CDAC

CARNEGIE / DOE ALLIANCE CENTER:
A Center of Excellence for
High Pressure Science and Technology

Russell J. Hemley

SSAA Program Symposium
Carnegie Institution
Jan. 20-22, 2010
OUTLINE

I. Overview of Center
   MOTIVATION
   TECHNIQUES
   EDUCATION, TRAINING, OUTREACH

II. Selected Science
   NEW METALS PHYSICS
   NOVEL COMPOUNDS
   LIQUIDS/AMORPH. CHEMISTRY
   LOW-Z SYSTEMS

III. Technical Developments
   INSTRUMENTATION
   FACILITIES

IV. Conclusions
Studies of extreme environments are opening up a new world of materials behavior
Understanding materials under extreme environments is central to the NNSA science mission.

1. OVERVIEW

Mission of CDAC

Develop techniques and training to examine the full complement of high P-T materials problems essential for stewardship science.
Components of the Center

**Academic Partners**
- CARNEGIE INST. (Hemley, H. K. Mao)
- UNIV. ALABAMA - BIRMINGHAM (Vohra)
- UNIV. CALIF. - BERKELEY (Wenk & Jeanloz)
- UNIV. CHICAGO (Heinz)
- UNIV. ILLINOIS (Dlott & Li)
- CALTECH (Fultz)
- PRINCETON UNIV. (Duffy)
- NEW MEXICO STATE/YALE UNIV. (Lee)
- FLORIDA INTERNATIONAL UNIV. (Saxena)
- TEXAS TECH (Ma)
- UNIV. NEVADA - RENO (Chandra)
- ARIZONA STATE UNIV. (Yarger)
- UCLA (Kavner)
- NORTHWESTERN UNIV. (Jacobsen)
- OHIO STATE UNIV. (Panero)
- WASHINGTON UNIV. ST. LOUIS (Schilling)
- UNIV. ARIZONA (Downs)
- STANFORD UNIV. (W. Mao)

**Academic Collaborators**
- FACILITY USERS

**NNSA Laboratory Partners**
- ALL HIGH P-T GROUPS AT LLNL, LANL, SNL
CDAC manages and coordinates activities at major facilities for high $P-T$ research

1. OVERVIEW

- Carnegie/Partner facilities:
  - High $P-T$ technology
  - Spectroscopy labs
  - Diffraction and microanalysis
  - Computational resources
  - CVD diamond growth

- Technique development/support for unique facilities at NNSA Labs

- Dedicated high-pressure synchrotron infrared beamline at the NSLS (U2A)
CDAC supports high $P-T$ facilities and activities at the Advanced Photon Source

1. OVERVIEW

High-Pressure Collaborative Access Team (HPCAT)
Carnegie Inst./Livermore Nat. Lab./
Univ. Nevada Las Vegas/Univ. Hawaii

**CDAC (Lab and Academic) is a 30% Member**
- 9 hutches
- 4 independently operating
- support lab

DOE NNSA/SC Partnership
CDAC supports high $P-T$ facilities and activities at the Advanced Photon Source

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DOE NNSA/SC Partnership
CDAC HIGHLIGHTS 2009: Education, training and outreach

1. OVERVIEW

- Growth of users at HPCAT (475+ to date)
- Expanded collaborations with all NNSA Labs
- CDAC supported 26 Ph.D. students
- 6 undergraduate/high school interns
- Student Winter Workshop held Feb. 2009
- Growing number of CDAC/HPCAT collaborations
  - 735 outside collaborators
  - 240 institutions
- Presentations at major national meetings
  - APS March – 23 abstracts
  - AIRAPT – 38 abstracts & presentations
  - Fall AGU – 56 abstracts & presentations (3 invited talks), including graduate session chair
CDAC HIGHLIGHTS 2009: Education, training and outreach

1. OVERVIEW

- 2009 CDAC Winter Workshop at APS Feb. 27-28, 2009

- 40 student attendees
- 46 posters presented
- 8 talks by CDAC students
- 9 talks by CDAC partners/collaborators
CDAC HIGHLIGHTS 2009:

**Education, training and outreach**

- **High Pressure Synchrotron Science Workshop, APS May 6-8, 2009**
  - 12 Scientific & Technical Sessions,
  - 10 talks by CDAC scientists

- **21st Century Needs and Challenges in Compression Science Workshop**
  - Santa Fe, Sept. 23-25, 2009

