EFree Energy Frontier Research in Extreme Environments Center

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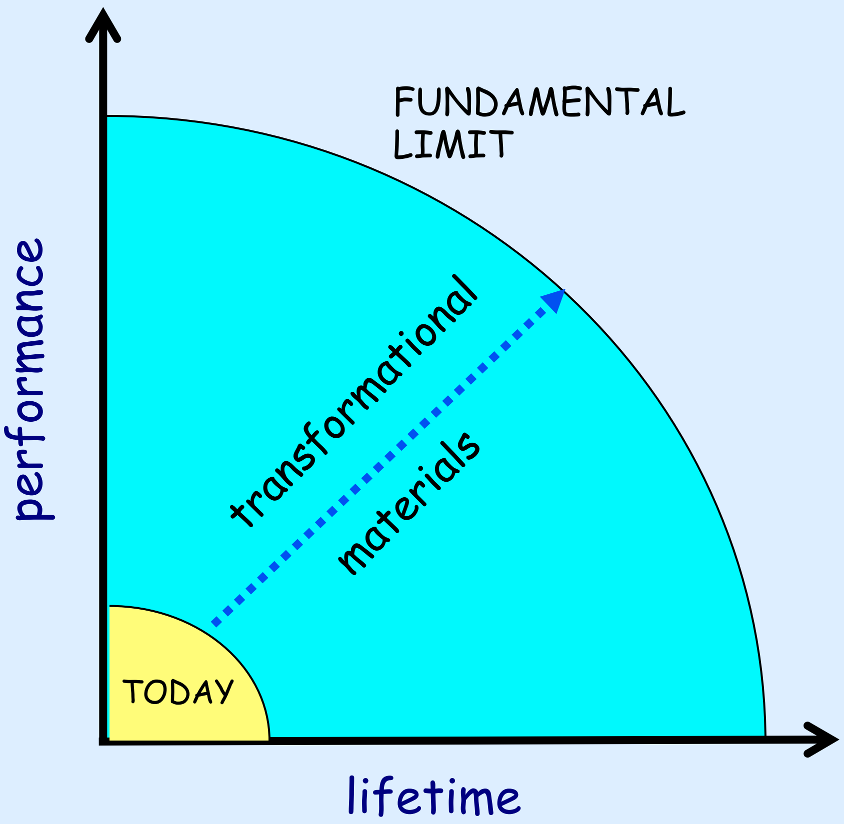
U.S. DEPARTMENT OF ENERGY Office of Science

Materials Under Extreme Conditions



Extreme Environments

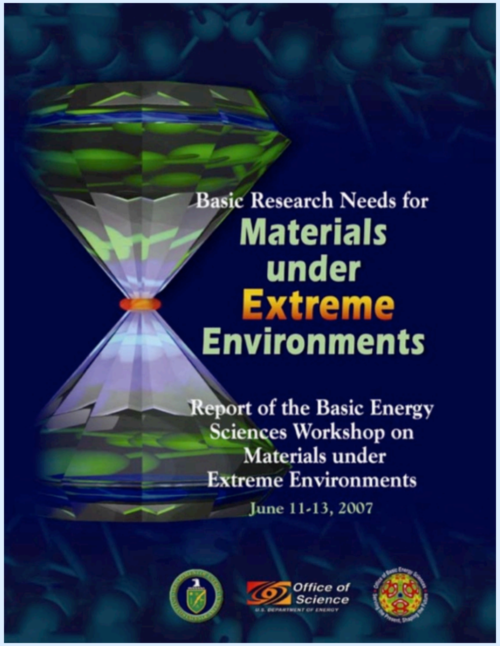
Energetic photon/particle flux

Chemical extremes

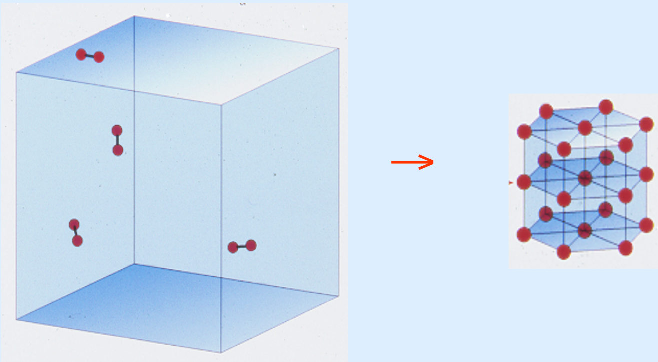
Electromagnetic extremes

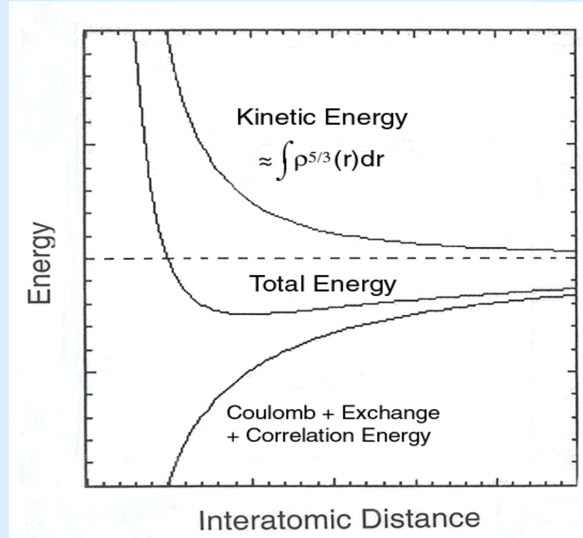
Pressures and temperatures

- ***Understanding materials behavior***
- ***Enhancing materials performance***
- ***Making new materials***

