predicted to occur. It is interesting to compare this combination with post-spinel transition, i.e., the dissociation of Mg_2SiO_4 ringwoodite to $MgSiO_3$ and MgO at pressure corresponding to the boundary between the upper and lower mantles of the Earth. Similarly, when $MgSiO_3$ coexist with SiO_2, they are predicted to combine into $MgSi_2O_5$. Therefore, depending on the atomic abundance ratio, Mg/Si, post-ppv transitions are very complex and consist of successive dissociations and recombinations [3]. Figure 1 shows phase boundaries of post-ppv transitions within the quasi-harmonic approximation for three types of Mg/Si.

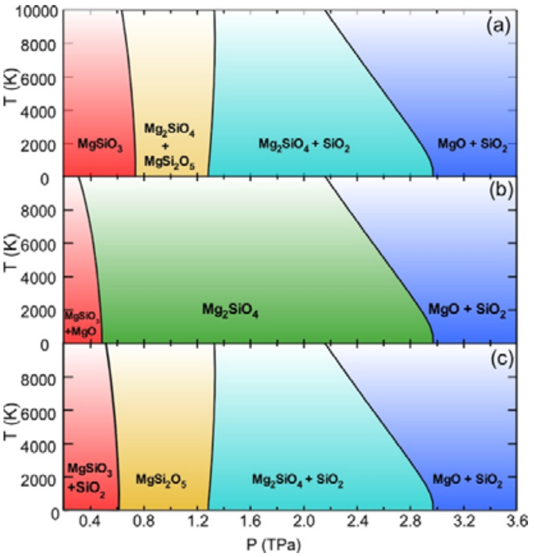

Figure 1. Phase boundaries of post-ppv transitions in Mg-Si-O ternary systems. (a) dissociation of pure MgSiO3 ppv, (b) recombination of $MgSiO_3$ and MgO, and (c) combination of $MgSiO_3$ and SiO_2. In (b) and (c), molar ratio between $MgSiO_3$ and MgO or SiO_2 is 1:1.

[1] S. Q. Wu et al., *J. Phys. Condensed Matter*, **26**, 035402 (2014).

[2] H. Niu, A. R. Oganov, X. Q. Chen, and D. Li, *Sci. Rep.* **5**, 18347 (2015).

[3] K. Umemoto et al., *Earth Planet. Sci. Lett.* **478**, 40 (2017).

Equations of state of carbon- and boron-materials by path integral Monte Carlo and density function theory simulations

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Keywords: equation of state, warm dense matter

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Accurate equations of state (EOS) from the cold condensed matter, across warm dense matter (WDM), to the hot plasma regimes are required for hydrodynamic modeling of experiments at the National Ignition Facility (NIF) and the OMEGA laser facility. Widely-used EOS tables based on Thomas-Fermi theory, although reasonably accurate for weakly-coupled plasmas and highly-degenerate materials, are relatively poor when describing real systems where bonding, electronic shell ionization, and many-body effects are often significant and coupled.

Among the many efforts toward improving the accuracy of EOS description for materials in various density and temperature regimes, path integral Monte Carlo (PIMC) and density functional theory molecular dynamics (DFT-MD) have demonstrated success (with uncertainty typically to the level of < 5% in pressure and < 2 Ha/atom in WDM conditions at which PIMC and DFT-MD are pushed to their respective limits) when being applied to a series of elements and compounds.

We apply PIMC and DFT-MD to study hydrocarbons and boron-materials—key ablator materials in shock-wave and inertial confinement fusion experiments. By pushing PIMC to low temperatures and DFTMD to high temperatures, we obtained coherent EOS at 10^6 K for CH and at 5×10^5 K for B. Tests using all-electron DFT calculations indicate consistency with the DFT-MD and PIMC data.

We find the Hugoniot curves of both hydrocarbons and boron show one peak structures, with a maximum compression ratio of ~4.7 for CH and ~4.6 for B. The peak originates from the *K* shell ionization of C and B respectively. We predict Hugoniot data that agree remarkably well with previous low-pressure experimental results as well as recent planar and spherically converged shock measurements at NIF.

In addition, we compare the EOS and shock Hugoniot curves of ideal carbon-hydrogen mixtures with direct first-principles simulations. The results show differences that are less than 1% around the compression maximum, which demonstrates the validity of the linear mixing approximation at WDM conditions.

We analyze the structure and chemical bonds in hydrocarbons at low pressures and temperatures and find evidences of stable carbon clusters and weak, short-lived C-H bonds, which gradually weaken with increasing pressure and temperature. We did not see any evidence of stable H-H bonds down to temperatures of ~0.6 eV. We observed a pseudo bandgap that gradually closes at 1.5-2.5 megabar, which indicates metallization of the system and is in accord with experimental findings of optical reflectivity changes.

Our results on the self-diffusion coefficient *D* of boron show a clear deviation from linearity between ln*D* and 1/*T* as temperature *T* increases, indicating breakdown of laws for ordinary condensed matter (here the Arrhenius relation) for one-component plasma across a wide temperature regime.

Our calculations provide accurate EOS data for carbon- and boron-materials over wide coupling and degeneracy regimes. We will show examples of the results being used to evaluate and build LEOS models.

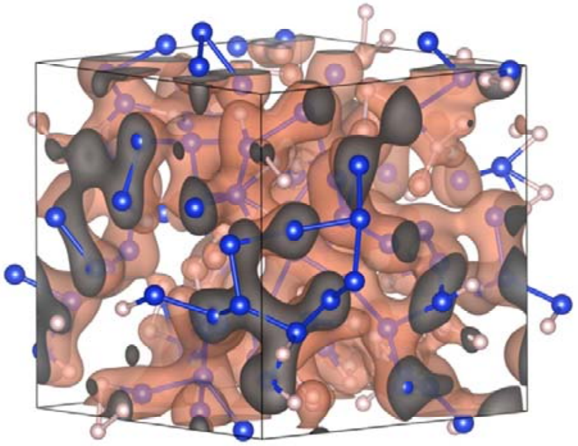

Figure 1. A snapshot of the electron density profile of CH around equilibrium at 3.15 g/cm^3 and 2×10^4 K. C and H atoms are represented by blue and pink spheres, respectively.

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[1] S. Zhang, et al., First-principles equation of state and shock compression predictions of warm dense hydrocarbons, *Phys. Rev. E* 2017, **96,** 013204.

[2] S. Zhang, et al., Path integral Monte Carlo simulations of dense carbon-hydrogen plasmas, *J. Chem. Phys.* 2018, **148,** 102318.

[3] S. Zhang, et al., Theoretical and experimental investigation of the equation of state of boron plasmas, *in review*. arXiv: 1804.11322

Structural prediction of host-guest structure in Lithium at high pressure

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Keywords: guest-host Structure, Phase transition, alkali metals

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Lithium (Li) is one of the most fascinating element in the periodic table and continues to attract a lot of attention due to the outstanding properties suitable for several applications, for example, battery technology, hydrogen storage, high electrical resistance, high superconducting transition temperature. Moreover, Li is one of central interest in many disciplines, especially in high pressure physics. There is huge interest in the theoretical study and the experimental observation as there is the stability of some of the complex structure. While the high-pressure phase of alkali metals, namely, sodium, potassium and rubidium, have also been found to be the complex structure. The complex structure of alkali metals was reported to have the host-guest (HG) structure. Interestingly, one important question that remains unresolved is the HG structure in Li at high pressure.

In our recent study, Ab initio random structure searching (AIRSS) technique is used to identify the high-pressure phases of lithium (Li). We proposed the transition mechanism from the fcc to host-guest (HG) structures at finite temperature and high pressure. This complex structural phase transformation has been calculated using ab initio lattice dynamics with finite displacement method which confirms the dynamical harmonic stabilization of the HG structure. The electron distribution between the host-host atoms has also been investigated by electron localization function (ELF). The strongly localized electron of p bond has led to the stability of the HG structure. This remarkable result put the HG structure to be a common high pressure structure among alkali metals.

Exploring the Earth's interior with the elasticity of minerals at high pressure and temperature

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Keywords: first-principles calculations,

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Elasticity of minerals at high PT is crucial for us in understanding the composition and dynamic properties of Earth's interior. However, measuring the elasticity of minerals at PT condition of Earth's interior is extremely challenge and calculating the elasticity of minerals at high T is usually expensive. We developed a method whose computational workload is less than tenth of the one of the usual method. The calculated results can be comparable to experimental data (Fig. 1). In this talk, I will firstly introduce briefly the method [1] and elastic results of several minerals. Then I will show two of our works on Deep Water Cycle: (1) constraining the water content at the top of the mantle transition zone with the elasticity of olivine and wadsleyite and (2) the effect of dehydration of superhydrous phase B on elasticity and evidences on the water transport to the lower mantle.

The seismic-velocity jumps at the depth of 410 km have been ascribed to the phase transformation from olivine to wadsleyite and provide the way to constrain the composition of the upper mantle because the values of 410-km jumps are determined by the velocity contrasts between olivine and wadsleyite and the amount of olivine. We investigated the elasticity of hydrous wadsleyite and obtained the velocity contrasts between olivine and hydrous wadsleyite. We found that the jumps are well matched by the transformation from olivine to hydrous wadsleyite for a pyrolitic mantle composition (~ 60% olivine) with ~ 0.5 wt% water and the wet transition zone reconciles the long-standing discrepancy on the upper-mantle composition.

The thermodynamic properties and elasticity of superhydrous phase B (ShyB) at high pressure and temperature are calculated using first-principles calculations based on density functional theory. The velocities and densities of ShyB are significantly lower than those of bridgmanite and periclase, the major minerals in the lower mantle. The decomposition of ShyB into bridgmanite, periclase, and water, which can occur at a depth around 800 km at a cold slab, will cause an increase of 7.5%, 15.0%, and 12% on shear velocity, compressional velocity, and density, respectively. Thus, the decomposition of a small amount of ShyB can produce a local discontinuity at the depth of ~800 km. The water released from the decomposition of ShyB may rise upward and promote the partial melt, which can further explain the the low-velocity zones just above 800 km discontinuity in Western-Pacific Subduction Zones [2].

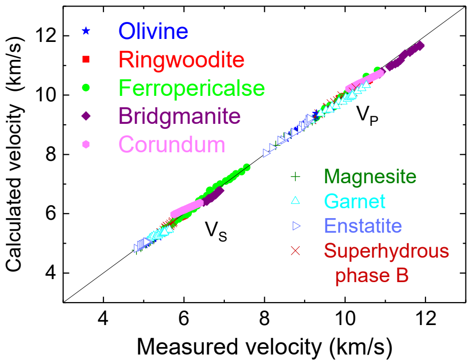

Figure 1. The calculated velocities agree well with the experimental data

Acknowledgments: This work is financially supported by Natural Science Foundation of China (41590621), State Key Development Program of Basic Research of China (2014CB845905), the Strategic Priority Research Program (B) of Chinese Academy of Sciences, grant XDB18000000.

[1] Z. Wu, R. Wentzcovitrch, *Phys. Rev. B* 2011, **83,** 184115.
[2] D. Yang, W. Wang, Z. Wu, *J. Geophys. Res.* 2017, **122**, 5026-5037

Measuring twinning and slip during shock-compression of Ta from in-situ x-ray diffraction

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Abstract

Understanding plasticity created by shock compression is critical for a number of fields such as planetary formation, asteroid impacts, spacecraft shielding, and ballistic penetrators. While in-situ x-ray diffraction (XRD) has emerged as an important tool for studying dynamic compression, progress has primarily focused on studying phase transitions. We report direct, in-situ observation of twinning and slip in shock compressed Ta using in-situ XRD. In this work, performed on the Matter in Extreme Conditions end station at LCLS, direct laser ablation was used to drive a shock, ranging in pressure from 10-300 GPa, into a Ta sample with an initial (110) fiber texture. The subsequent changes in texture were observed in-situ by examining the azimuthal distribution of the diffraction intensity and matched to twinning or lattice rotations about specific lattice planes. Measurements of the twin fraction and lattice rotation were used to calculate the equivalent plastic strain from twinning and slip. Contrary to the common association of twinning with strong shocks, we find a transition from twinning to slip for shocks above 150 GPa.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract No. DE-AC52-07NA27344.

The electronic ground state of FeO_2

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From the oxygen-rich atmosphere to the iron-rich core, the iron-oxygen (Fe-O) system spreads the entire pressure-temperature-composition range of our planet, iron oxides are important materials of Earth's interior, and play an important role in geological and biological processes. It is believed that under different pressures and temperatures, from the Earth's surface to the core, the electronic properties, oxidation states, spin states and magnetism of different iron oxides are distinctive. Recently, a pyrite-structured FeO_2 which has the lowest Fe/O compositional range to date [1] with a formal oxidation state of +4 was synthesized under the deep lower-mantle conditions. Here, we employed a variety of First Principles electronic structure calculations using different density functionals and correlated treatments to investigate the electronic ground state at high pressures. For calculations using functionals including correction to the self-interaction,(e.g. Hartree-Fock exchange and GGA+U), FeO_2 is found to be a ferromagnetic insulator with a formal oxidation state close to +2 at lower-mantle conditions. The Mossbauer isomer shift and high spin to low spin transition pressure are predicted. The theoretical information will help to characterize the electronic state of this novel material by experiments.