- **Advances in High Pressure Science Using Synchrotron X-rays, Oct. 4, 2008**
CDAC also support research by undergraduate and high-school summer scholars

1. OVERVIEW

2009 Carnegie Summer Scholars

N. Foley (Carleton Coll.)
Fractionation of Sulfur Isotopes in the Formation of Mars

Z. Liang (Lehigh Univ.)
Crystallization of Periodic Mesoporous Organosilicas

A. Savello (Emory Univ.)
Measurement of the Thermal Conductivity of (MgFe)SiO₃ Perovskite at High P and T

2009 High School Summer Scholars

C. Barkett (Good Counsel High School, Olney, MD)
Low-Temperature Synthesis of Fe-Bearing Solid Solutions

E. Sandford (Glenelg Country School, Ellicot City, MD)
High-Pressure Brillouin Spectroscopy of Polymers
A broad range of fundamental problems in high $P-T$ science is being investigated.

- **STRUCTURES AND PHASE RELATIONS**
- **EQUATIONS OF STATE**
- **ELASTICITY, RHEOLOGY, STRENGTH**
- **ELECTRON AND PHONON DYNAMICS**
- **TRANSPORT PROPERTIES**
- **EXTREME CONDITION CHEMISTRY**

**2009:** 129 Publications  

**SELECTED SYSTEMS**
- Metals physics
- Novel compounds
- Liquids/Amorphous Materials
- Chemistry
- Low-Z systems

**TO DATE:** 750+ Publications  
Unexpected phase behavior and complexity in ‘simple’ metals

[Gregoryanz et al., *Science* (2008)]

Sodium undergoes a metal to insulator transition at multimegabar pressures.

Synchrotron IR-Visible Reflectivity (U2A)

Reflectivity measurements and first-principles calculations indicate a sudden decrease in free electron metallic behavior across the cl16-oP* transition.


[Lazicki et al., PNAS (2009)]

[see also, Ma et al., Nature (2009)]
2. SCIENCE

Continued studies of phase transformations and \( P-V-T \) EOS of elemental metals

- *Eu is the ‘newest’ elemental superconductor*

  - High strength and incompressibility

- *\( P-V-T \) EOS of interest for metals systematics*

\[ \text{Os} \]

\[ \text{BCC} \]

\[ \text{HCP} \]

\[ \text{orthorhombic (Pmna)} \]

\[ \text{Pmna + P2_1/c} \]

\[ \text{monoclinic (P2_1/c)} \]

W. Bi (CDAC graduate student, Washington Univ.)

Matt Armentrout (CDAC graduate student, UCLA)
Twinning is a significant deformation mechanism in hexagonal metals at high pressure.

DAC in radial diffraction geometry to impose stress and pressure on pure osmium and zinc, inducing elastic and plastic deformations. The two hcp metals behave very differently.

Os at 24 GPa (2.0 m.r.d.)

Zn at 34 GPa (3.1 m.r.d.)

W. Kanitpanyacharoen
P. Kaecher, CDAC graduate students (UC Berkeley)
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The visco-plastic self-consistent (VPSC) polycrystal model is used to provide insight into which slip systems and twinning modes are active under a given set of conditions.

W. Kanitpanyacharoen
P. Kaecher, CDAC graduate students (UC Berkeley)

Carnegie/DOE Alliance Center
Lattice dynamics of iron is directly measured at extreme $P-T$ by inelastic x-ray scattering (IXS)
Lattice dynamics of iron is directly measured at extreme $P-T$ by inelastic x-ray scattering (IXS).

**HERIXS on Hot Dense Fe**

High energy resonant IXS (resolution of ~2 meV and beamsize of 25 μm at XOR3, LA phonon dispersions of hcp-Fe. HT has a strong effect on the Vp.

**NRIXS on Textured hcp-Fe**

Nuclear Resonant IXS

Vs is 4.1 % faster along the c relative to a axis giving elastic, vibrational, and thermodynamic parameters.

Hcp-Fe in cubic BN/Be gasket

**Phonon Density of States**

Z. Mao, J. F. Lin, G. Xu, A. Alatas, Compressional wave velocity of hcp-Fe at high pressures and temperatures, in prep., 2010.