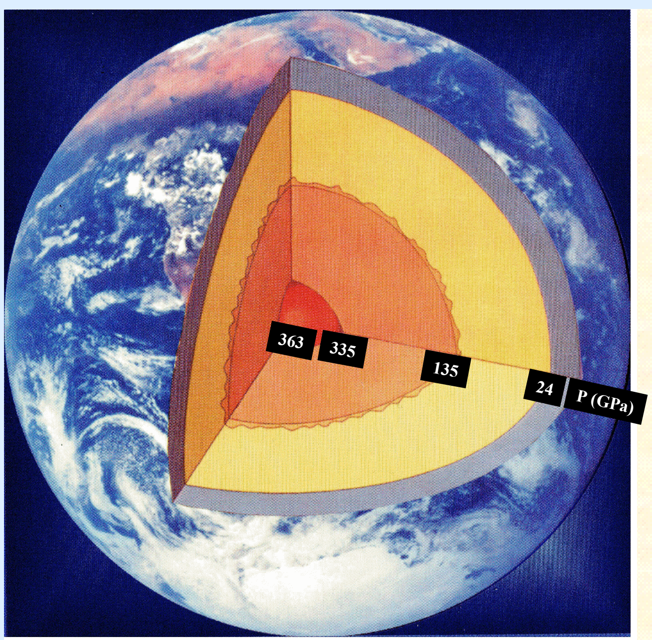


Effects of Extreme Pressures on Materials





$$P = -\frac{\partial E}{\partial V}$$

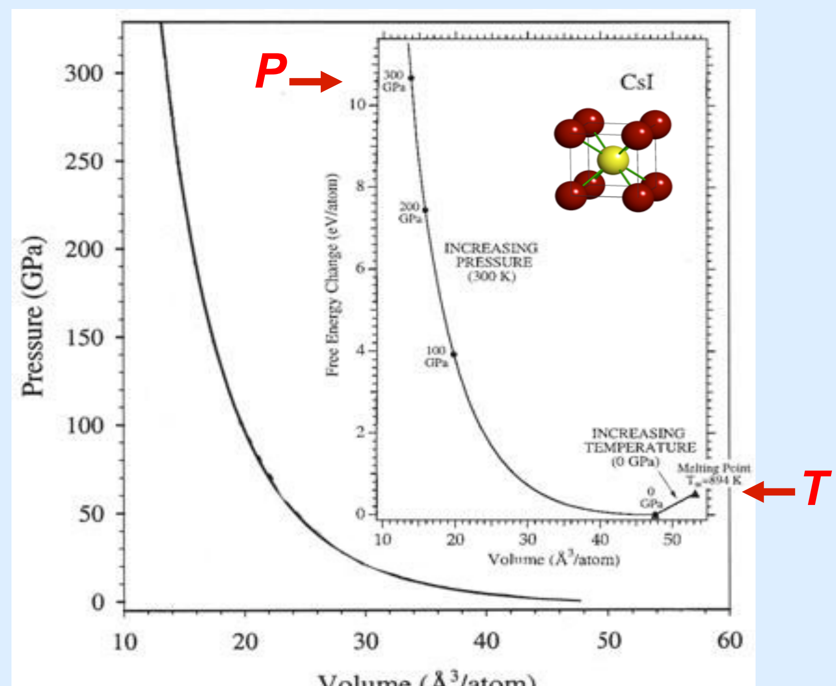


$P\Delta V$ ~ eV

chemical

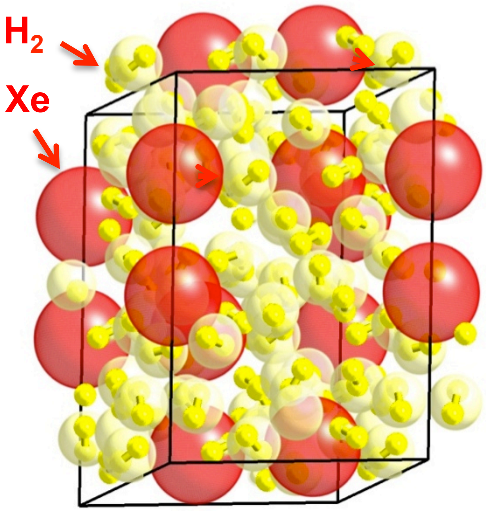
bond

strengths



Novel Materials Discovered under Pressure

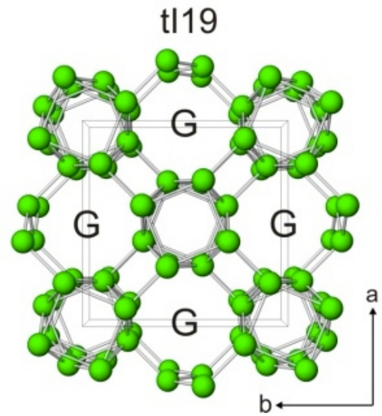
Novel Compounds



$Xe(H_2)_8$

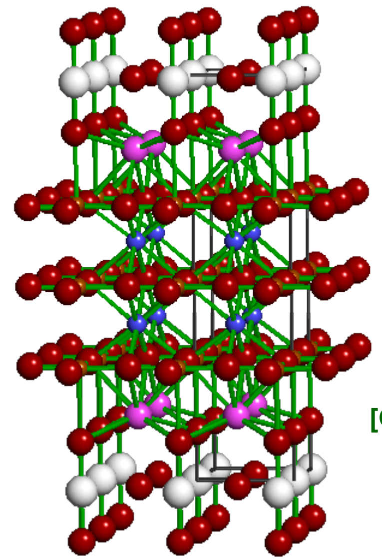
[Somayazulu et al., *Nature Chem.* (2009)]

'INSULATING' METALS



Na >200 GPa

Ma et al., *Nature* 2009); Lazicki et al., *PNAS* (2009)]



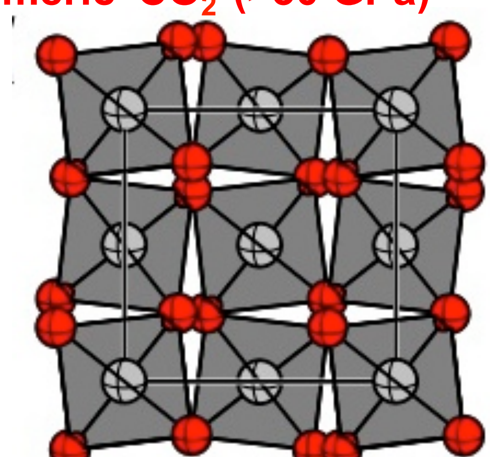
HIGHEST T_c SUPER-CONDUCTIVITY 164 K at 30 GPa

$HgBa_2Ca_2Cu_3O_{8+}$

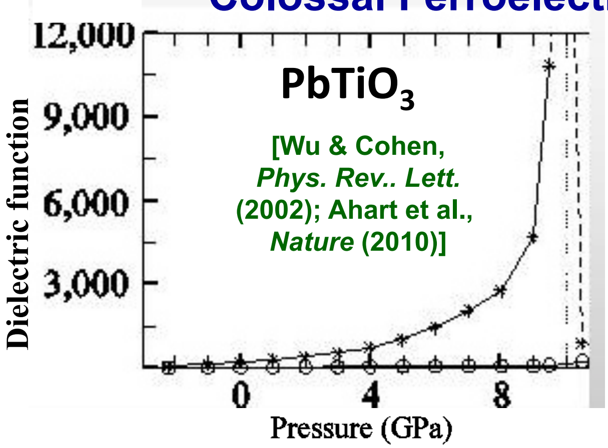
[Gao *et al., Phys. Rev. B* (1994); Lokshin *et al. ibid.* (2002)]