[1] Hu et al., (2016) *Nature* **534**, 241

The effect of electronegativity and size of divalent metal ion on pressure evolution of DmAMF

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Keywords: Dimethyl ammonium metal formates, High pressure, IR, Hydrogen bonds

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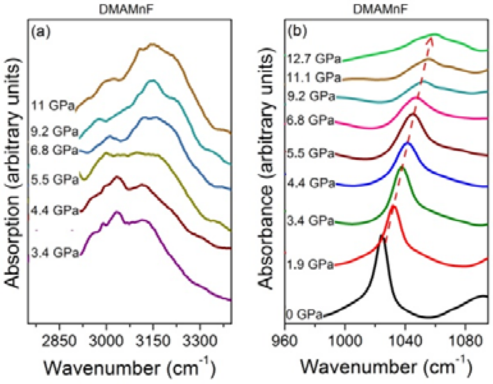
Dimethyl ammonium metal formates (DmAMF) are important metal organic framework compounds (MOF). Though, they have been extensively studied at low temperature, to perceive their ferroelectric transition due to H-bonding [1], thermal expansion properties, stress-strain dependence, magneto-electric tunability [2] etc., very few studies have been carried out on these materials at high pressure. As per our studies, application of pressure deforms the formate network. This results in the distortion of the cubo-octahedral cavities formed by it, leading to the structural phase transition [3]. However, the role of size and electronegativity of the transition metal ion, on this phase transition, has not been addressed so far.

We have studied the dependency of divalent metal ion on pressure evolution of DmAMF (M = Ni, Co, Mn, Cd). O-C-O stretching modes shift towards higher wavenumber for the DmAMF with smaller metal cation, due to strong M-O hence weak C-O bond. Our IR spectroscopic studies show that the framework structure of the formates with transition metal cations having smaller ionic radii [Ni^{2+}(0.69A^{o}) < Co^{2+}(0.745A^{o}) < Mn^{2+}(0.83A^{o}) < Cd^{2+}(0.95A^{o})] distort at higher pressures and the degree of distortion is less than the formates with higher cationic radii. It was also observed that the lower flexibility of the formate network in these compounds can be attributed to the stronger metal-formate coordination bond. In addition, on application of pressure the CNC mode softens [Fig (c) & (d)] and some of the hydrogen bonds weaken [Fig (a) & (b)] in the formates having smaller ionic radii cations (DmANiF & DmACoF), indicating that the electronegativity of the metal ion plays a vital role in the high pressure behavior of the coordination and hydrogen bonds. This information can help us to design new MOF's with tailored properties. Further results will be discussed.



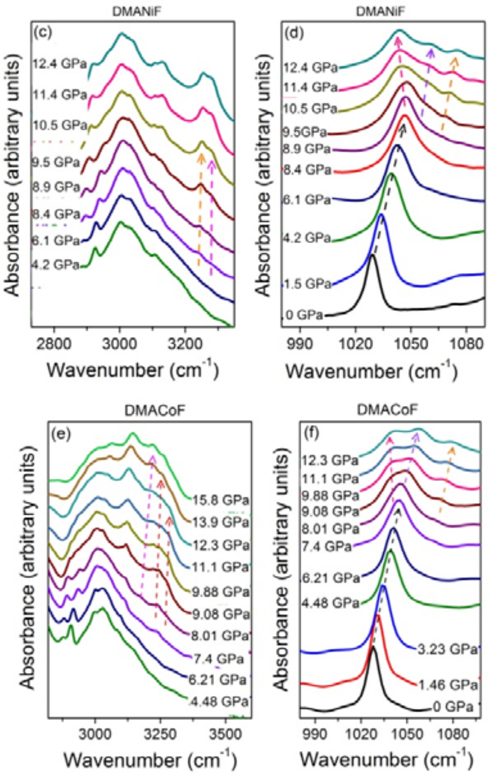


Figure 1.: In (c) and (e) arrows indicate appearance of new modes correspond to H-bonds which are not visible in (a) i.e. DmAMnF. In (b), (d) and (f) arrows trace the degenerated C-N-C stretch. Newly appeared modes show softening in DmANiF and DmACoF.

[1] M. Mączka, A. Gągor, B. Macalik, A. Pikul, M. Ptak, and J. Hanuza, Inorg. Chem. **53**, 457, 2014.

[2] W. Wang, L. Q. Yan, J. Z. Cong, Y. L. Zhao, F. Wang, S. -P. Shen, T. Zou, D. Zhang, S.G. Wang, X. F. Han & Y. Sun, Scie. Rep. **3**, 2024, 2013

[3] Abhishek Chitnis, H. Bhatt, M. Maczka, M. N. Deo, Nandini Garg, (submitted to *Inorganic Chemistry* on 15 Feb 2018)

X-ray diffraction of ramp-compressed copper up to 1.2 TPa

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Keywords: Coopper, high-power lasers, x-ray diffraction

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Copper is an abundant element that has been extensively studied, both, experimentally and theoretically by itself and along with the different alloys it forms. It is also commonly used as a pressure standard, flyer plate and ablator material within the high-pressure community. Its electronic structure is simple, with the 3d shell completely filled, availability of accurate shock wave and ramp-compressed data up to few Mbar [1-5] and its FCC phase structure is predicted to remain stable up to very high pressures [6].

Along the Hugoniot Cu melts above 200 GPa. Thus to determine its stable solid phase structure, a high-pressure and low-temperature off-Hugoniot compression path is required. Here we present recent x-ray diffraction data of ramp-compressed Cu up to 1.2 TPa acquired at the Omega Laser at the University of Rochester. Our results, as shown in Fig 1., indicate that along the isotherm copper remains in the FCC phase structure up to the highest pressures explored in this study, 1.2 TPa. These results supplement the recent EOS ramp-compressed data measured at the National Ignition facility up to 2.4 TPa [7].

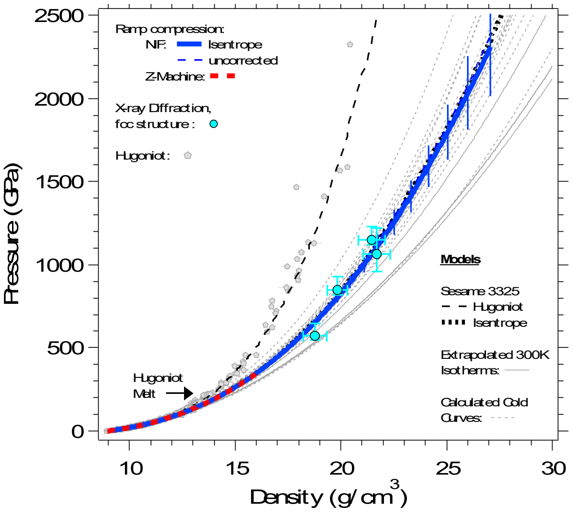

Figure 1. Pressue-density plot of copper. Hugoniot data [3], ramp compressed data (red [5] and blue curves [7]), and several theoretical cold curves (dashed grey lines) and the extrapolated isotherm at 300 K (solid grey line) are shown. The corresponding fcc pressure states measured at the Omega Laser are indicated with filled blue circles.

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[1] H. K. Mao *et al*., J. Appl. Phys 1978, **49**, 3276.
[2] A. D. Chijioke *et* al., J. Appl. Phys. 2005, **98**, 073526.
[3] Y. Wang *et al*., J. Appl. Phys. 2002, **92**, 6616.
[4] A. Dewaele *et al.*, Phys. Rev. B 2004, **70**, 094112.
[5] R. G. Kraus *et al.*, Phys. Rev. B 2016, **93**, 134105.
[6] C. W. Greeff *et al..,* J. Phys. Chem. of solids 2006, 67, M. Svandrlik, F. Parmigiani, *Nat. Photonics* 2014, **8,** 82.
[7] R. F. Smith, private communication.

Structure at terapascal pressures from *in-situ* powder x-ray diffraction of laser ramp-compressed magnesium

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Magnesium is predicted by first-principles to undergo structural phase transformations near 450, 650 and 1000 GPa to electride structures featuring electron localization in void spaces within the crystal lattice. These pressures are out of range for most diamond anvil cell measurements so we have used laser ramp-compression at the National Ignition Facility to reach pressures in excess of 1 TPa while simultaneously probing the structure using x-ray diffraction. We will present results spanning the pressure range of predicted new phases, and compare with first-principals studies.

Acknowledgments: This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

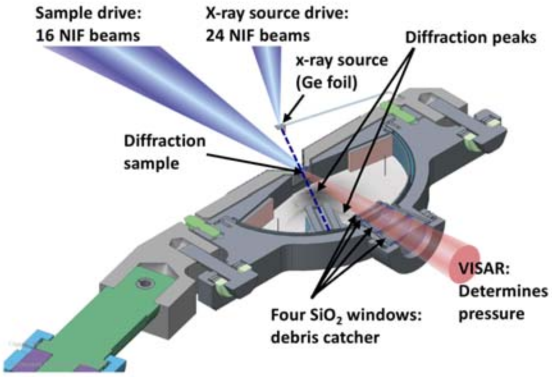

Figure 1. Powder x-ray diffraction diffraction diagnostic developed for the National Ignition Facility and used in this study to probe Mg to >1 TPa.

High-pressure phases of feldspars with five- and six-fold coordinated aluminium

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Keywords: high-pressure single crystal diffraction, feldspars

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Feldspars with a general formula MTO_8 (M= Na^+, K^+, Ca^{2+}, Sr^{2+} and Ba^2; T = Si^{4+} and Al^{3+}) are rock-forming minerals that make up over 50% of Earth's crust. A knowledge of the high-pressure and high-temperature behavior of feldspars is crucially important for the understanding of the chemical and thermodynamic processes within the lithosphere. A series of high-pressure single-crystal X-Ray diffraction (SCXRD) studies have been conducted up to 5-7 GPa on selected feldspar minerals with the aims of determining the variation of equation-of-state parameters with compositions and state of order [1]. Recent advances at third-generation synchrotron facilities allow to extend the pressure range of previous experiments and to get a new insight into the variation of feldspar crystal structures upon compression. Here we report on high-pressure SCXRD diffraction studies of two feldspars of high geological relevance, anortite (An), $Ca(Al_2Si_2O_8)$, and microcline (Mc), $(KAlSi_3O_8)$.

Diffraction experiments were performed at the P02.2 experimental station (Extreme Conditions Beamline) at synchrotron Petra III (Hamburg, Germany) up to 21 and 26 GPa for An and Mc, respectively. At ambient conditions the crystal structures of An and Mc consist of a three-dimensional framework of strongly-bonded TO_4 tetrahedra formed by the sharing of oxygen atoms between tetrahedra. Ca^{2+} and K^+ atoms occupy the larger voids in the tetrahedral framework to provide charge balance. According to the previous observations [2,3], the compression of An and Mc at low pressures is controlled by changes in T-O-T angles whereas TO_4 units do not undergo significant distortion. We have discovered that at elevated pressures the AlO_4 units start to undergo pressure-induced geometrical distortion resulting in Al coordination number increase. Thus, between 8 and 13 GPa An transroms into a new high-pressure polymorph. The new phase possesses 8 Al atoms in its asymmetric units: six Al sites are tetrahedrally coordinated, two are pentacoordinated (trigonal bipyramidal geometry) and two are octahedrally coordinated. This An phase is persistant until the sample amorphisation at about 21 GPa. In a similar pressure range, between 10 and 12 GPa, Mc undergoes a phase transition as well. The high-pressure Mc features octahedrally coordinated Al and is stable up to the highest studied pressure. In both An and Mc silicon atoms remain tetrahedrally coordinated in the whole pressure ranges.

The new high-pressure phases of An and Mc are another examples of geologically important minerals that reveal increase of cation coordination number upon the compression, also passing through exotic pentacoordinated state [4]. The compression routes of An and Mc as well as application of the results to the current geological models would be discussed in detail.

[1] Angel R.J. In: Parsons I. (eds) Feldspars and their Reactions. NATO ASI Series (Series C: Mathematical and Physical Sciences). 1994, **421**. Springer, Dordrecht.
[2] Angel R.J., *Am. Mineral.* 1992, **77**, 923
[3] Allan R.D, Angel R.J., *Eur. J. Mineral.* 1997, **9**, 263
[4] Hu Y., Kiefer B., Bina C. R., Zhang D., Dera P. K. *Geophys. Res. Lett.* 2017, **44**, L24307.

Ascertaining structural responses of porous soft crystals in comparatively moderate-high pressure environments

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Keywords: single crystals, anomalous behaviour, high pressure

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Porous crystalline materials have attracted much interest in a wide range of applications, namely, gas storage, molecular separation and catalysis.[1] A plethora of novel porous structures are being designed and developed with industrial application in mind. The chemistry of novel porous structures constitutes tuneable pore sizes and adjustable pore surface functionality. Barbour's group [2-4] and others have investigated the effect of host structure dynamics triggered by guest adsorption as well as pressure, light, and temperature variation (baro-, photo- and thermo-responsive properties, respectively). The fundamental studies are poised on revealing the underlying factors responsible for structural transitions and adjustments upon guest uptake. The innovation in Barbour's lab [5] enabled us to study the behaviour of materials under the controlled environmental gas cell with pressure ranges up to 100 bar. Considering the safety of handling gases, this might be the only reason for having limited pressure studies restricted to this threshold. There is therefore good potential to explore porous crystalline structure behaviour at higher pressures, potential up to a few GPa in diamond anvil cells (DACs), where gasses or liquids may be loaded as pressure transmitting media. The possibility of such comparatively enormous environment pressures affords a wide breadth of tenability. Moreover the diamond windows permit in-situ structural characterisation by way of single-crystal x-ray diffraction (SCD) and Raman spectroscopy (RS). We believe that this kind of research on porous structures has opened up new avenues of possible discovery of new properties.