**System setup at XOR3, APS**

**Phonon Dispersions**

46GPa/700K
Pressure-induced Invar effect has been discovered in Pd$_3$Fe

- It is possible to tune Invar behavior with pressure, rather than composition.
- The electronic structure at the Invar transition is the same for either composition-tuned or pressure-tuned Invar.
Infrared reflectivity of studies of pressure-induced insulator-metal transitions

Reflectivity of the diamond-GaP interface at high pressure. The main peak in the spectrum is due to the TO phonon mode which shifts to higher wavenumber and decreases in intensity as pressure is increased. The disappearance of the phonon mode and sharp rise in the magnitude of the reflectivity are associated with the metallization of GaP at 20 GPa.

Far IR of FeO under pressure
[Seagle et al., Phys. Rev. B (2009)]
Structural and magnetic phase transitions in NdCoAsO

- Iron-based layered compound SmFeAsO$_{1-x}$F$_x$ is known to exhibit superconductivity at 55 K
- NdCoAsO is isostructural to layered superconductors

Designer diamond anvil for electrical studies at high pressures and low temperatures
Structural and magnetic phase transitions in NdCoAsO

- Iron-based layered compound SmFeAsO\textsubscript{1-x}F\textsubscript{x} is known to exhibit superconductivity at 55 K
- NdCoAsO is isostructural to layered superconductors
- Magnetic ordering and superconducting transitions are detected by four probe electrical resistance measurements

W. Uhoya (CDAC grad. student, UAB)

Designer diamond anvil for electrical studies at high pressures and low temperatures

Material shows anti-ferromagnetic behavior to 53 GPa
EOS, phase transitions, and ‘polyamorphism’ of liquids and amorphous solids

Brillouin spectroscopy, ultrasonic, and diffraction techniques

Brillouin spectra of soda-lime glass powder at ambient conditions ($P = 0$ GPa, $T = 290$ K) in back-scatter (top and bottom spectra: $\theta = 180^\circ$) and reflection geometries (middle two spectra: $\theta' = 110^\circ$),

Measured DAC EOS for amorphous red phosphorus. The three sets of symbols represent separate runs. The compression data is in black and the decompression data is in red. Inset:

A Gleason (CDAC grad. student, UC Berkeley)

E. Oelker (CDAC graduate student, ASU)
Surface chemistry and spectroscopy under extreme conditions

Sum Frequency Generation (SFG)

Raman spectrum of benzenethiol monolayer on photonic substrate in the DAC at 10.2 GPa.

SFG spectra of HMX of surface nitro groups in two polarization conditions (SFG, vis, IR) as the crystal is rotated. Spectra such as these should determine the orientation of surface nitro groups.

A. Lozano
(CDAC grad. student (UIUC)

K. Brown
(CDAC grad. student (UIUC)
There are new findings in high-pressure strength and toughness

Hardness from EOS of ZrO$_2$

\[ H(\text{OII}) < H(\text{MI}) < H(\text{OI}) \]
\[ G(\text{OII}) < G(\text{MI}) < G(\text{OI}) \]
\[ K(\text{OII}) > K(\text{OI}) > K(\text{MI}) \]

For all phases, \( H \approx 10 \text{ GPa} \)

Y. Al-Khatatbeh
(CDAC Grad. student, NMSU)

Understanding the behavior of hydrogen in materials under pressure is fundamental.

Be(OH)$_2$

Polyhedral image of the six-membered ring of silicate tetrahedra in cristobalite

Xe(H$_2$)$_7$

Equivalent ring of Be(OH)$_4$ tetrahedra in behoite

- Novel dimer structure
- Highest mole percent hydrogen
- Pressure-induced covalency

Madison Barkley (CDAC grad. student, Univ. Arizona)

[Somayazulu et al., *Nature Chem.* (2009)]
Novel intermolecular interactions in high-pressure van der Waals compounds

- SiH$_4$ is a metal/superconductor at 100 GPa
- Discovery of SiH$_4$(H$_2$)$_2$
Novel intermolecular interactions in high-pressure van der Waals compounds

- SiH₄ is a metal/superconductor at 100 GPa
- Discovery of SiH₄(H₂)₂

**Tim Strobel**
(postdoctoral fellow, Carnegie)

- Intramolecular H-H bond weakens significantly
- Pathway for dissociation/metallization of H₂

[Strobel et al., *Phys. Rev. Lett.* (2009)]
New high $P-T$ Raman measurements constrain the phase diagram of hydrogen

- Melting behavior studied to 110 GPa from observation of vibron discontinuity
- Possibility of a high temperature solid-solid transition above 110 GPa?
3. NEW TECHNIQUES