'Polymeric' CO_2 (>30 GPa)

[Santoro et al. *PNAS (2012]];* Datchi et al., *Phys. Rev. Lett.* (2012)

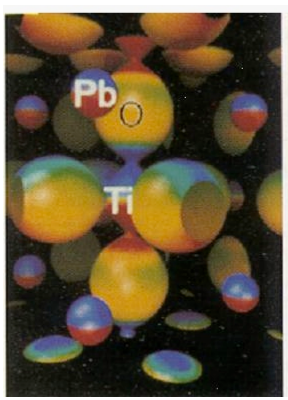


Colossal Ferroelectricity



$PbTiO_3$

[Wu & Cohen, *Phys. Rev.. Lett.* (2002); Ahart et al., *Nature* (2010)]

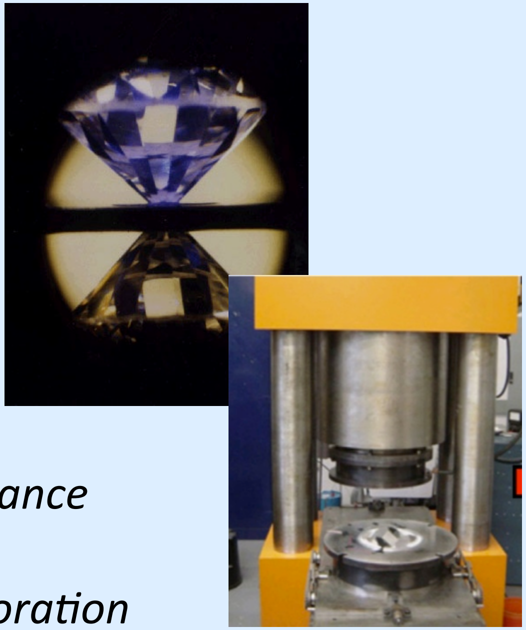


DEEP CARBON OBSERVATORY

Motivation for the Center

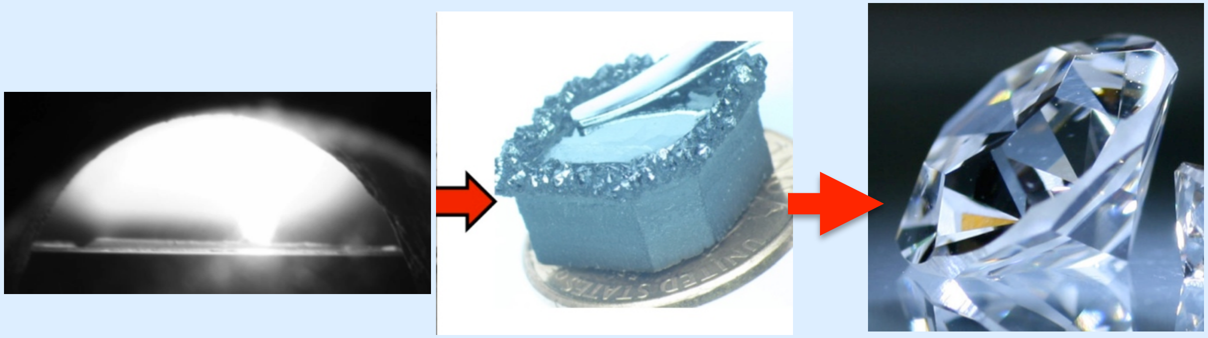
- Intrinsic limitations of available materials

  Deficiencies in performance, cost, stability



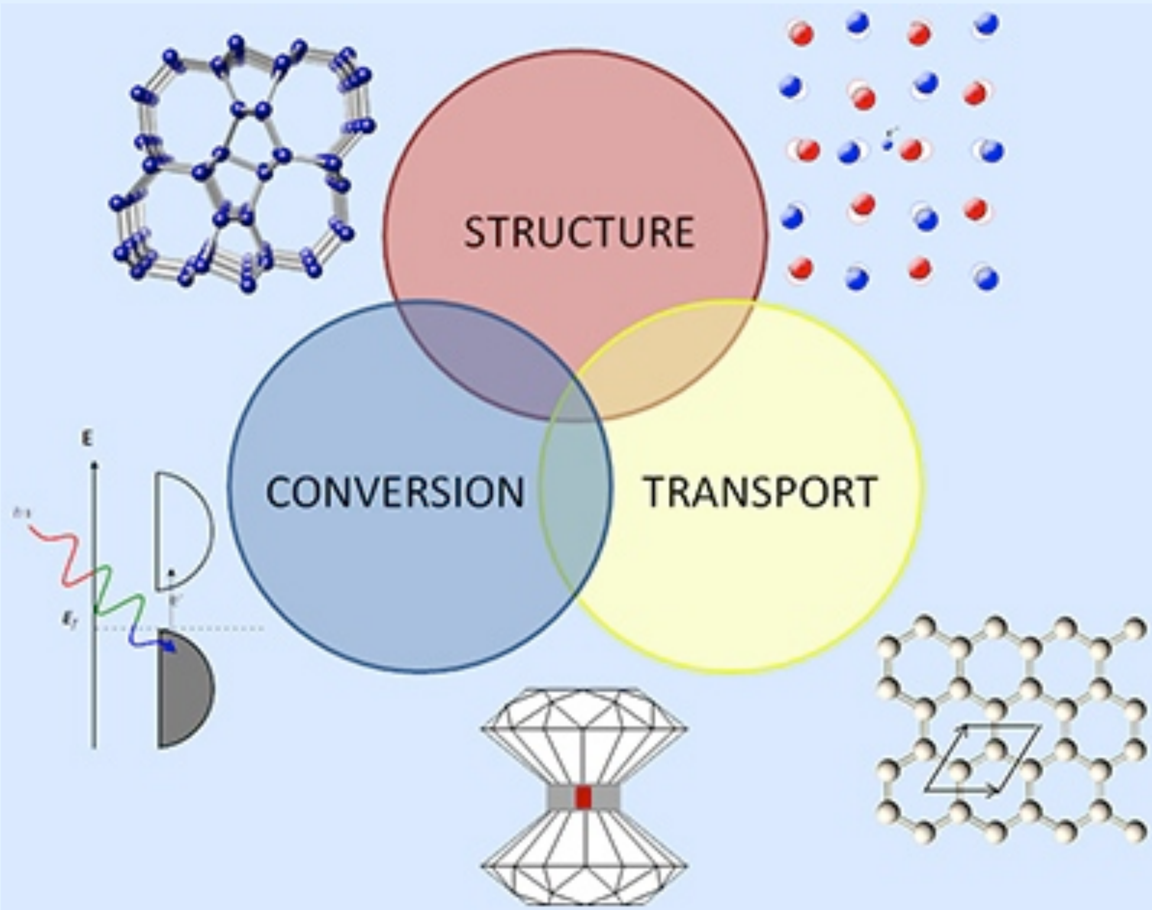
- New strategies needed to develop paradigm-shifting, transformative materials
  - *Exploit extreme environments—manipulate matter for next-generation materials*
  - *Understand fundamental factors that control performance*
  - *Synthesis and/or stabilization at ambient pressure*
  - *Broad university, national laboratory, industrial collaboration*