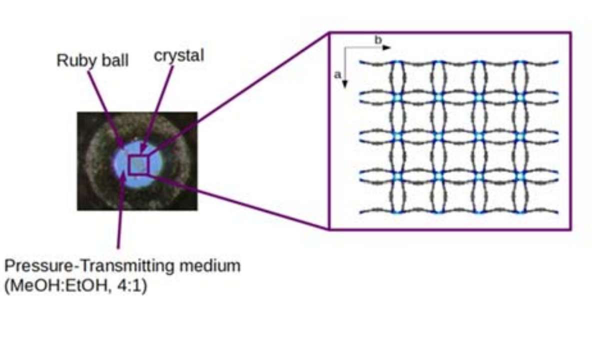

Figure 1. single crystals loaded in the DAC and crystal structure of the synthesised framework showing double wall wine rack

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[1] Shen, K.; Zhang, L.; Chen, X.; Liu, L.; Zhang, D.; Han, Y.; Chen, J.; Long, J.; Luque, R.; Li, Y.; Chen, B. Science 2018, 359, 206.

[2] Engel, E. R.; Smith, V. J.; Bezuidenhout, C. X.; Barbour, L. J. Chemistry of Materials 2016, 28, 5073.

[3] Das, D.; Jacobs, T.; Barbour, L. J. Nature Materials 2009, 9, 36.

[4] Grobler, I.; Smith, V. J.; Bhatt, P. M.; Herbert, S. A.; Barbour, L. J. Journal of the American Chemical Society 2013, 135, 6411.

[5] Lama, P.; Barbour, L. J. Journal of the American Chemical Society 2018, 140, 2145.

The dynamic diamond anvil cell (dDAC) at the HED instrument of the European XFEL

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Keywords: dynamic diamond anvil cell, free-electron laser, HED instrument

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Experimental conditions reached by static high-pressure and high-temperature techniques utilizing diamond anvil cells and those that result from dynamically driven shock waves, such as in laser/magnetic or gas gun shock compression experiments, differ greatly in their thermodynamic pathways. Moreover, the two high pressure techniques yield very different strain rates whose impact on the physical properties of matter is unclear. A piezo driven dynamic DAC [1] is a technique developed to reach intermediate strain rates between those from static and dynamic compression. Higher compression rates, however, require use of fast X-ray probes, of high brilliance, and fast large area detectors for diffraction experiments – a unique combination offered by the High Energy Density (HED) instrument at the European XFEL [2].

The HED instrument will feature a second interaction chamber (IC2) with a setup dedicated to research using diamond anvil cells. With the unique hard energy X-rays (up to 25 keV) and high sampling rate (220 ns between two successive pulses), provided by the European XFEL, one can efficiently probe the structural properties of material as the stress state countinuously increases up to the mechanical limit of the DAC.

Here we present preliminary studies on fast compression of metals in membrane DAC conducted at the Extreme Conditions Beamline P02.2 of Petra III, DESY, Germany [3]. The materials of choice (Fe [4], Pt, RE, stainless steel) give us hint on microstrain behavior of the sample and gasket assembly during the compression/decompression ramps, which yields better understanding of sample preparation for future dDAC experiments. Further, we will show some capabilities of the dDAC techniques in terms of reachable compression rates and discuss further developments of these experiments at FEL sources.

Our future plan is to explore the structural behaviour and properties of MgO, FeO and (Mg,Fe)O solid solutions (Fe% = 20, 40, 60, 80) at different strain rates and at multimegabar pressures. dDAC experiments combined with pulsed laser heating will enable us to cover large P,T space using an approach complementary to the static and dynamic techniques.

Acknowledgments: This work is supported by the DFG Project grant no. KO 5262/1.

[1] Evans, W.J. et al. (2007). Rev. Sci Inst. 78, 073904.
[2] Nakatsutsumi, M. et al. (2014) Technical Design Report, Scientifc Instrument High Energy Density Physics (HED).
[3] Liermann, H.-P. et al. (2015). J. Synchrotron Radiat. 22, 908–924.
[4] Konopkova, Z. et al. (2015). Phys. Rev. B 91, 144101.

High-pressure single-crystal diffraction at PX^2

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Keywords: synchrotron radiation, high pressure, crystallography

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The Partnership for eXtreme Xtallography (PX^2) program is a research initiative focusing on high pressure diamond anvil cell research, supported by the Consortium for Materials Properties Research in Earth Sciences (COMPRES). PX^2 is a collaboration between the University of Hawaii at Manoa and GeoSoilEnviroCARS (GSECARS), located at the Advanced Photon Source (APS) experimental station 13-BM-C. This beamline provides focused X-rays at 29 keV energy, and a unique 6-circle heavy duty diffractometer, optimized for a variety of advanced crystallography experiments including interface studies, powder and single crystal structure determination, equation of state studies and thermal diffuse scattering. Multiple auxiliary experimental capabilities, including online ruby fluorescence pressure determination, Raman spectroscopy, and remotely-controlled resistive heating, are available for high pressure research. Diffraction studies at P-T conditions of more than 150 GPa and 2000 K have been carried out at PX^2, and several materials of interest to Earth's deep interior have been studied. These new capabilities are available to all researchers interested in studying deep earth materials through the APS General User Proposal system.

Acknowledgments: PX^2 was supported by COMPRES under NSF Cooperative Agreement EAR-1606856 and by GeoSoilEnviroCARS through NSF grant EAR-1634415 and DOE grant DE-FG02-94ER14466. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

[1] Zhang, D., Dera, P.K., Eng, P.J., Stubbs, J.E., Zhang, J.S., Prakapenka, V.B., and Rivers, M.L. (2017), High pressure single crystal diffraction at PX^2. Journal of Visualized Experiments, 119, e54660.

High-pressure compressibility of synthetic tourmaline of near end-member compositions

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Keywords: high-pressure single-crystal X-ray diffraction, diamond anvil cell, tourmaline, bulk modulus, P-V EOS

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Tourmaline is the most common and widespread boron-bearing mineral, occurring as an accessory phase and primary boron host in rocks of various bulk compositions and formation conditions throughout the crust. This borosilicate is a supergroup mineral comprising at least 33 end-member species represented by the general structural formula $XY_3Z_6T_6O_{18}(BO_3)_3V_3W$. Despite strong interest in tourmaline as a petrogenetic indicator mineral, knowledge of its non-ambient elastic properties is scarce and largely limited to studies on natural samples to <18 GPa. As a result, it remains unclear if reported variation in the bulk moduli of tourmaline reflect variation in composition or data collection method.

Before tourmaline can be included in petrological models, we need an understanding of its end-member thermodynamic parameters and crystal chemistry at high pressure and temperature. Synthetic crystals allow the properties of different end-members to be investigated directly, which can be combined to reflect the properties of their solid solution in natural samples. We present data for synthetic tourmaline representing the following end-member compositions:

dravite	$NaMg_3Al_6Si_6O_{18}(BO_3)_3(OH)_3(OH)$
oxy-uvite	$CaMg_3Al_3Si_6O_{18}(BO_3)_3(OH)_3O$
magnesio-foitite	$(Mg_2Al)Al_3Si_6O_{18}(BO_3)_3(OH)_3(OH)$
olenite	$NaAl_3Al_6Si_6O_{18}(BO_3)_3O_3(OH)$

The synthetic magnesio-foitite, oxy-uvite [1], and olenite [2; columnar crystal] used are compositionally and structurally well-characterized. Dravite was newly synthesized from its constituent oxides and a NaCl-saturated fluid at 4.0 GPa and 700ºC using the chamber method [3] modified for the piston-cylinder press and characterized by electron microprobe analysis and powder X-ray diffraction. For each experiment, an individual tourmaline crystal was loaded with ruby and Au pressure standards and Ne as a pressure-transmitting medium in a symmetric diamond anvil cell with 300-µm culets and a Re gasket. High-pressure single-crystal X-ray diffraction data for each tourmaline composition was collected up to 50 GPa in 3-5 GPa pressure steps at beamline 13BM-C (PX^2) of the Advanced Photon Source in Chicago.

Every synthetic tourmaline crystal was indexed to a rhombohedral unit cell up to the maximum pressure of each experiment. The resultant unit cell parameters are fit to a third order Birch-Murnaghan P-V equation of state (K_o'=4) (*Fig. 1*) with the following isothermal bulk moduli:

dravite	K_o=116 ± 3 GPa
oxy-uvite	K_o=112 ± 1 GPa
magnesio-foitite	K_o=107 ± 2 GPa
olenite	K_o=129 ± 3 GPa

In addition to varying as a function of composition, tourmaline's compressibility is highly anisotropic. Each investigated crystal is ~3 times more compressible along the crystallographic *c* axis than along the *a* axis at ambient conditions. With increasing pressure, anisotropy in the axial compressibility gradually decreases.

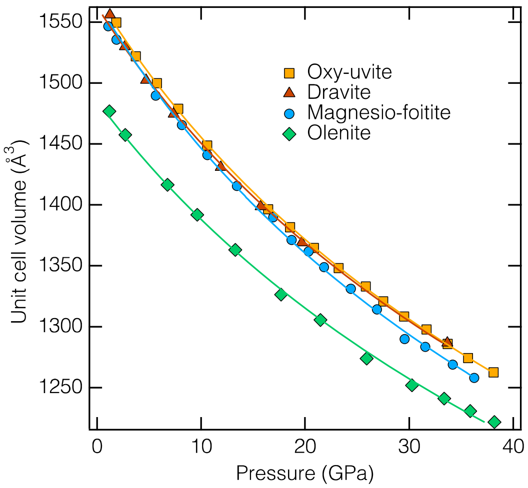

Figure 1. Unit cell volume (Å³) of synthetic tourmaline (oxy-uvite, dravite, magnesio-foitite, and olenite) as a function of pressure. The solid lines show the fit to the corresponding third order Birch-Murnaghan P-V EOS.

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[1] E.J. Berryman et al., *Phys Chem Minerals* 2016, **43**, 83-102.
[2] M. Kutzschbach et al., *Am Min* 2016, **101,** 93-104.
[3] G. von Goerne, G. Franz, R. Wirth, *Eur J Mineral* 1999, **11**, 1061-1077.

Structural Phase Transitions of 1T-$TiTe_2$: Experiment and Theory

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Keywords: topological insulator, transition metal dichalcogenides, phase transition.

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Due to its time-reversal symmetry protected, topological insulators (TIs) offer promising aspirations in many quantum applications such as spintronic-logic, data storage, and low power consumption devices [1]. TIs are materials with zero band gap surface states exhibiting linear dispersion at the Fermi surface. At the surface of TIs, the spin current flows in the absence of charge current flow. The strong spin-orbit coupling plays an important role which can exert spin-orbit torques and spin-momentum locking state at its surface. In another words, the spin of the electron is locked at a perpendicular direction of momentum. Therefore, this interplay is the effect of diffusion at the interface between TI and transition metals. It has been predicted that 1T-$TiTe_2$ materials are topological insulators, [2].

1T-$TiTe_2$ materials belong to an extensive family of layered transition metal dichalcogenides, consisting of alternating close packed titanium and tellurium layer. At the ambient conditions, 1T-$TiTe_2$ is a semimetal or semiconductor with the crystal structure described by the space group of $P\bar{3}m1$. There are three atoms with Ti and Te atoms in a unit cell located at (0, 0, 0) and (⅓, ⅔, z = 0.25) Wyckoff sites, respectively. The Ti atom is ionicly or covalently bond to the Te atom, and van der Waals forces is linked between the two Te atoms in a unit cell. Hence, a layer situation is happening between the Te atoms due to this van der Waals forces.

At low temperature, the charge density wave (CDW) and superconducting (SC) states are competing to dominate the system. As pressure increases, the CDW state becomes unstable as the SC state emerges [3]. This puzzling behavior of 1T-$TiTe_2$ is believed to be a product of strong electron-phonon coupling due to the softening of the phonon mode. However, fermi-surface nesting is irresponsible to this behavior. The strong electron-phonon coupling hardens the phonon frequency and overthrows the system to favor the SC state. Hence, the superconducting state is phonon mediated [4]. In addition, 1T-$TiTe_2$ experiences two topological phase transitions at around 2 GPa and 4 GPa [5]. In consequence, a high-pressure structural study of 1T-$TiTe_2$ is required in order to gain insight to this system.

In situ high-pressure synchrotron powder X-Ray diffraction (XRD) in diamond anvil cell experiments were performed on 1T-$TiTe_2$ powder up to 50 GPa at the High Pressure Collaborative Access Team, Sector 16 BM-D at the Advanced Photon Source. In addition, structure searches had been performed with evolutionary algorithm, USPEX method to predict the high-pressure phases of 1T-$TiTe_2$. 1T-$TiTe_2$ experiences two first-order phase transitions at 8 GPa and 35 GPa. According to our theoretical calculations with USPEX, there are two novel stable phases: P21/m (8 GPa) and $P\bar{6}2m$ (35 GPa).