CDAC
Cdac

gigahertz-ultrasonic interferometry
elastic properties of superhard materials

3. NEW TECHNIQUES

Y. Chang
(CDAC grad.
student,
Northwestern)

Application to CVD diamond:
benchmark for elasticity studies

Acoustic wavelengths are <20μm at GHz-frequencies. Accurate $C_{ij}$ can be obtained on transparent or opaque single-crystal and glassy materials as thin as 20μm, as well as at high P-T inside diamond-anvil cells for application to equations of state.
CVD single crystal diamond for a new generation of anvils

[Meng et al., PNAS (2008)]
Major upgrade of the U2A beamline for spectroscopic studies under extreme conditions

3. NEW TECHNIQUES

Major Beamline Upgrades

- New capability: far-IR reflection
- Routine high pressure experiments in the range of 10-1000 K
- Extended side station to achieve ideal performance in terms of diffraction limited resolution
- Path to NSLS II
Many new tools are coming on line at HPCAT and HPSynC

- **Nano imaging (TXM), diffraction**
- **Coherent diffraction imaging (CDI)**
- **High energy scattering (PDF)**
- **High energy resolution:**
- **HERIX and MERIX**
- **Time resolved: shock wave, XPCS**
- **Magnetic circular dichroism (XMCD)**

Spin transition of Fe$_3$O$_4$ discovered by XMCD technique
[Ding et al, Phys. Rev. Lett (2009)]

Coherent diffraction imaging
3D reconstruction from a single crystal of Au at 6 GPa

[Yang et al, to be published]

Phase reconstruction

Magnitude reconstruction

3d full field imaging (TXM)
30 nm spatial resolution
[Ding et al, to be published]

Tin_TXM_tomo.mpg
Using nanoscopes and nanobeams to measure anvil strains to maximize pressure

30 nm resolution radiography

[Xradia nanoscope

Nanodiffraction (< 200 nm beams) mulitimegabar pressures measures the pressure gradient

[Wang et al. PNAS (2010)]
A new generation of large facilities are coming on line

### X-ray Sources
- Higher brightness synch.
- Dynamic compression
- Energy Recovery Linacs
- Fourth Gen. Sources (LCLS).

### Neutron Sources
- Dedicated beamlines
- >100 GPa neutron scattering

### Pulsed Power
- Ultrahigh P-T conditions
- Larger samples
- Static/dynamic

### Laser Sources
- Still higher P-T conditions
- New diagnostics
- Static/dynamic
GRAND CHALLENGES

- New inelastic scattering in new domains
- Time dependent (<ps-scale) diffraction/imaging
- Heterogeneous/complex assemblages: nm-diffraction
- Interfaces/grain boundaries
- New domains of P-T-t

- Ultrahigh P-T conditions
- Larger samples
- Static/dynamic
- Still higher P-T conditions
- New diagnostics
- Static/dynamic
CDAC is supporting studies with ultrastrong shocks and isentropic compression techniques

- Hydrogen and helium at TPa pressures
- Fast ramp wave loading
- Chemistry at ultraextreme conditions
- Rigidity and plasticity
- Going beyond the EOS
- Wave-velocities in super-giant planets
- Rigidity of material properties
- Gigabar pressures
- Support of ICF

3. NEW TECHNIQUES

- Combined static/dynamic compression
- Ultra-fast diagnostics

NIF Planetary Interiors Science Team
CONCLUSIONS AND OUTLOOK

1. Education and Training
   - Expanded student program with increased partners
   - High-pressure summer school/workshops
   - Continued increase in number of CDAC collaborators

2. Science Program
   - Growing number of publications
   - Novel phenomena over a broad range of extreme conditions
   - Many new opportunities, including time resolved methods

3. Technique Development
   - New x-ray techniques (<100 nm beams, time-resolved)
   - New developments in neutron methods
   - Continued need for high $P$-$T$ device developments
   - Many new opportunities for combined static/dynamic compression
Improved measurements of stress and strain at multimegabar pressures

Measurements of differential stress in a platinum sample for various pressure media.

3D reconstruction of coherent diffraction from a single crystal of Au at 6 GPa

Magnitude reconstruction

Phase reconstruction

[Yang et al, to be published]
There have been major technical advances at HPCAT/HPSynC

3. NEW TECHNIQUES

A second undulator installed to enhance brightness

New diamond anvil cell techniques

17-element analyzer array commissioned in June 2009

Microfocused X-Ray Diffraction Symmetric DAC in gearbox assembly