- Archetypal model
  - *Diamond synthesis by CVD instead of pressure*



EFree Energy Frontier Research in Extreme Environments Center

Mission: To accelerate the discovery and synthesis of new energy materials using extreme conditions



Carnegie:

- **Director:** R. J. Hemley
- **Assoc. Director:** T. S. Strobel
- **Admin.** S. Gramsch, M. Phillips
- **Carnegie Partners:** R. Boehler, Y. Fei, D. Kim, Z. Liu, H. K. Mao, I. Naumov, V. Struzhkin, W. Yang

University Partners:

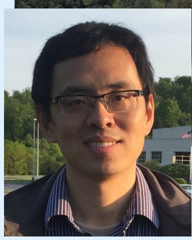
- **Penn State:** J. Badding, N. Alem, V. Crespi
- **Cornell:** R. Hoffmann, N. Ashcroft
- **Colorado School Mines:** C. Taylor
- **Caltech:** B. Fultz
- **Lehigh:** K. Landskron

DOE Facilities

- ***APS, ANL (X-ray)***
- ***SNS, ORNL (Neutron)***
- ***NSLS II, BNL (IR)***

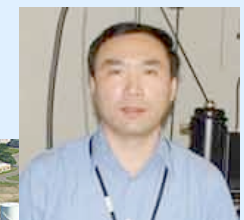
DOE National Laboratory facilities provide key support for EFree projects through technical coordinators/leads

Spallation Neutron Source (ORNL) - *NEUTRON SCATTERING*



Chen Li
Neutron Scattering Coordinator

Advanced Photon Source (ANL) – *X-RAY*



Zhenxian Liu
Carnegie IR Lead

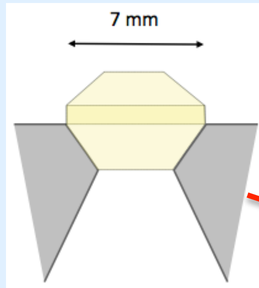
Maria Baldini
X-ray Coordinator

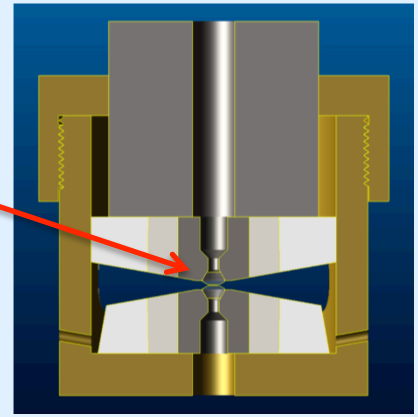
National Synchrotron Light Source II (BNL) - *SYNCHROTRON IR*

EFree coordinators support high *P-T* technique developments and computational theory

Reini Boehler

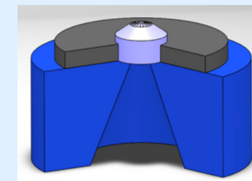
High P-T Technique Coordinator





Large volume diamond cells (x100 volume)

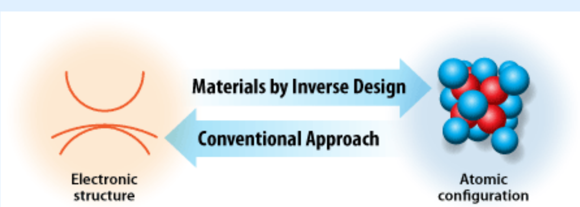
Single Crystal CVD Diamond

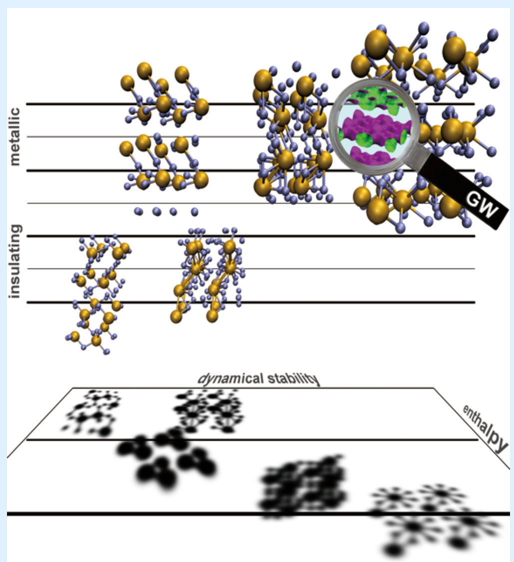


www.washingtondiamondscorp.com

DuckYoung Kim

Computational Theory Coordinator





<u>Electronic structure analysis</u>

<u>Crystal structure predictions</u>

USPEX

Universal Structure Predictor: Evolutionary Xtallography

Ab Initio Random Structure Searching

UCL

Meta dynamics

Argonne NATIONAL LABORATORY

TACC

NERSC

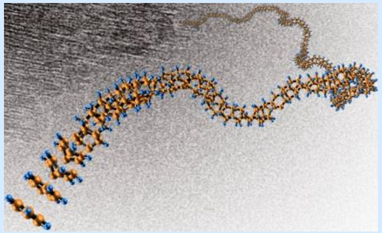
Efree highlights to date

https://efree.gl.ciw.edu

Since 2009

- **280 Publications**
  - **66 High impact**
  - **58 Efree only**
- **38 Students / Postdocs supported**

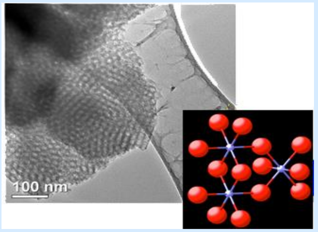
EFree currently supports five center-wide projects



Carbon Nanothreads

1. New Nanophase Carbons

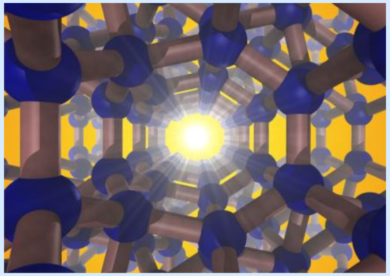
Goal: To stabilize and characterize new forms of carbon through tailored synthetic processes for the development of new structural materials (*Lead*: *Badding, Penn State*).