In the 2018 International Union of Crystallography (IUCr) on High Pressure, I will present a high-pressure XRD structural study of 1T-$TiTe_2$ and its theoretical implications. In addition, I will present comparison between our predicted new stable structures with reported structures in literature.

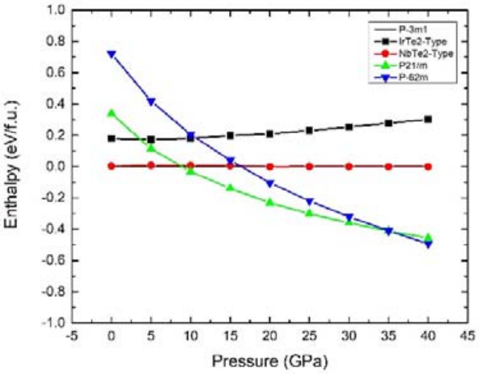

Figure 1. Enthalpy formation of 5 different structures: $P\bar{3}m1$, $IrTe_2$-type (C2/m), $NbTe_2$-type (C2/m), P21/m, and $P\bar{6}2m$ phases. $P\bar{3}m1$ phase is laying underneath the $NbTe_2$-type phase.

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[1] Y. Wang, D. Zhu, Y. Wu, Y.Yang; J. Yu, R. Ramaswamy, R. Mishra, S. Shi, M. Elyasi, K. Teo, Y. Wu, H. Yang, *Nat. Commun*. 2017, **8**.

[2] Q. Zhang, Y. Cheng, U. Schwingenschlögl, *Phys. Rev. B* 2013, **88**.

[3] U. Dutta, P. S. Malavi, S. Sahoo, B. Joseph, S. Karmakar, *Phys. Review B* 2018, **97**.

[4] M. Calandra, F. Mauri, *Phys. Rev. Lett.* 2011, **106**.

[5] V. Rajaji, U. Dutta, P. C. Sreeparvathy, S. C. Sarma, Y. A. Sorb, B. Joseph, S. Sahoo, S. C. Peter, V. Kanchana, C. Narayana, *Phys. Rev. B* 2018, **97**.

High-temperature and high-pressure shock causes the decomposition of Ankerite to produce diamond and high-pressure iron magnesium oxide

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Abstract:

We have found a new high-pressure polymorph of $MgFe_2O_4$ (HP-$MgFe_2O_4$-Maohekite) and diamond decomposed directly from ankerite [$Ca(Fe,Mg)(CO_3)_2$] in shock-metamorphic gneiss of the Xiuyan crater in China , which could have important implications for understanding the high-pressure behavior of Fe-rich carbonates in the subducting slabs, carbonates on the Earth's surface may sink into the deep mantle via subduction. The behavior of carbonates under high pressure and high temperature has important implications for the Earth's deep carbon cycle.

The mechanism of diamond formation is not by chemical reduction in contact of metals as in the industrial process, but by self oxidation-reduction.

We use ankerite [$Ca(Fe,Mg)(CO_3)_2$] sample for shock-wave experiment at Institute of High Temperature and High Pressure Physics, Wuhan University of Technology. Under high pressure and high pressure impact, that ankerite decompsite to diamond , HP-$MgFe_2O_4$, calcite, and some ankerite remains as it is.That were produced at shock-wave speed 293Km/S, inpact pressure 79.1GPa and ~1000^{O}C via the following chemical reaction: $3Ca(Fe,Mg)(CO_3)_2 = 3CaCO_3 + MgFe_2O_4 + 3C + 5/2O_2$, which results in oxidation of Fe2+ to Fe3+ and reduction of part of carbon.

At the BL 15U1 beamline of the synchrotron radiation facility (SSRF) in Shanghai, China, using monochromatic radiation with microfocus incident beam(beam size of 2μmX3μm) and beam energy of 20.0KeV, the angle dispersive x-ray diffraction (AD-XRD) patterns were implemented with a MarCCD detector ,a good determination of diamond C, HP-MgFe2O4, and calcite $CaCO_3$, and residual as-prepared ankerite.

It shows that HP-MgFe2O4 is one of potential carriers for Fe3+ in the Earth's mantle. And the diamond decomposed directly from cambanate such as ankerite [$Ca(Fe,Mg)(CO_3)_2$].

The energy CH_4 gas extraction by CO_2 substitution in clathrate hydrate through bimolecular iteration

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Keywords: Neutron diffraction, Clathrate Hydrate

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Methane hydrates (MH) are promising energy resourcestoday, although the controllableextraction of $CH_4$from it is still challenging. Using CO_2 to gently replace CH_4 in MH is one of the most attractive exploiting schemes for its benefits toboth geologic hazard consideration and cost efficiency (extract energy and CO_2 sequestration). However, the practicability of this exploiting method is still ambiguousaccording to previous studies.

Here, through the in-situ neutron diffraction investigation, it is clearly confirmed CH_4 in bulk structure-I (sI) clathrate hydrate can be efficiently substituted by gaseous CO_2 witha high substitution ratio of ~44% in the large cages at high-T/low-T conditions and the conservation of the hydrate framework. We proposea squeezing mechanism with the help offirst-principles calculations, where the energy barrier of CH_4 diffusing through the clathrate hydrate is significantly decreased by ~50% by experiencing an intermediate state that one hydrate cage is doubly occupied by CO_2/CH_4 molecules. Therefore, the replacement reaction is not only energetically favorable but also kinetically feasible. The experimental and theoretical evidences to the feasibility of CH_4-CO_2 substitution are of great significance in taking advantage of the rich combustible ice resources on earth.

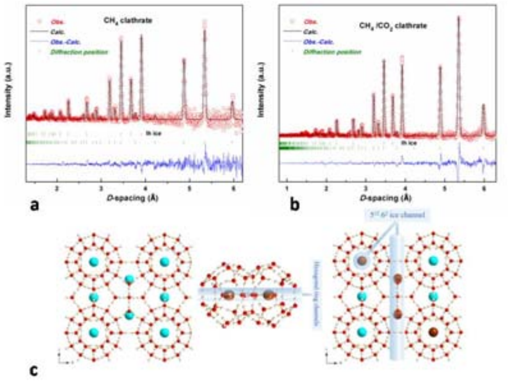

Figure 1. Time-dependent neutron diffration patterns showing CH_4 clathrate formation (a); CO_2 substitution of CH_4 in mechane clathrates for 48 h; and schematic shows of sI clathrate with CH_4 (balls in cyan), partial CO_2 (balls in wine) substitution and proposed gas molecular pathway through the hexgonal rings of $5^{12}6^2$ large cage. The red and white balls represent the oxygen and disordered deuterium in D_2O frame.

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Pseudosymmetry in high-pressure phosphorus and the phase relations in group 15 elements

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Keywords: pnictogens, pseudosymmetry, phase trasitions

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Although black phosphrous is the thermodynamic ground state polymorph of the element, it was synthesised for the first time only in 1914 by Bridgman using high pressure techniques. Since then, the high pressure behavior of phosphorus and other group 15 elements (pnictogens) has been studied extensively. A number of crystal phases have been discovered, including exotic incommenurately modulated host-guest structures at very high pressures. It appears, however, that the phase diagrams of pnictogens, are still not well understood even considering the seemingly simpler structural relations.

In black phosphorus (bP) atoms are arranged into puckered single atomic layers of trivalent P. Quite recently it was found that the individual layers can be exfoliated yielding phosphorene, a two dimensional material which can be viewed as a single layer of black phosphorus, much in the same way that graphene is a single layer of graphite. Since the pristine phosphorene, unlike graphene is an intrinsic semiconductor and has a band gap which can be effectively tuned, it is exstensively studied for its potential novel applications in electronics and optoelectronics.

At ~5 GPa bP (*Cmce*, *Z*=8) transforms to a hexagonal (*R*-3*m*, *Z*=2) A7 structure. bP was reported to transform further to a simple cubic (sc, *Pm*-3*m*, *Z*=1) 3D metallic modification upon compression, around ~11 GPa. It can be therefore considered as the stability limit for the layered phases of phosphorus, the point at whcih the layers eventually combine into a 3D network. We have shown, however, that this phase tranformation has a much more complex, gradual mechanism [1].

While at ~10.5 GPa we observed a discontinuity of all parameters, at higher pressure the measured powder XRD pattern does not reflect the sc symmetry, which is broken by the presence of previously unreported peaks of low intensity. This finding led us to the conclusion that above this presure P is pseudosymmetric: while the rhombohedral cell metrically resembles a cubic one ($\alpha \approx 60.0°$) the P atom does not reach the position of the highest symmetry Wyckoff site ($u < 0.25$) up to at least ~30 GPa. It implies that in this range a previously overlooked pseudo-simple cubic (p-sc) phase exists rather than the sc one.

This result has important implications. First, it increases a pressure limit to which layered structures of phosphorus exist. It also explains the long-debated anomalous pressure evolution of the superconducting critical temperature, T_c. Finally, comparing the data for P to the literatue reports on the other heavier pnictogens (As, Sb and Bi) our findings bring order to the sequence of the layered A7 phases of these elements, regarding the pressure stability ranges and 2D-3D transition tresholds [2]. Notewhorty, once again it has appeared that also in this case high pressure behavior of elemnts within one periodic table group corroborates well with the chemical intuition.

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[1] D. Scelta, A. Baldassarre, M. Serrano Ruiz, K. Dziubek, A. B. Cairns, M. Peruzzini, R. Bini, M. Ceppatelli, *Angew. Chem. Int. Ed.* 2017, **56,** 14135.
[2] D. Scelta, A. Baldassarre, M. Serrano Ruiz, K. Dziubek, A. B. Cairns, M. Peruzzini, R. Bini, M. Ceppatelli, *Chem. Comm.* 2018, in press.

10^9-fold conductivity enhancement of Li_2C_2: Pressure-induced polymerization and disproportionation

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Keywords: carbide • high pressure • polymerization • conductivity• Li-battery materials

Li-C compounds are well focused due to their applications in Li-battery materials. For example, Li-intercalated graphite is used in the anode of rechargeable Li-battery, because it is conductive and the dendrite of Li will be avoided.[1] Very recently, a very simple Li salt, lithium acetylide (Li_2C_2), was investigated as a promising high energy density electrode material for Li-battery[2], but suffered from its low conductivity. Here we found its conductivity was enhanced by 10^9-fold under high pressure, which is recoverable to ambient pressure. We investigated the phase transitions and reactions of Li_2C_2 under external pressure and room temperature by in situ and ex situ X-ray diffraction (XRD), Raman, IR, Gas Chromatography-Mass Spectrometry (GC-MS) and theoretical calculations, and identified the polymerized carbon species from C_2^{2-}, like ribbon structures. The pressure-induced polymerization (PIP) of C_2^{2-} is responsible for the irreversible enhancement of conductivity. The polymerized Li_2C_2 species disproportionate into C-rich and Li-rich phases, implying it is highly electrochemically active. Our works demonstrates that applying pressure is an effective method to drive charged monomers like C_2^{2-} to polymerize, and hence provide the possibility to synthesize novel carbon-based electrode materials.

[1] F. Chevallier, F. Poli, B. Montigny, M. Letellier, *Carbon* **2013**, *61*, 140-153.

[2] N. Tian, Y. Gao, Y. Li, Z. Wang, X. Song, L. Chen, *Angew. Chem.* **2016**, *128*, 654-658; *Angew. Chem. Int. Ed.* **2015**, *54*, 1-6

Femtosecond x-ray diffraction studies of the reversal of the microstructural effects of plastic deformation during shock release of tantalum

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An understanding of the rapid deformation mechanisms in crystals occurring during the shock process at the lattice level, such as the generation and motion of defects, or deformation twinning, has long been sought [1–3]. Of particular interest is the observation that in many cases the high rates of plastic strain observed at the shock front not only cannot be mediated by pre-existing dislocations, but are also inconsistent with the defect densities found via *post facto* analysis. That is to say a direct application of Orowan's equation [4] implies (under the assumption of sub-sonic dislocations) dislocation densities behind the shock front that can be several orders of magnitude greater than both those initially present, and those found in recovered samples.

Whilst defect densities consistent with observed plastic strain rates are not found in recovered samples [5, 6], such high densities are observed in many MD simulations [7, 8], and long prior to those simulations the generation of high densities of homogeneously nucleated dislocations at the shock front had been proposed [2]. A resolution to this discrepancy is suggested by further MD simulations that show that upon the shock unloading at a free surface, and subsequent rarefaction, most of the dislocations annihilate [9] implying that post facto analysis of recovered samples may at best not provide a full picture of the conditions present during the passage of the shock itself.

It is within the context outlined above that we present the results of experiments where, via femtosecond x-ray diffraction, we directly observe the microstructural effects of shock-induced plasticity being reversed in polycrystalline tantalum during shock breakout as the rarefaction wave travels back into the sample. In particular, we directly observe the reduction of shock-induced twins as well as a significant reversal in the lattice rotation imparted during the shock-compression process. These results, which are in good agreement with MD simulations, provide conclusive evidence that the release of stress after shock events, and the associated subsequent rarefactions and reverberations, can significantly alter the microstructure of the sample from that extant during the shock itself, highlighting the importance of *in situ* measurements.

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1. C. S. Smith, TMS-AIME **212**, 574 (1958)
2. M. A. Meyers, Scr. Metall. **12**, 21(1978)
3. F. A. Bendak et al. Phys. Rev. B **46**, 3228 (1992)
4. E. Orowan, Proc. Phys. Soc. **52**, 8 (1940)
5. C. H. Lu et al. Acta Mater. **61**, 7767 (2013)
6. L. L. Hsiung, J. Phys Condens. Matter **22**, 385702 (2010)
7. E. M. Bringa et al. Nat. Mater. **5**, 805 (2006)
8. D. Tramontina et al. High Energy Density Pays. **10**, 9 (2014)
9. H. N. Jarmakani et al. Acta Mater. **56**, 5582 (2008)

Metastable Synthesis of Gas Clathrates

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Keywords: hydrogen-rich, diffraction, clathrates, metastable transitions

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Under high pressure, gases such as molecular hydrogen, oxygen and helium have been known to form host-guest van der Waals compounds with H_2O ice known as gas clathrates. These compounds are of interest as the 'host' H_2O molecules typically adopt networks not readily adopted by pure H_2O [1]. In addition, gas clathrates may be used as gas separation/storage materials if the gas:H_2O ratio is high enough. One of the most useful tools for increasing the gas:H_2O ratio is pressure, as generally the gas content of a gas clathrate increases with the appliction of high pressure[1-4]. Here we report the results of neutron diffration experiments on the synthesis and stability of various gas clathrates at low pressure.

Although the hydrogenous analogue of the D_2-D_2O system has been well explored in the regimes above 1 GPa, and below 0.2 GPa, there have been very few studies in the region between these pressures [5-10]. The recent discovery in the range 0.5-0.7 GPa of a new phase, C_0, that possesses a new clathrate structure with a new H_2O network , along with the proposal of another structure stable at similar conditions, has prompted further studies of the hydrogen-water system in this intermediate pressure region [8-11]. This work observed transitions from metastable to stable structures in the D_2-D_2O system around 0.2 - 0.3 GPa between 130 K and 280 K. These metastable structures were observed in the stability region of the sII hydrogen hydrate clathrate and computational studies of their relative enthalpies suggest that transition sequence observed is in line with Ostwald's 'Rule of Stages'. In addition, the results of neutron-diffraction experiments exploring the possible metastable synthesis of high-pressure phases in other gas clathrate systems such the He-D_2O system will be presented.

[1] J. S. Loveday and R. J. Nelmes, *Phys. Chem. Chem. Phys.*, **10**, 937–950, 2008.
[2] Y. Song, *Phys. Chem. Chem. Phys.*, **15**, 14524–14547, 2013.
[3] T. A. Strobel, K. C. Hester, C. A. Koh, A. K. Sum and E. D. Sloan, Jr., *Chem. Phys. Lett.*, **478**, 97–109, 2009.
[4] D. â. D'Alessandro, B. Smit and J. Long, *Angew. Chem. Int. Ed.*, **49**, 6058–6082, 2010.
[5] W. L. Vos, L. W. Finger, R. J. Hemley & H-K. Mao, *Phys. Rev. Lett*., 71 (19), p3150-3153, 1993.
[6] W. L. Mao, H. K. Mao, A. F. Goncharov, V. V. Struzhkin, Q. Z. Guo, J. Z. Hu, J. F. Shu, R. J. Hemley, M. Somayazulu and Y. S. Zhao, *Science*, **297**, 2247–2249, 2002.
[7] K. A. Lokshin, Y. S. Zhao, D.W. He, W. L. Mao, H. K. Mao, R. J. Hemley, M. V. Lobanov and M. Greenblatt, *Phys. Rev. Lett.*, **93**, 125503, 2004.
[8] V. S. Efimchenko, M. A. Kuzovnikov, V. K. Fedotov, M. K. Sakharov, S. V. Simonov and M. Tkacz, *J. Alloys. Compd.*, **509**, S860–S863, 2011.
[9] T. A. Strobel, M. Somayazulu and R. J. Hemley, *J. Phys. Chem. C*, **115**, 4898–4903, 2011.
[10] T. A. Strobel, M. Somayazulu, S. V. Sinogeikin, P. Dera and R. J. Hemley, *J. Am. Chem. Soc.*, **138**, 13786–13789, 2016.
[11] G.-R. Qian, A. O. Lyakhov, Q. Zhu, A. R. Oganov and X. Dong, *Sci. Rep.*, **4**, 5606, 2014.

Deformation in olivine during rapid compression as an analogue for shock processes

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Keywords: Keywords: fast compression, olivine deformation, kinetics
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Meteorite impacts produce a suite of deformation features and high-pressure phases that can be used to suggest the pressure and temperature conditions reached during the impact [1, 2]. Olivine is common in meteorites, and it is an important component of numerous planetary bodies. In olivine, with increasing shock pressures and temperatures, initially optical extinction is observed, followed by mosaicism, several types of deformation features, and mineral transformations to higher pressure phases. We use a new technique, rapid compression, to assist with identifying the specific deformation processes that result in shock deformation. We compare our results to previous terrestrial deformation maps in order to identify compression rate effects on deformation.

Using a membrane diamond anvil cell, we compressed two samples, synthetic olivine $(Mg_{0.5},Fe_{0.5})_2SiO_4$ and San Carlos olivine $(Mg_{0.9},Fe_{0.1})_2SiO_4$ at compression rates of 0.04(6) - 1.79(1) GPa/s to peak pressures of approximately 50 GPa. *In-situ* X-ray diffraction images were taken every 1 second. All experiments were non-hydrostatic and were conducted at room temperature. The diffraction patterns were analyzed using multiple techniques. LeBail fitting was performed to determine unit cell and peak shapes parameters. Peak width measurements were made in order to create Williamson-Hall plots. These plots allow determination and separation of the contributions of size and micro-strain to peak broadening. Recovered samples were investigated by SEM.

The study produced several novel findings: 1) From the LeBail fitting, samples compressed at faster rates were more brittle. 2) In faster compression rate experiments, lattice parameter ***a*** ceased to change above 10 GPa. 3) Both peak strain (Figure 1.) and differential stress build-up at higher pressures with increasing rate. 4) Based on our measurements of differential stress vs. strain rate, samples compressed at slower compression rates reached a cataclastic regime. Samples compressed at faster rates, remain in either discrete obstacle resistance or Peierl's mechanism dominated plastic regimes. 5) Despite compression at different rates, our recovered samples appeared to have extremely similar grain sizes and morphologies. Cataclastic (superplastic) flow has no strain rate dependence and produces similar flattened morphologies. Therefore, we suggest the deformation observed during our experiments was a form of low temperature plasticity followed by cataclastic flow at higher pressures. Our experiments produced micro-strain values that are commensurate with those of an experimental shock study that uses the same technique to calculate micro-strain [3]. Given the micro-strain measurements and the lack of significant mechanism change between the 0.42(8) and 1.79(0) GPa/s compression rates, similar deformation mechanisms and regimes may be occurring during meteorite impacts.

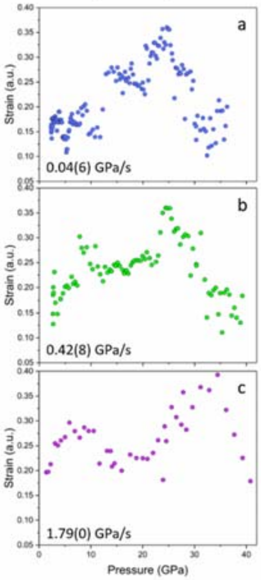

Figure 1. Plot of strain broadening with pressure for a) 0.04(6) GPa/s b) 0.42(8) GPa/s and c) 1.79(0) GPa/s compression rate experiments. Strain error bars should be around 0.03.

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[1] R.A. Binns, R.J. Davis, and S.J.B. Reed, *Nature* 1969, **221,** 943.
[2] D.K. Stöffler, Geochim. Cosmochim. Acta 1991, **55**(12), 3845-3867.
[3] A. Uchizono, et al., Mineral. J. 1999, **21**(1), 15-23.

High-throughput experiment technology for synchrotron radiation high-pressure diffraction

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Keywords: wide-band synchrotron radiation, high throughput, high pressure diffraction

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The synchrotron radiation high pressure experiment has important applications in many fields such as materials, geology, environment, energy and so on. However, due to the particularity of the sample environment, the high-pressure diffraction experiment signal is very weak, which seriously restricts the structural analysis and dynamic research. How to increase flux, improve experimental efficiency and data quality is very important for synchrotron radiation high pressure experiment. In this paper, combining the frontier technology with the development of the detector, the application of pink beam and white light in high pressure experiment is introduced in detail. According to the theoretical analysis and preliminary experimental results, it shows that the broadband light has only a slight influence on the resolution in high pressure experiment, but it can improve the efficiency and improve the quality of the data effectively.

Structure and behavior of the Ni end-member schreibersite, (Ni_3P), under deep Earth conditions

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Keywords: schreibersite, diamond anvil cell, the Earth's core

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Natural schreibersite consists of iron-nickel phosphide [$(Fe, Ni)_3P$], is common in iron meteorites [1] and is believed to have a similar composition as that of Earth's core [2]. Although, there are a few environments to find schreibersite, the implication of its preseence might be important for the Earth's life. It is believed that meteoritic phosphides minerals including schreibersite could have beena source of phosphorus on the early Earth. [3,4].

Current knowledge about the chemical and physical properties of the Earth's deep interior mostly comes from seismic observations, the chemistry of meteorites, and geophysical modeling of the Earth's interiors with data obtained from high pressure and pressure experiments. Seismic velocity measurements of Earth's core indicate that the density of the outer core and inner core is about 10% and 3% lower than pure iron at the relevant pressure and pressure conditions [5,6]. The density deficit of the core with respect to pure iron can be explained by assuming the presence of Fe-Ni- light element alloys.

Although, there have been numerous previous studies investigating solid solutions between Fe and light elements, including the schreibersite Fe end-member (Fe_3P), the effect of Ni, the second major element in the core, on the high-pressure and temperature behavior and physical properties of Fe_3P has not been systematically investigated.

We examined the crystal structure and behavior of the Ni end-member schreibersite at high pressure and temperature conditions by using single-crystal synchrotron-based X-ray diffraction and using Vienna ab-initio simulation package (VASP) in MedeA program.

The compression experiment at ambient temperature shows that at approximately 35 GPa, the trend of c/a ratio changes from negative to positive, which might be a sign for a magnetic transition. At ambient conditions both Ni3P is and Fe3P schreibersite end members are Pauli paramagnets. Magnetic transitions have been reported to take place in Fe3P and at high pressure.

A better understanding of the effects of the potential presence of light element alloys of Fe and Ni, such as schreibersite, will provide new constraints on the evolution and formation of the Earth, and will improve our ability to interpret seismic observations of the Earth's core.

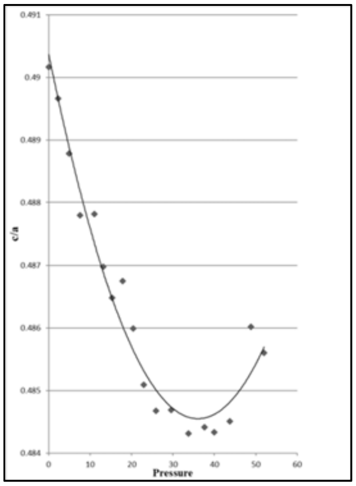

Figure 1. The c/a axial ratio at different pressure

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[1] V. Geist, G. Wagner, G. Nolze, O Moretzki, *Crystal Research and Technology* 2005, 40(1-2), 52-64.

[2] W.F. McDonough, S.-s. Sun, *Chemical Geology* 1995, 120, 223 – 253.

[3] M. Gull, M.A. Mojica, F.M. Fernández, D.A. Gaul, T.M. Orlando, C.L. Liotta, M.A. Pasek, *Scientific reports* 2015, 5.

[4] M.A. Pasek, *Geoscience Frontiers* 2017, 8(2), 329-335.

[5] F. Birch, *Journal of geophysical research* 1952, 57, 227 – 286.

[6] C.J. Allègre, J.P. Poirior, E. Humler, A.W. Hofmann, *Earth and Planetary Science Letters* 1995, 134(3-4), 515-526.

In situ XRD measurement for Se under pressure over 200GPa

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Keywords: synchrotron radiation, in situ XRD, phase transitions

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A series in situ synchrotron XRD experiments with pressure up to 210 GPa has been carried out on selenium at room temperature. Rapid compression was applied on the sample by means of two membrane-controlled diamond anvils cell. The phase transitions upon various compression rate within 45 GPa on selenium was studied. The compression rate effect on phase transition pressure and sequence on selenium was investigated.

Trigonal Se was used in the current experiment. Fig.1 shows typical XRD patterns during compression of Se at room temperature with various compression rates in different pressure regions. With the pressure increasing the XRD patterns showed a series of phase transition which are consistent with the published ones from the experiments done by the traditional static compression [1-3]. With the rapid compression and short exposing time, the dynamic processes of the phase transitions are shown clearly. According to the current work, the series of phase transitions is found less sensitive to the compressing rate below the rate of 0.66GPa/s. And in the pressure above 140 GPa, the Se VI (bcc) stays stable up to 210 GPa.