Mesoporous Stishovite

2. Next Generation Mesoporous Materials

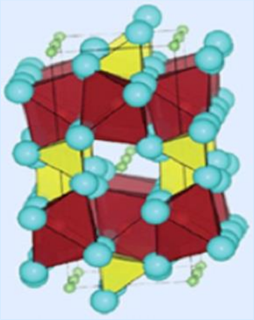
Goal: To obtain mesoporous and mesostructured crystalline materials through templated synthetic routes at high pressure for catalysis and related applications (*Lead*: *Landskron, Lehigh*).



Open-Framework Si_{24}

3. New Solar Energy Materials

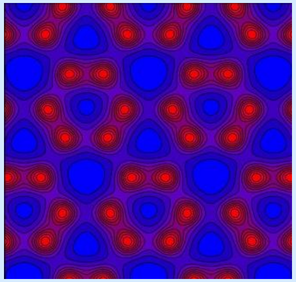
Goal: To synthesize new materials that will have a transformative impact on solar light absorption, conversion efficiencies and manufacturing costs (*Lead*: *Strobel, Carnegie*).



$Li_x FePO_4$

4. Ion Transport Processes

Goal: To characterize the structural features that underlie ion transport in battery materials (*Lead*: *Fultz, Caltech*).



Graphenic Hydrogen

5. Novel Transport in Hydrogen-Rich Materials

Goal: To uncover novel electron transport in hydrogen-rich materials for enhanced electrical transport (*Lead*: *Hemley, Carnegie*).

Benzene-Derived Carbon Nanothreads

Scientific Achievement

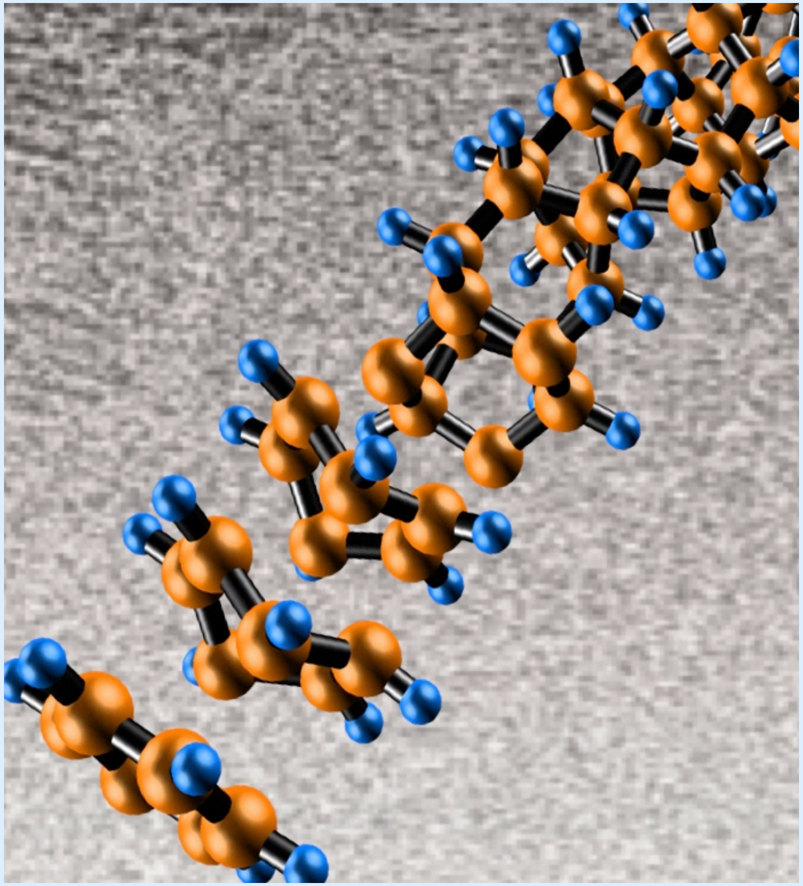
Synthesis of a new carbon nanomaterial from benzene under pressure that is the thinnest possible thread of the diamond structure

Significance and Impact

These nanothreads should have diverse applications owing to their unique properties, including strength, compared to conventional carbon nanotubes

Research Details

- Slow compression/decompression of benzene allows recovery to ambient pressure of carbon nanothreads capped by hydrogen.
- Threads were characterized by synchrotron x-ray diffraction, neutron diffraction, TEM, Raman spectroscopy, NMR, and first principles calculations.



Facilities: SNS, Oak Ridge; APS, Argonne;
MRRC, Arizona State; Geophysical Lab, Carnegie Institution;
Penn State Materials Characterization Lab

[Fitzgibbons, T.C., Guthrie, M., Xu, E.-S., Crespi, V.H., Davidowski, S.K., Cody, G.D., Alem, N., & Badding, J.V., *Nat Mater, 10.1038/nmat4088 (2014)]*

Discovery of Graphenic Dense Hydrogen

Scientific Achievement

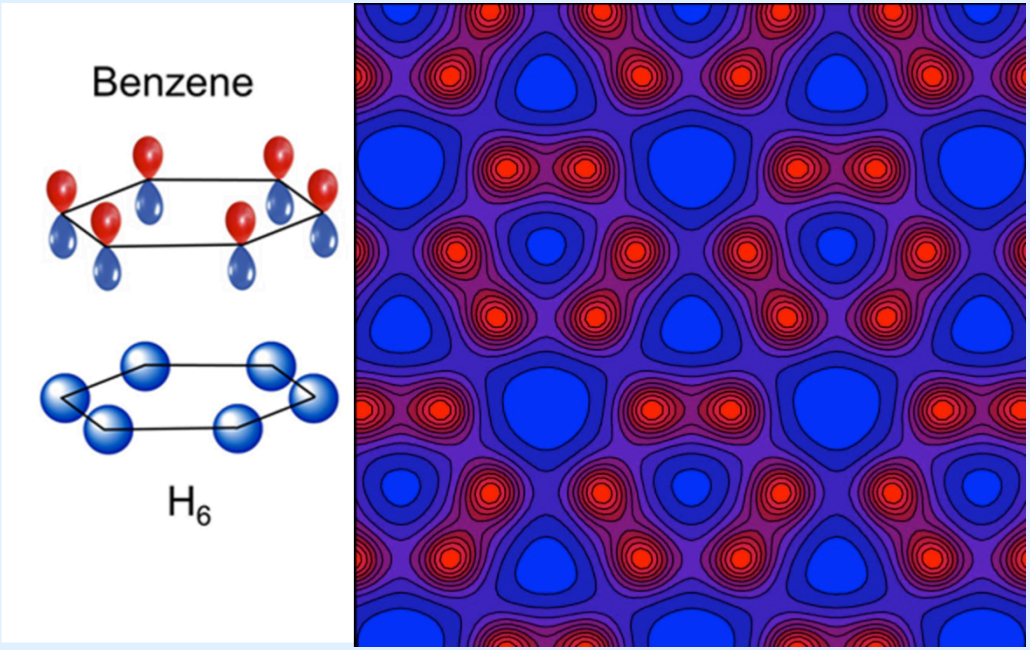
The atomic and electronic properties of dense hydrogen at very high pressures are controlled by closed-shell effects that parallel those of graphene