The lattice parameters of Se in the high-pressure region from 90 GPa to 200 GPa are obtained from the profile refinement of the synchrotron x-ray diffraction. The lattice parameter a is noticed to decrease with the increase of pressure. In the region of pressure below 160 GPa, the lattice parameter a decreases more dramatically compared to that above 160 GPa. This observation is consistent with the message shows by Figure 1, where the phase of Se VI starts to show up around the pressure of 140 GPa, and the Se V disappears gradually in the following higher pressure until it reaches 160 GPa. Above 160 GPa, not much change in either the lattice parameter a or the Unit cell volume V is observed, which shows the structure becomes more stable in the region of pressure from 160 GPa to 210 GPa where selenium has transited to the high-pressure phase Se VI.

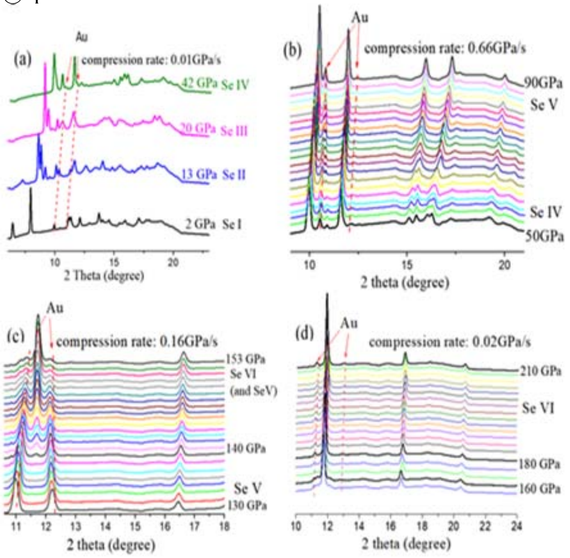

Figure 1. XRD patterns during the rapid compression of Se at ambient temperature, (a) the compression rate of 0.01GPa/s within 45 GPa, and the pressure-induced phase transitions between Se I, II, III, IV; (b) the compression rate of 0.66 GPa/s from 50 GPa to 90 GPa, and pressure-induced phase transitions between Se IV, V; (c) the compression rate of 0.16 GPa/s from 130 GPa to 153 GPa, and pressure- induced phase transitions between Se V, VI; (d) the compression rate of 0.02 GPa/s from 180 GPa to 210 GPa, Se VI phase remains stable within this region.

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[1] H. Liu, L. Wong, X. Xiao, F. Carlo, J. Feng, H-K. Mao and Hemley R J 2008 PNAS. 105 13229–13234
[2] W. Holzapfel, T. Krüger, W. Sievers and V. Vijayakumar 1993 Phys. Rev. B 32 16-21
[3] O. Degtyareva, E. Gregoryanz, H-K. Mao and R. Hemley 2005 High Pressure Res. 25 17-33

Is there a liquid-liquid phase transition in Cs?

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Keywords: synchrotron radiation, x-ray absorption density measurement, liquid-liquid phase transition

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Abstract

To verify the first-order liquid-liquid phase transition (LLT) in liquid Cs reported by Falconi et al. [1], the pressure dependence of liquid density was measured up to 5 GPa by an x-ray absorption method. The results showed that the density continuously increases over the entire pressure region investigated, without showing the previously reported large volume jump (□V/V= ~17%) at 3.9 GPa. No existence of the volume jump is also suggested from the slopes of the melting curve in the phase diagram. Although the electronic transition is one of the most promising candidates that may cause LLT, it is unlikely to occur in liquid Cs because of the gradual nature of the 6*s*-5*d* electron transfer [2].

Introduction

First-order phase transitions between two crystalline states are quite common, whereas those between liquid states (LLT) are very rare. The investigation of the LLT is important for revealing the mechanism of transitions between phases with the same symmetry and the prerequisite conditions for them. Among many liquids, elemental liquids, i.e., liquids comprising a single element have attracted considerable attention because this system does not have a degree of freedom with respect to the chemical composition, which prevents misinterpretation of the LLT caused by a change in the chemical composition of multicomponent systems.

In 2000, a first-order LLT was discovered in liquid phosphorus, in which the local structure drastically changed at 1 GPa, accompanied by a large volume change of 40% and macroscopic phase separation [3]. Succeedingly, the LLT was repored in Cs [4], in which the density of liquid abruptly changes by 17% at 3.9 GPa [1] accompanied by the change in its electronic structure (6*s*-5*d* electron transfer). This has attracted considerable attention because it was the first example of a LLT caused by electron transfer, which will open the way to observe LLTs in many other liquid metals. However, the data which led to the discovery, i.e., the liquid density, were indirectly calculated from the structure factor S(Q) and the volume of the crystalline phase before melting, thus there is still room for reconsideration. In this study, we investigate the existence of the LLT by directly measuring the liquid density using an in situ x-ray absorption method [5].

Experimemt

The experiments were conducted at beamline BL22XU at the SPring-8 synchrotron radiation facility, using a multianvil press (SMAP180). A fresh Cs sample was placed in a teflon capsule together with a diamond cylinder. The empty space below and above the cylinder was filled with the sample so that the sample could be continuously supplied into the cylinder under high-pressure conditions. The density of the sample was calculated by fitting the transmission profile of the sample confined in the diamond cylinder with a known dimesion. The liquid density was measured up to 5GPa both at 232 and 350 °C, which is almost the same as the condition of the previous study.

Result

Figure 1 shows the pressure dependence of liquid density at two temperatures. Here, the values of previous studies [1, 6, 7] are also shown. With increasing pressure, the density of the liquid gradually increased along the line for crystalline phases. In all experimental runs, no discontinuous change was observed at 3.9 GPa wherein a large density jump was previously reported [5]. This indicates that the liquid does not show LLT. The origin of the misinterpration in the previous study and the related anormlous compression behavior due to 6*s*-5*d* transition will be discussed.

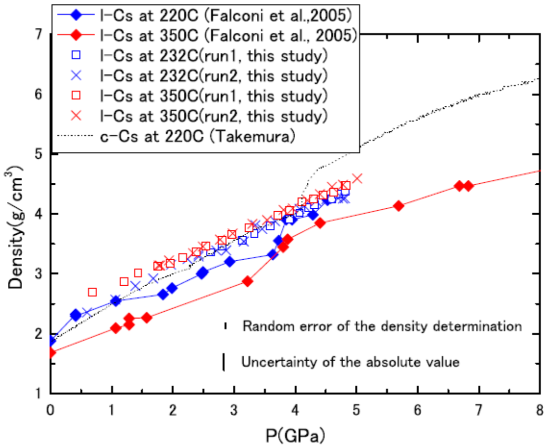

Figure 1. Pressure dependence of density of liquid Cs at 232 and 350 ◦C. The values of the previous study [1] and those of the crystalline phases[6,7] are also shown together.

References

[1] S. Falconi *et al.*, *Phys. Rev. Lett.* **94**, 125507 (2005).
[2] T. Hattori, *Phys. Rev. B* **97**, 100101(R) (2018).
[3] Y. Katayama *et al.*, *Nature* **403**, 170 (2000).
[4] Y. Katayama *et al.*, *Science* **306**, 848 (2004).
[5] Y. Katayama *et al.*, *J. Synchrotron Radiat.* **5**, 1023 (1998).
[6] K. Takemura *et al.*, *Phys. Rev. Lett.* **49**, 1772 (1982) and references therein.
[7] M. I. McMahon *et al.*, *Phys. Rev. Lett.* **87**, 255502 (2001).

Recent Developments of High-Pressure Neutron Experiments in J-PARC

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Keywords: Pulsed neutron source, J-PARC, PLANET

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Introduction

Neutron interacts with atoms differently from x-rays. By utilizing this character, neutron experiments enables observation of hydrogen, magnetic moments and excitations in materials. Despite its usefulness, neutron experiments under high-pressure condition have not been common due to incompatibility of a small neutron flux and a tiny sample used in high-pressure experiments. Intense pulsed neutron source recently constructed at Tokai in Japan is about to change this situation. In this talk, I will introduce the current status and recent developments in high-pressure elastic and inelastic neutron experiments at J-PARC.

J-PARC is a complex of several facilities utilizing intense proton accelerator. Neutron experiments are conducted at Materials and Life Science Experimental Facility (MLF), in which 21 beamlines are currently operated and utilized for studies of various fields of sciences. The large beam flux and slow reputation rate enable us to observe atomic arrangements and movements on a wide spatial and time scale.

Elastic Scattering Experiments

The high-pressure neutron diffraction experiments are mainly conducted at High-Pressure Neutron Diffractometer(PLANET) specialized to high-pressure experiments[1]. This beamline is equipped with various high-pressure devices, such as the six-axis press[2] for high-PT experiments, Paris-Edinburgh press[3] for room temperature experiments and Mito-system[4] for low-T and high-P experiments. Figure 1shows the PT condition at which *in-situ* high-pressure experiments are possible. By coupling with optics customized for high pressure experiments, the beamline give us the opportunity to precisely determine hydrogen positions in crystals, liquid and amorphous solids, as well as a magnetics structure of crystals. In addition to diffraction experiments, neutron radiography is also possible by using a neutron camera, which enables *in-situ* observation of diffusion of hydrogen in materials under high-PT conditions. These capabilities are utilized in studies of geoscience[5], materials science[6] and chemical physics [7]. The performance of the beamline and recent results will be introduced.

Inelastic Scattering Experiments

Another merit to use neutrons is the ability to observe the motion of atoms. However, intensity of inelastic scattering is usually much weak compared to elastic scattering, thus inelastic scattering experiments under high pressures are much more difficult. Recently, we are challenging to realize it in beamlines of SIKI[8] and AMATERAS[9] in J-PARC.

In the experiments at SIKI, we tried to observe vibrational excitation of hydrogen in ZrH_2, in which hydrogen is located in a harmonic potential formed by metal lattice. A P-E press (VX4) was used as a high-pressure device. The clear excitation of hydrogen vibration was successfully observed up to about 20 GPa. The results showed following pressure dependences: the increase in the excitation energy, the increase of the harmonicity of the potential and the localization of the wave function of a hydrogen atom.

In the experiments at AMATERAS, we have observed magnetic excitation of $(CuCl)LaTa_2O_7$ in the quantum spin system. A cramp cell [10] with a large sample volume($0.74 cm^3$) was used as a high-pressure cell. By subtracting the background, a clear magnetic excitation was successfully observed at temperatures down to 4.5 K.

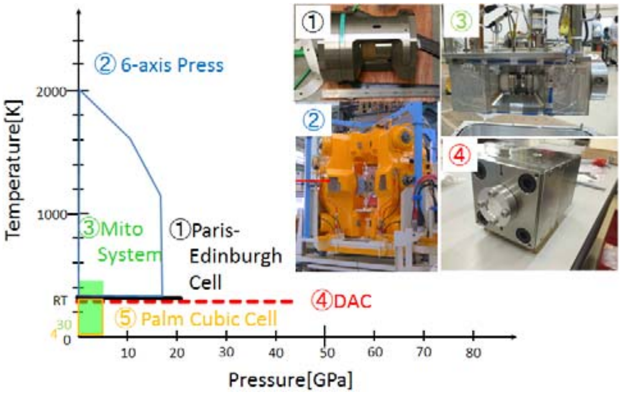

Figure 1. Various high-pressure devices used at PLANET and *PT* condition at which *in-situ* high-pressure experiments are possible.

References

[1] T. Hattori *et al., Nuclear Instrum. Meth. A* **780**, 55 (2015).
[2] A. Sano-Furukawa, *et al., Rev. Sci. Instrum.*, **85**, 113905 (2014).
[3] S. Klotz *et al., High Press. Res.* **24**, 291 (2004).
[4] K. Komatsu *et al., High Press. Res.* **33**, 208 (2013).,
[5] R. Iizuka *et al., Nature Communications*, **8**, 14096 (2017).
[6] A. Machida et al., Nature Com. **5**, 5063 (2014).
[7] S. Klotz *et al, Scientific Reports*, **6**, 32040 (2016).
[8] R. Kajimoto *et al., J. Phys. Soc. Jpn* **80**, SB025 (2011)
[9] K. Nakajima et al., *J. Phys. Soc. Jpn* **80**, SB028 (2011).
[10] N. Aso *et al., AIP Conf. Proc*. **850**, 705 (2006)

Single-crystal X-ray diffraction of grunerite up to 25.63 GPa: A new high-pressure clinoamphibole polymorph

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Keywords: Amphibole, high-pressure, phase-transition, synchrotron radiation

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High-pressure single-crystal X-ray diffraction experiments were conducted on natural grunerite crystals with composition $(Fe_{4.421}Mg_{0.829}K_{0.489}Mn_{0.027}Ca_{0.03}Ti_{0.004}Na_{0.026}Cr_{0.002}Al_{1.04})(Si_{7.728}Al_{0.272})O_{22}(Cl_{0.01,}OH_{1.99})$ using a synchrotron X-ray source. Grunerite has C2/m symmetry at ambient conditions. The samples were compressed at 300 K in a diamond-anvil cell to a maximum pressure of 25.6(5) GPa. We observe a previously described phase transition from C2/m (α) to $P2_1/m$ (β) to take place at 7.4(1) GPa, as well as a further transition from $P2_1/m$ to C2/m (γ) at 19.2(3) GPa. The second-order Birch-Murnaghan equation of state fit to our compressional data, yielded the values V_0 = 914.7(7) Å^3 and K_0 = 78(1) GPa for α, V_0 = 926(5) Å^3 and K_0 = 66(4) GPa for β and V_0 = 925(27) Å^3 and K_0 = 66(13) GPa for γ. The β – γ phase transition produces a greater degree of kinking in the double silicate chains of tetrahedra accompanied by a discontinuous change in the a and c unit cell parameters and the monoclinic β angle. At 22.8(4) GPa the O5-O6-O5 kinking angle of the new high-pressure C2/m phase is 137.5(4)°, which is the lowest reported for any monoclinic amphibole. This study is the first structural report to show the existence of three polymorphs within an amphibole group mineral. The high pressure γ-phase illustrates the parallel structural relations and phase transformation behavior of both single and double chain silicates.