Significance and Impact

The results are essential to understanding of how the dense hydrogen becomes metallic – the state predicted to have exotic properties including high-T_c superconductivity

Research Details

- Hydrogen in different forms - molecular clusters, 2D and 3D crystals – was studied using modern quantum chemistry and solid state approaches.
- The stability of dense hydrogen structures (at >200 GPa) arises from the intrinsic stability of its 6-member rings and has properties similar to carbon graphene.



[Naumov, I.I., and Hemley, R.J. *Accts. Chem. Res.*, **47**, 3551 (2014)]

Novel Fullerene-Graphene Hybrid Material

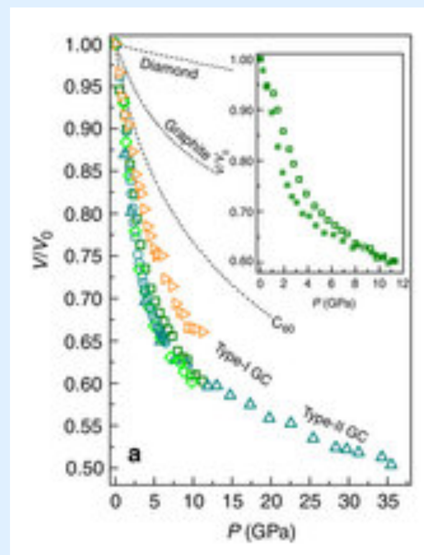
Scientific Achievement

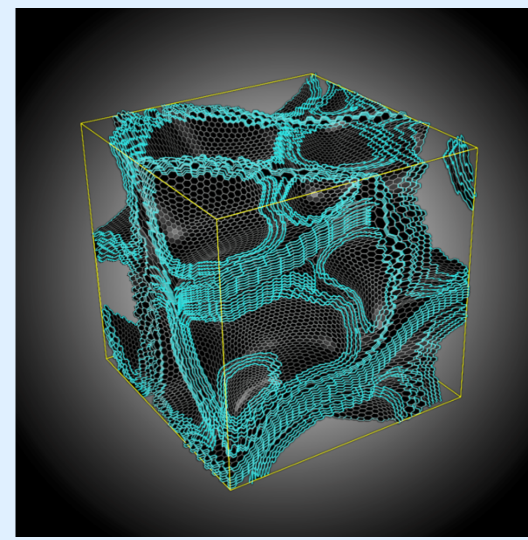
Discovery of a fullerene-graphene hybrid carbon with superior properties such as high strength, high volume compression, superelastic recovery from large volume deformation and high uniaxial strain, and variable Poisson's ratio.

Significance and Impact

This study will stimulate additional work on carbon-based materials, including new composites that feature combinations of two or more carbon allotropes.

- Fullerene-like spheroids encased in a disordered, multi-layer graphene matrix were identified in glassy carbon by using HRTEM.
- In-situ techniques for direct volume determination, acoustic wave velocity measurements, and x-ray diffraction, along with molecular dynamics simulations, were employed to explore the nature of the unusual and pressure-tunable, compression and elastic properties.



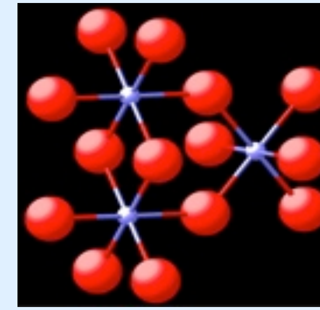


[ZS Zhao, EF Wang, HP Yan, Y Kono, B Wen, LG Bai, F Shi, JF Zhang, C Kenney-Benson, CY Park, YB Wang, GY shen, *Nature Commun*. **6**, 6212 (2015)]

Synthesis of Mesoporous Stishovite

Scientific Achievement

Mesoporous stishovite (SiO_2) has been synthesized using a nanocasting methodology with a large-pore mesoporous silica composite as a precursor.

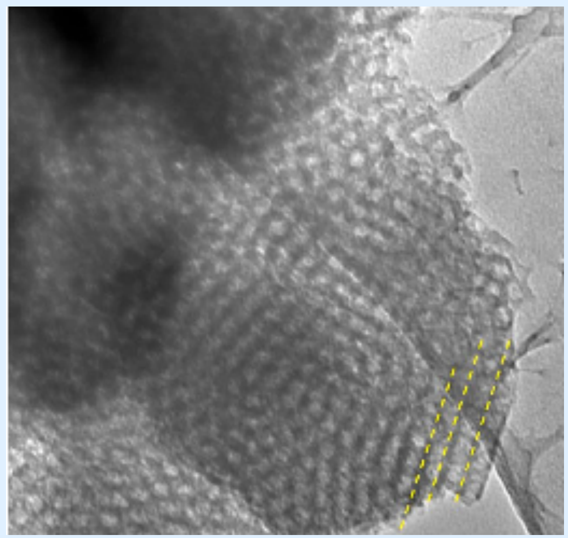


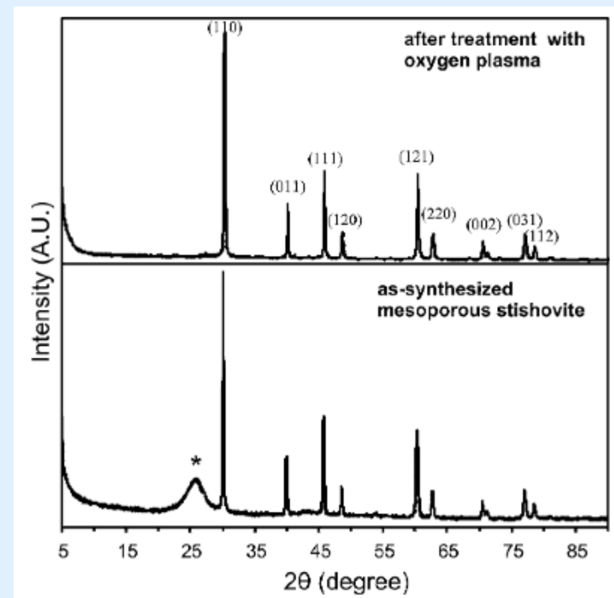
Significance and Impact

Synthesis of mesoporous stishovite offers the opportunity to investigate thermochemical properties for the interaction between stishovite and complex aqueous fluids to <u>model fluid sequestration</u> under relevant conditions.

Research Details

- Synthesis carried out at 9 GPa and 500 ^{o}C in a multianvil apparatus and characterized by TEM, electron microscopy and gas adsorption.
- Material has accessible mesopores with a wide pore size distribution, ~ 45 m^2/g, and pore volume ~ 0.15 cm^3/g

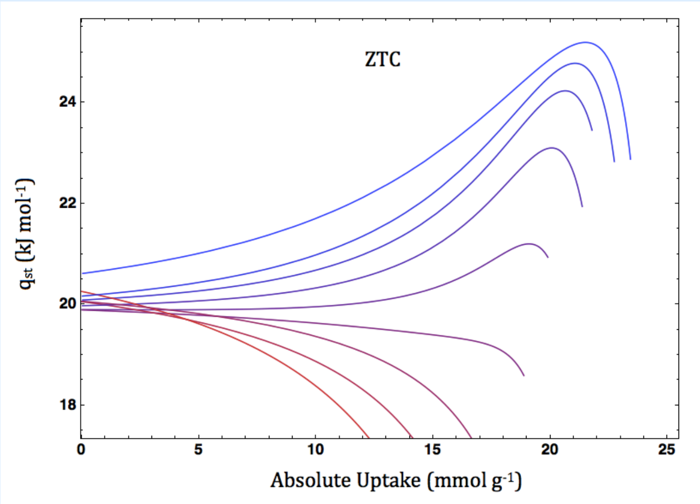




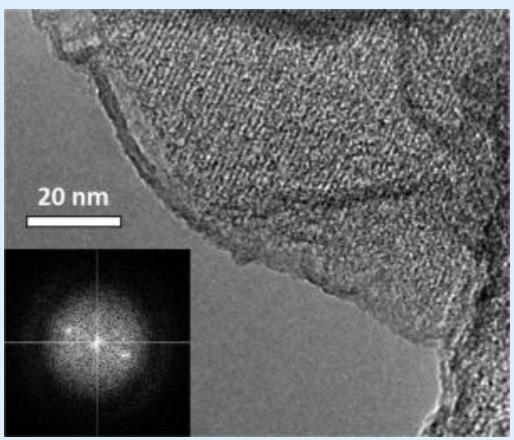
Facilities: Carnegie Institution, Lehigh University

[Stagno, V., et al. *Phys. Chem. Minerals* 10.1007/s00269-015-0739-8 (2015)].

Thermodynamics of Ethane and Methane Adsorption



Above: The isosteric heat of ethane adsorption on zeolite-templated carbon (ZTC) between 253 K and 423 K, showing an anomalous increase at low T.



Left: High-resolution TEM micrograph of ZTC showing regular porosity with a pore spacing of ~1.2 nm. Inset: A confirmation of the regularity by FFT of the image.

Scientific Achievement

The enthalpy of gas adsorption on surfaces was altered by nanostructures that promote interactions between the adsorbed molecules.

Significance and Impact

Attractive interactions between adsorbed methane and ethane molecules can be used to enhance gas densification at high pressures. This could be beneficial for natural gas storage.

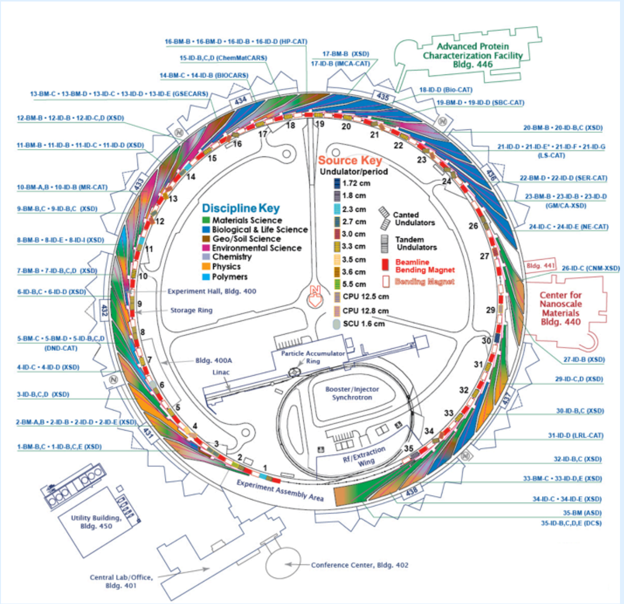
Research Details

- In previous studies, the enthalpy of adsorption of gases on carbon surfaces was found to decrease with surface coverage because the more favorable sites are filled first.
- By controlling the <u>adsorbent pore size distribution</u>, the adsorbed molecules show enhanced intermolecular interactions, leading to an isosteric heat that increases with surface coverage.
- An increasing enthalpy of adsorption substantially improves gas storage (e.g. methane delivery would be improved by 50% with ZTC at 60 bar and -40°C.)
- The effects found for methane, ethane, and krypton scale with the interaction strengths between free molecules, and depend on the surface structure.