Cutting-edge synchrotron facilities for advanced sample characterization at extreme conditions

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Keywords: synchrotron radiation, extreme conditions

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Understanding the complex nature of the deep interiors of the Earth and giant planets requires knowledge of physical and chemical properties of their constituting elements and compounds at relevant extreme P-T conditions. To provide new constrains on models for planetary evolution and origin, essential properties (melting, structure, phase relation, chemical reactions, and kinetics, transport, elastic, electronic properties, etc) of a wide range of minerals must be studied in-situ at ultra-extreme conditions of pressure, temperature up to 1TPa and 10,000K. These formidable experiments can only be conducted at dedicated synchrotron beamlines, like GSECARS (Sector 13, Advanced Photon Source), where state-of-the-art high-pressure on- and off-line techniques have been implemented and are currently being developed. Recent progress in continues and pulse laser heating technique, including application of fiber lasers and flat top laser beam shaping optics, result in significant improvement of the quality of x-ray data collected in-situ at high pressures and high temperatures in the diamond anvil cell [1]. Combining the double stage anvils technique [2] with pulse laser heating [3] coupled with the gating options of the new, large area CdTe 1M Pilatus detector, we will be able to study materials in-situ in the TPa pressure range and temperatures up to 10,000K for both static and dynamic experiments. Such unique capabilities at ultra-high P-T conditions approaching the warm dense state of matter will open an entire new research area creating a bridge between shockwave and DAC experiments that provides fundamental structural, thermodynamic, and transport property information for understanding the composition, origin and evolution of planetary systems.

Details and future developments of cutting-edge techniques at GSECARS for comprehensive characterization of materials in-situ at extreme conditions in view of planned APS diffraction limited storage ring upgrade will be discussed.

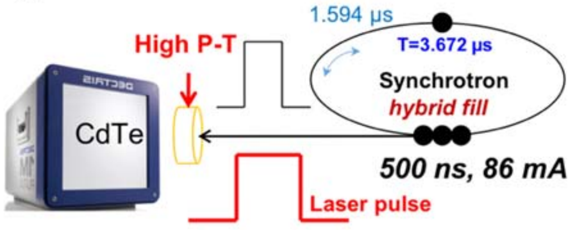

Figure 1. Schematic illustration of pulse laser heating combined with high resolution XRD in the diamond anvil cell and synchronized with APS bunch mode structure

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[1] V. Prakapenka, A. Kubo, A. Kuznetsov at al. High Pressure Research. 28 (3), 225-235 (2008)

[2] L. Dubrovinsky, N. Dubrovinskaia, V. Prakapenka et al. Nature Communications 3, 1163-1-1163-7 (2012)

[3] A. Goncharov, V. Prakapenka, V. Struzhkin et al. Review of Scientific Instruments, 81 (11), 113902-1-113902-5 (2010)

Study of the high-pressure phase transition of ZnO with wide-band synchrotron radiation

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Keywords: wide-band synchrotron radiation, high pressure experiment, phase transition

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An approach using wide-band synchrotron radiation for studying high pressure powder diffraction is described in this work. The wide-band synchrotron radiation means the energy resolution of the X-ray is 10^{-3}- 10^{-2}. Compared to the traditional monochromatic X-ray ($\Delta E / E = 10^{-5} - 10^{-4}$) high pressure diffraction experiments, the advantages and disadvantages of this method are discussed. Theoretical calculation of the effect of energy broadening on diffraction data has been conducted and experiments to demonstrate the application of this method have been performed on the wurtzite to rocksalt phase transition in ZnO at high pressure using a DAC. Result of the theoretical calculation shows that when the energy resolution is less than 10^{-2}, the effect on the diffraction data is not significant and the experimental results are in accordance with the theoretical calculation.

[1] Yan, X., et al., Sci Rep. 2016, 6: 24958.
[2] Prabhu, Y. T., et al., World Journal of Nano Science and Engineering 2014, 04(01): 21-28.

Design of high-pressure beamline at HEPS

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Keywords: synchrotron radiation, high pressure, beamline

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High Pressure Beamline (HPB) is one of the 14 beamlines in the first phase of HEPS project at Beijing, China. The total length of HPB is 95m. In addition to the front end and beamline optical hutches, an experimental hutch for XRD method is included.

The insert device of HPB is an in-vacuum permanent magnetic undulator. The magnetic field period, the minimum magnetic gap and the maximum magnetic field strength of the undulator are 20.2mm, 5mm and 1.02T respectively. The 4.2m length undulator provides high brilliance X-rays for high-pressure experiments in the energy range 20-50 keV. The source size (FWHM) is 22.09 μm (H) × 9.50 μm (V), and the source divergence (FWHM) is 13.88 μrad (H) × 12.09 μrad (V).

The first optical component after the front end is white beam mirror (WBM) which is used to reject the high orders harmonics. The distance from WBM to source is 35.5m, and the acceptance angles of the WBM is 20μrad (H) × 18μrad (V). In order to obtain higher reflection efficiency around 50keV, Pt is selected for the mirror coating, and the grazing incidence angle is set to 1.5mrad.

To improve the flux at sample position, the pink beam mode with ~0.1% energy resolution is set-up during beamline design. The pink beam and mono beam can be switched by tuning the high-heat load double plain mirrors (DPM) and the Si (111) double-crystal monochromator (DCM). The distances from beam source to DPM and DCM are 38m and 40m separately. In order to improve beam stability, the DCM and DPM are vertically placed and the X-ray is diffracted in the horizontal direction. The acceptance angles of the DPM and DCP are both 20μrad (H) × 18μrad (V).

To improve the X-ray focus spot stability at the sample position, a secondary light source is placed in the beamline. The secondary light source bending mirrors, with scaling ratios of ~1.83, are located at 42m away from the source. The acceptance angle of the bending mirrors is 18μrad (H) × 16μrad (V). Secondary light source slit is located at 65m from the source.

The experimental hutch is dedicated for high pressure XRD experiment. There are two experimental tables in this hutch, general purpose table (GPT) and laser heating table (LHT). The sample position at GPT and LHT are at 89m and 94m away from source respectively. The GPT configuration allows a wide range of experimental techniques, such as powder/single-crystal/multi-grain XRD, rapid de/compression XRD, under high pressure and at room temperature, high temperature (with external heating) or low temperature (with cryogenic cooling). The GPT provides an X-ray focused spot size <5μm with flux > 2×1013ph/s@30keV, or a focal spot size of < 200nm in sub-micron diffraction experiments. The LHT is dedicated for in situ double-side laser heating XRD under high pressure, furthermore the pulse laser heating method will be established in the LHT.

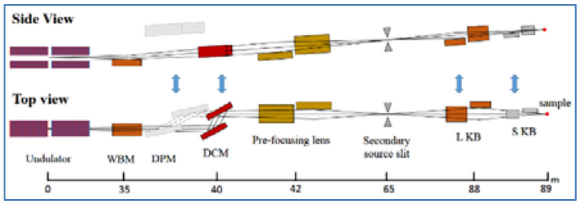

Figure 1. Design of beamline. WBM: with beam mirror, DPM: double plain mirrors, DCM: double crystal monochromator, L KB: long KB mirror, S KB: short KB mirror.

High-pressure equation of state of schreibersite $Fe_{2.15}Ni_{0.85}P$

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Keywords: schreibersite, high pressure, equation of state

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Introduction: In the veinlet of iron meteorites, iron-nickel phosphides are often observed as common accessories, such as $(Fe,Ni)_3P$-schreibersite [1], $(Fe_{0.58}Ni_{0.42}Co_{0.003})_{1.95}P$-barringerite [2], $(Fe,Ni)_2P$-allabogdanite [3], and $(Ni_{2.30}Fe_{1.64}Co_{0.01})_{\Sigma=3.95}P_{1.05}$-melliniite [4]. Phosphorus is thought to be an important light element existing in planetary cores [5,6]. As a volatile element, phosphorus could become highly siderophile at high pressure and high temperature, for example, 4 wt% of phosphorus could dissolve in crystalline iron at 23 GPa and 1275 °C [7], and its core-mantle partition coefficient is in a likely range of 20-50 [8]. The information supports that phosphorus could migrate to planetary cores during crystallization differentiation of a magma ocean and become one of the light elements in planetary cores, such as ~0.20 wt% phosphorus in the Earth's core [5] and ~0.32 wt% in the Martian core [9]. Thus, understanding the high-pressure and high-temperature behaviors of Fe-Ni-P compounds is of significance to discuss and constrain the properties of planetary cores. So far, investigations on Fe_2P, Fe_3P and Fe_4P compounds have been applied. Fe_3P exhibits an electronic state transition of Fe^{3+} from high-spin to low-spin at around 20-40 GPa and a phase transition from $I\bar{4}$ to $P4/mnc$ at 64 GPa and 1600 K [10]. Alloying effect of Ni on physical properties and structure of Fe and Fe-light elements alloys is also very important. Previous studies indicate that adding nickel into iron phosphides would change its structure and phase stability. Such as, a small amount of Ni and Co in the allabogdanite-Fe_2P may stabilize its orthorhombic structure [11]. The doping of nickel also slightly increases the bulk modulus of the allabogdanite phase [11]. Furthermore, incorporation of nickel in Fe_4P results in reduction of compressional and shear wave velocities while enhances their anisotropy [12]. In this work, we compressed a natural single-crystal sample of $(Fe,Ni)_3P$-schreibersite up to 50 GPa at room temperature, and *in-situ* characterized its compressibility by synchrotron-radiation X-ray diffraction (XRD) combined with a diamond anvil cell (DAC).

Experimental Data and Discussions: A natural schreibersite single crystal occurring in an iron meteorite was used as the sample. The chemical formula of the sample was determinded to be $Fe_{2.15}Ni_{0.85}P$ based on electron microprobe analysis (EMPA). The sample was identified as $I\bar{4}$ structure, determined by micro X-ray diffraction (Micro-XRD). *In-situ* high-pressure XRD experiments were conducted at 13IDD beamline (GSECARS) of the Advanced Photon Source (APS), Argonne National Laboratory (ANL). The sample was compressed up to 47.3 GPa at room temperature. Peaks from the tetragonal phase were observed and could be fitted to the highest pressure, indicating that the tetragonal structure ($I\bar{4}$) is stable to at least 47 GPa. Unit-cell parameters are obtained. a/a_0 and c/c_0, the normalized axial length, keep nearly equal, and the c/a ratio keeps almost constant at 0.493 up to 50 GPa, indicating that $Fe_{2.15}Ni_{0.85}P$ is compressional isotropic. In contrast, the c/a ratio reported by Scott et al. [13] and Gu et al. [10] exhibit compressional anisotropy of Fe_3P at high pressure. This indicates that the doping of Ni in Fe_3P weakens compressional anisotropy. The pressure-volume (P-V) data of $Fe_{2.15}Ni_{0.85}P$ were fitted by the Birch-Murnaghan equation of state (EoS), yielding K_0 = 185(1) GPa, K_0' = 4.0 (fixed), V_0 = 365.8(1) Å^3 (the second order equation), and K_0 = 184(4) GPa, K_0' = 4.1 (2), V_0 = 365.9(1) Å^3 (the third order equation). $Fe_{2.15}Ni_{0.85}P$ is less compressible than Fe_3P (K_0 = ~160 GPa) [10,13], which means the substitution of Ni tends to enhance incompressibility.

Implication: To survey the doping effect of Ni and P on the density of the Martian core, densities of $Fe_{2.15}Ni_{0.85}P$ together with those of Fe_3S, Fe_3P, FeS and FeP have been computed at 18-40 GPa and 2100 K (see Figure 1). The high-temperature Birch-Murnaghan EoS was used. Density profile of γ-Fe [14] and the density profile of the Martian core (based on the R11-DW84 model) [6,15] has been used as reference curves for comparison. Under the pressure and temperature conditions of the Martian core, the density of Fe_3P is lower than that of Fe_3S, and the density of $Fe_{2.15}Ni_{0.85}P$ is even lower. With the increment of pressure, such a difference becomes more apparent. This result evidences that the presence of Ni and P could efficiently decrease the density of Fe_3S. FeP has a much lower density than FeS, suggesting the adding of P into FeS could lower its density under the Martian core conditions. This suggests that existence of Ni and P could be important, and $(Fe,Ni)_3P$-schreibersite would be a possible mineral in the Martian core. Although the density of γ-Fe - Fe_3S system doesn't match that of the Martian core, given that Fe_3S, Fe_3P, Ni_3S, and Ni_3P are isostructural, a comprehensive understanding of $(Fe,Ni)_3(S,P)$ would be helpful for studying the Martian core.