This work was performed at the California Institute of Technology

[M. Murialdo, N. P. Stadie, C.C. Ahn, B. Fultz, J. Phys. Chem. C. **2015**, 119, 944-950.
N. P. Stadie, B. Fultz, C. C. Ahn, M. Murialdo, Patent Application US20140113811 A1, **2014**.
N. P. Stadie, M. Murialdo, C. C. Ahn, B. Fultz, *J. Am. Chem. Soc.* **2013**, 135, 990-993]

EFree Supported X-ray Techniques



Spectroscopy, scattering and imaging

In-situ characterization
Micro, nano, amorphous
Magnetic and electronic properties
Structure and dynamics
Chemical bonding
Phonon density/oxidation state

x-ray diffraction, PDF, EXAFS= Structural characterization
x-ray absorption x-ray, Raman spectroscopy= chemical bonding (sp2/sp3 bonding in C-related compounds)
Transmission X-ray Microscopy (TXM), imaging= strain analysis, volume determination
Small angle scattering= shape and distribution of porous

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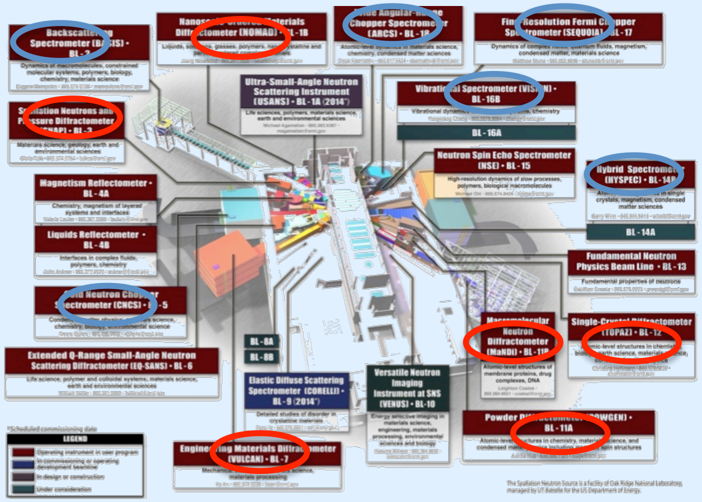
LEHIGH

EFree
Energy Frontier Research Center

Facility/Techniques Available: Spallation Neutron Source

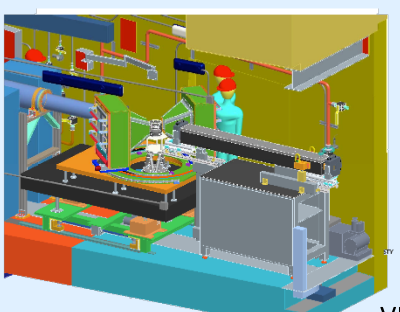


Available Instruments at SNS

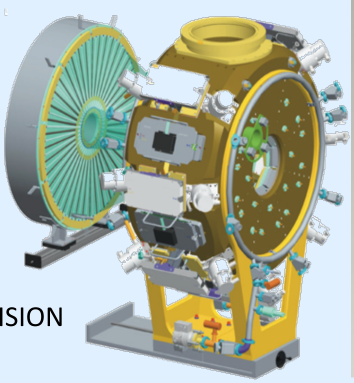
6 diffractometers and 6 spectrometers for understand materials at a large range of length, energy, and time scales under various environments: temperature, pressure, electric and magnetic field.

Structure : diffraction and PDF

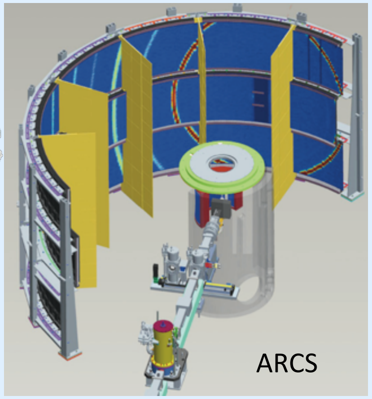
- Local and long–range order of single crystal, crystalline, and amorphous materials.
- In-situ material behavior studies during processing, synthesis. In-situ studies of working system.
- Magnetic ordering.



SNAP



VISION



ARCS

Dynamics: vibrations and diffusion

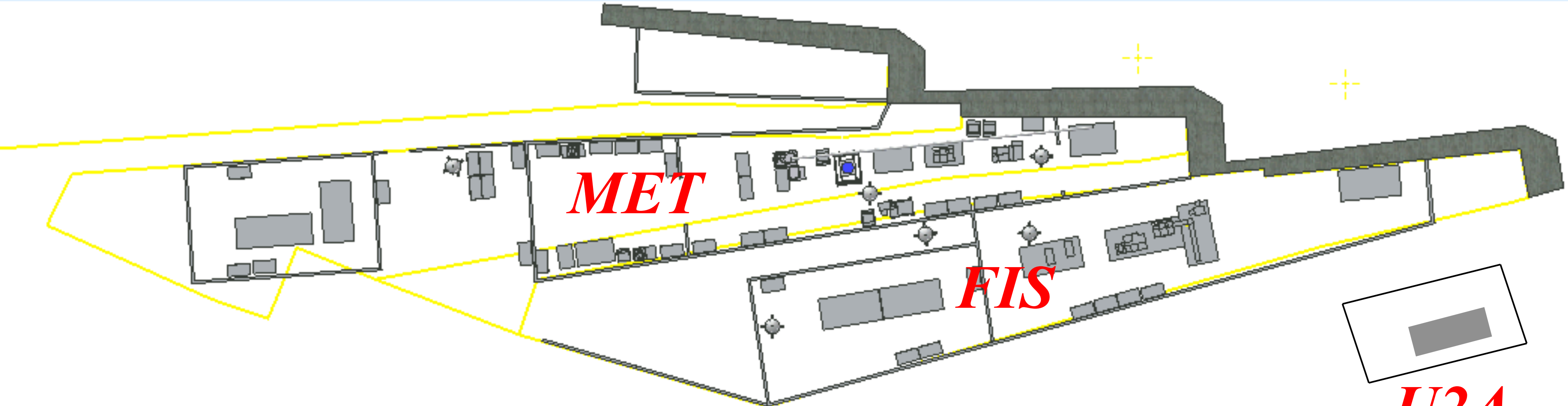
Energies from μeV~eV to understand femtosecond to nanosecond dynamical processes

- Transport properties.
- Phase transitions and structure stability.
- Thermal expansion.
- Especially effective for hydrogen.

Frontier Infrared Spectroscopy (FIS) beamline at NSLS-II

- **FIS is the successor of NSLS-U2A dedicated to optical studies at extreme conditions;**
- **The first infrared beamline to be built at NSLS-II (available late 2017);**
- **Near IR through far IR/THz spectral range with diffraction-limited performance and high S/N ratio;**
- **In situ reflectivity, absorption, Raman and fluorescence measurements at ultra-high pressure and temperature.**

Location of FIS/MET infrared beamlines at NSLS-II



Floor layout of FIS/MET infrared beamlines

Role of EFree for DOCCSS?

1. **Discovering novel materials**
   - *Recovery from high P-T*
   - *Scale up*
2. **New mesoprous materials**
   - *Expanded range of compositions*
   - *Functional structures*
2. **Center for extreme conditions science**
   - *Interactions with national lab facilities*
   - *Technique development*
3. **Synergy between theory and experiment**
   - *Collaborations with labs and industry*