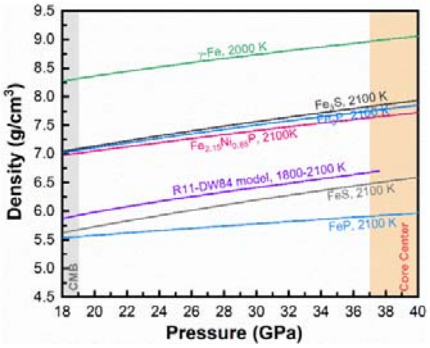

Figure 1. Calculated densities of Fe_3S, Fe_3P, $Fe_{2.15}Ni_{0.85}P$, FeS, and FeP at pressure-temperature conditions correspond to the Martian core, compared with the density of γ-Fe [14] and the density profile of R11-DW84 model [6,15]

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[1] R. Skála, I. Císařová, *Phys Chem Minerals* 2005, **31,** 721
[2] P. R. Buseck, *Science* 1969, **165,** 169
[3] S. N. Britvin, N. S. Rudashevsky, S. V. Krivovichev, P. C. Burns, Y. S. Polekhovsky, *Am Mineral* 2002, **87,** 1245
[4] G. Pratesi, L. Bindi, V. Moggi-Cecchi, *Am Mineral* 2006, **91,** 51
[5] W. F. McDonough, *Treatise on geochemistry* (Carlson Editors, New York 2003)
[6] A. Rivoldini, T. Van Hoolst, O. Verhoeven, A. Mocquet, V. Dehant, *Icarus* 2011, **213,** 451
[7] A. J. Stewart, M. W. Schmidt, *Geophys Res Lett* 2007, **34,** L13201
[8] A. N. Halliday, B. J. Wood, *Treatise on geophysics* (Stevenson Editors, Amsterdam, the Netherlands 2007)
[9] L-K. Sha, *Geochim Cosmochim Ac* 2000, **64,** 3217
[10] T. Gu, Y. Fei, X. Wu, S. Qin, *Earth Planet Sc Lett* 2014, **390,** 296
[11] J. Nisar, R. Ahuja, *Earth Planet Sc Lett* 2010, **295,** 578
[12] X. Wu, M. Mookherjee, T. Gu, S. Qin, *Geophys Res Lett* 2011, **38,** L20301
[13] H. P. Scott, S. Huggins, M. R. Frank, S. J. Maglio, C. D. Martin, Y. Meng, J. Santillán, Q. Williams, *Geophys Res Lett* 2007, **34,** L06302
[14] T. Komabayashi, Y. Fei, *J Geophys Res* 2010, **115,** B03202
[15] G. Dreibus, H. Wänke, *Meteoritics* 1985, **20,** 367

Inelastic x-ray scattering of silica glasses beyond megabar pressure

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Despite implications for dense magmas in the Earth's interiors, the detailed structures of silicate glasses at elevated pressure conditions, especially beyond megabar pressures, are among the challenging problems in geophysics. As a simplest model for silicate glasses and also as an archetypal oxide glass, structure of amorphous silica at elevated pressure conditions has been studied using diverse experimental probes, including elastic and inelastic x-ray scattering, neutron scattering, molecular dynamics, and Brilluion scattering [1-6]. The direct silicon coordination environments above megabar pressures, however, remain to be further explored and reconciled. Recent advances in synchrotron techniques, especially in x-ray collimating optical devices, allow us to successfully refocus the weak inelastically scattered photons from ~60 μm sized-sample in a diamond anvil cell [7,8]. Here we collected the O *K*-edge and Si $L_{2,3}$-edge inelastic x-ray scattering spectra of silica glasses with varying pressures up to 1.24 Mbar and revealed its unique densification paths.

Progress in inelastic x-ray scattering provided insights into the pressure-induced bonding changes in diverse oxide glasses [8-10]. Theoretical calculations of inelastic x-ray scattering spectrum can provide useful constraints on the atomistic origin of the pressure-induced changes in inelastic x-ray scattering features. Thus, we calculated O *K*-edge and Si $L_{2,3}$-edge inelastic x-ray scattering spectra of crystalline silica polymorphs and used it to closely investigate the structural changes in silica glasses at high pressure.

Features in O *K*-edge inelastic x-ray scattering spectra shift to higher energy loss as pressure increases, implying a pronounced decrease in O-O distances. Overall shape of excitation band also varies with increasing pressures, which can potentially be interpreted as a formation of highly coordinated silicon. Whereas O *K*-edge inelastic x-ray scattering spectra are represented as a single broad excitation features, Si $L_{2,3}$-edge mainly consists of three peaks. Features in Si $L_{2,3}$-edge inelastic x-ray scattering spectra with increasing pressures show clear evidence of formation of octahedral Si and decrease in Si-O distances. Si $L_{2,3}$-edge features for silica glasses at 124 GPa and its crystalline analogue seifertite are similar, indicating potential similarity in their atomic packing at high pressure.

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[1] C. Prescher et al., *Proc. Natl. Acad. Sci.* 2017, **114**.
[2] J. F. Lin et al., *Phys. Rev. B* 2007, **75**.
[3] H. Fukui et al., *Phys. Rev. B* 2008, **78**.
[4] A. Zeidler et al., *Phys. Rev. Lett.* 2014, **113**.
[5] M. Wu et al., *Sci. Rep.* 2012, **2**.
[6] M. Murakami et al., *Phys. Rev. Lett.* 2010, **104**.
[7] P. Chow et al., *Rev. Sci. Instrum.* 2015, **86**.
[8] S. K. Lee et al., *Proc. Natl. Acad. Sci.* 2018,
[9] S. K. Lee et al., *Nat. Mater.* 2005, **4**.
[10] S. K. Lee et al., *Proc. Natl. Acad. Sci.* 2008, **105**.

Super-hydration from zeolites to clay

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Keywords: Super-hydration, natrolite, MOF, kaolinite, subduction, water cycle

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Super-hydration is defined as a special case of pressure-induced insertion whereby water molecules are injected into the pores of microporous materials. Since its first discovery in a natural zeolite natrolite ($Na_{16}Al_{16}Si_{24}O_{80}x16H_2O$) in 2002 [1], super-hydration has been established to be a systematic property of this class of small-pore zeolites [2]. Depending on the type of extra framework cations (Li, Ag, K, Rb, Cs, Ca, Sr, Pb, Cd), the degree of volume expansion and its onset pressure are controlled by up to 21% and in the pressure range of 0.4 – 3.0 GPa, respectively. Such a unique high-pressure chemistry occurring in nanopores under low-to-intermediate pressure-temperature conditions is also being extended to MOFs (Metal-Organic Framework materials) to design novel means in guest exchange and high-pressure storage [3].

More recently, we have reported that super-hydration occurs in the subduction interface where a clay mineral kaolinite becomes super-hydrated at conditions corresponding to a depth of about 75 km in a cold subducting slab (ca. 2.7 GPa and 200 °C) in the presence of water [4]. This super-hydrated kaolinite has a unit cell volume that is about 31% larger, a density that is about 8.4% lower than the original kaolinite and, with 29 wt% H_2O, the highest water content of any known aluminosilicate mineral in the Earth. As pressure and temperature increase to 19 GPa and about 800 °C, super-hydrated kaolinite undergoes sequential breakdowns into hydrous mantle minerals. The formation and subsequent breakdown of super-hydrated kaolinite in cold slabs subducted below 200 km leads to the release of water that may affect seismicity and help fuel arc volcanism at the surface.

In this talk, I will summarize our evolving efforts in high pressure crystallography focused on super-hydration and developments of high-pressure research opportunities at PLS-II and PAL-XFEL in Korea.

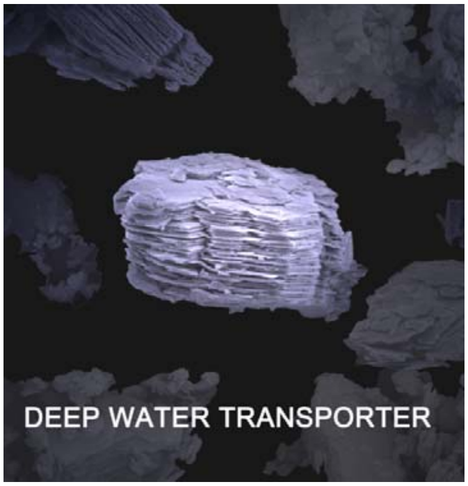

Figure 1. The first observation of a super-hydrated phase of the clay mineral kaolinite could improve our understanding of water transport in the deep Earth that lead to volcanism and affect earthquakes on the surface.

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[1] Lee et. al., JACS 2002, **124,** 5466; Lee et. al., Nature 2002, **420,** 485.
[2] Lee et. al., Chem. Eur. J. 2013, **19,** 10876; Lee et. al., Chem. Mater. 2016, **28,** 5336
[3] Lee et al., JACS 2016, **138,** 11477; Lee et al., Chem. Mater. 2016, **28,** 5336.
[4] Lee et al., Nature Geoscience 2017, **10,** 947.

Shock recovery of high-pressure bismuth-II

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Keywords: synchrotron radiation, shockwave

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Bismuth displays a remarkable variety of high-pressure phases, including an incommensurate structre and one of the few isotypes of α-Po. [1] High-pressure bismuth (Bi) phases have been examined in static compression experiments; however, none could be recovered to ambient conditions. The narrow stability range and multiple phases present at low pressure make for difficult recovery. [2] Here we report the recovery of Bi-II α-Po type structure from a decaying shockwave recovery experiment.

During dynamic compression, voids, grain boundaries and other heterogeneities existing prior to shock compression affect local stress and temperature. We are studying bismuth crystals through a series of shock recovery experiments to understand the stress and temperature evolution upon shock loading. Before shock, samples are characterized using an X-ray tomography technique at the Advanced Photon Source (APS) on the Argonne National lab (ANL) campus. A shock recovery experiment is performed on this sample at the UNLV gas gun laboratory. After shock the sample is analyzed at the APS with X-ray microdiffraction.

Chemically pure bismuth crystals (0.3 mm – 1 mm) are pressed into a copper retainer ring with 3 mm inner diameter and 8 mm outer diameter. X-rays at the 16 IDB beamline at the APS were focused to 1 x 2 μm^2 at monochromatic x-ray energies of 40 keV. Initially a 2D tomographic image was recorded on a 3.9 x 3.9 mm^2 grid with 13 x 13 μm^2 spacing. This tomographic map shows distribution of voids, cracks and density differences in polycrystalline aggregates of single or multiple phases due to spatial contrast in attenuation of the X-ray beam. Here the tomographic maps serve to identify regions that could generate local temperature or stress excursion during shock. Diffraction data shows the sample is pure Bi in the Bi-I structure, stable at ambient conditions. Afterwards samples were subjected to the following shock compression experiment.

A tungsten flyer and stainless steel driver produced a peak shock pressure of 15 GPa stepping down to 10 GPa then 6 GPa followed by 4 GPa down to ambient conditions, with duration 12 ns per step on a 0.37 mm thick bismuth sample. Upon shock loading it is expected that void- collapse will generate regions of increased temperature (hot spots), which can cause local melting, and transformation to high P-T phases of bismuth in the area around the hot spots. [3] The complex phase diagram of bismuth helps provide constraints on pressure and temperature conditions reached based on melting and structures present.

X-ray micro-diffraction maps were collected with a primary beam focused to 3 x 7 μm2 at 40 keV energy in transmission geometry using a MAR165 CCD detector. These maps were sampled over a 0.39 x 0.60 μm^2 region with a 0.010 μm spacing while oscillating the sample at each location on the goniometer from -5 to 5 degrees omega. The most dominant peaks are intense reflections from recrystallized Bi-I with symmetric peak shapes and narrow rocking curves. Much weaker sharp single crystal reflections occur at 2θ angles not matching the lattice of Bi-I. Streaky features of lower intensity indicate the presence of a finer grained Bi-I and Bi-II fraction, which have also experienced plastic deformation. SEM analysis indicated the shock-recovered sample is pure bismuth so we know these diffraction features are from a different phase of Bi, not from a reaction product.

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[1] Mcmahon, M. I., Degtyareva, O., & Nelmes, R. J. (2000). Ba-IV-Type Incommensurate Crystal Structure in Group-V Metals. Phys. Rev. Lett., 85(23), 4896-4899. doi:10.1103/physrevlett.85.4896

[2] Gorman, M. G., Briggs, R., Mcbride, E. E., Higginbotham, A., Arnold, B., Eggert, J. H., . . . Mcmahon, M. I. (2015). Direct Observation of Melting in Shock-Compressed Bismuth With Femtosecond X-ray Diffraction. Phys. Rev. Lett.,115(9). doi:10.1103/physrevlett.115.095701.

[3] Shan, Tzu-Ray, & Thompson, Aidan P (May 2014). Shock-induced hotspot formation and chemical reaction initiation in PETN containing a spherical void. Journal of Physics Confer- ence Series, 500(17), 6. doi:101088/1742-6596/500/17/172