

# LA-UR-13-21887

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Title: High-Pressure research of energy and environmental materials: In-situ synchrotron/ Neutron diffraction study

Author(s): Yu, Xiaohui

Intended for: Job interviews



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# **High-Pressure research of energy and environmental materials:**

## **In-situ synchrotron/ Neutron diffraction study**

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**[yuxh-jl@hotmail.com](mailto:yuxh-jl@hotmail.com)**

***March 20th, 2013***

- **Outline:**

- **1) High pressure background and technique**

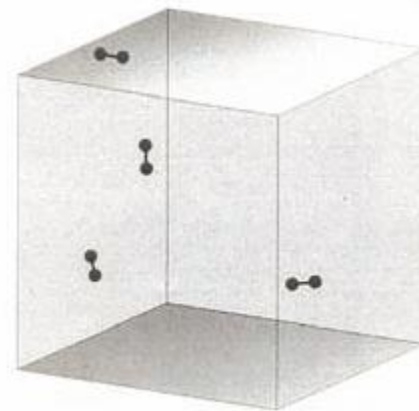
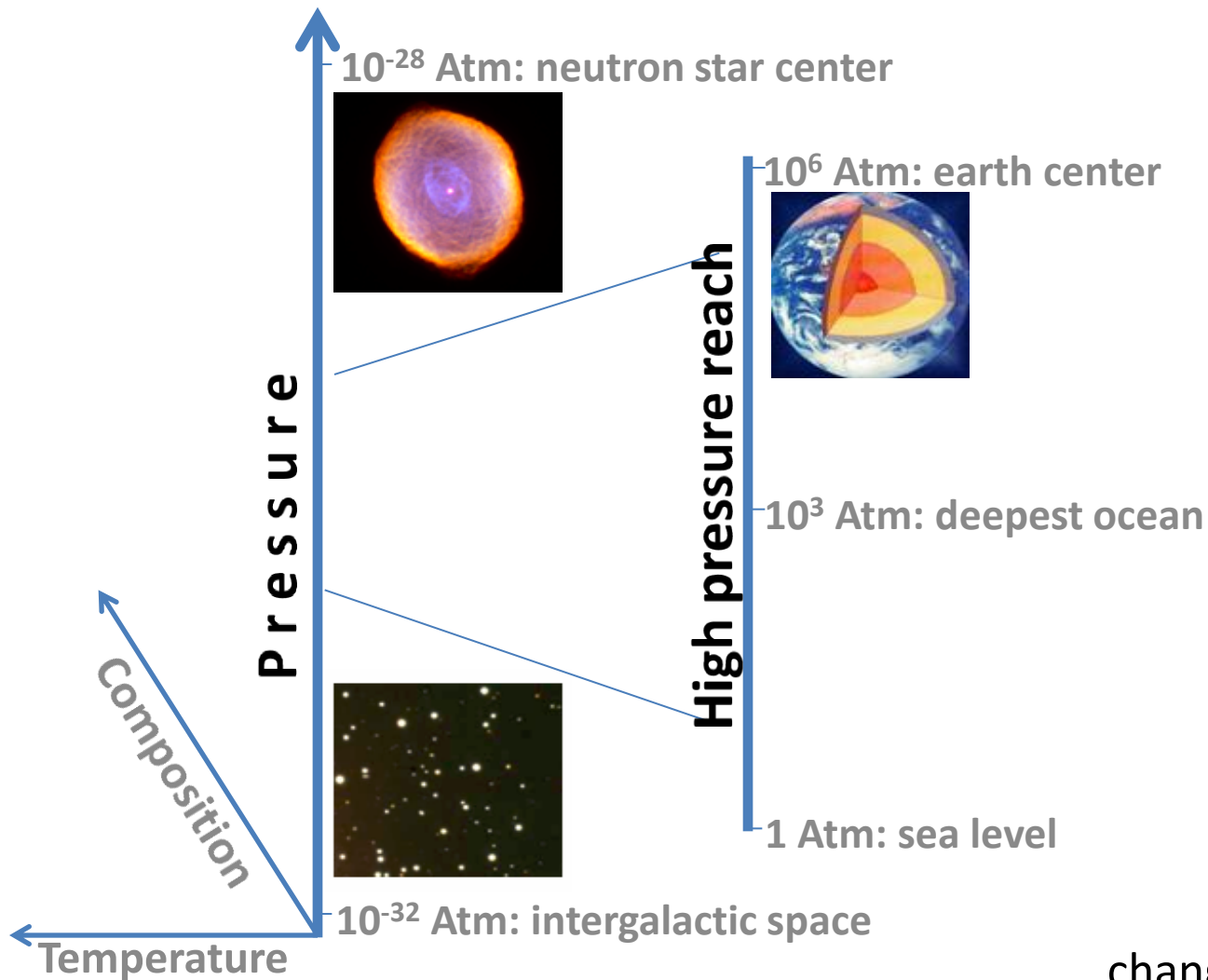
- **2) In-situ high pressure neutron diffraction study of Clathrate (gas cell): CO<sub>2</sub>-CH<sub>4</sub> (SI); CO (SII); Ne (ice-II).**

- **3) Nano mechanics under tri-axial (dia press) and uni-axial (deformation dia press) deformation: Nano Fe, Co, Ni.**

- **4) High pressure mechanics: omega phase Zr, diamond, Nitride (WN<sub>x</sub>, CrN).**

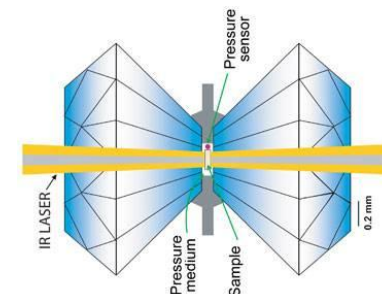
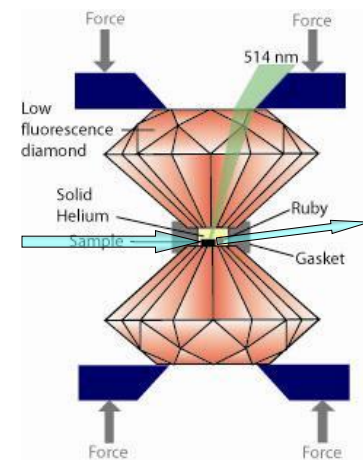
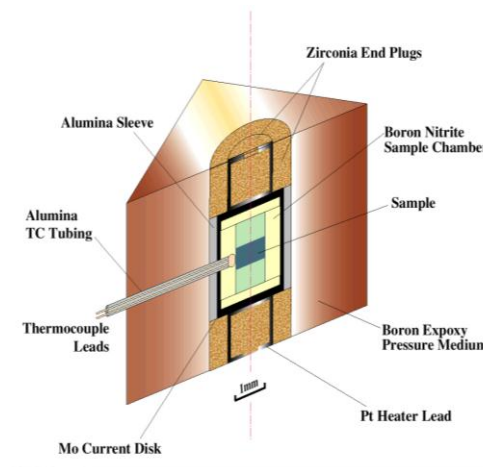
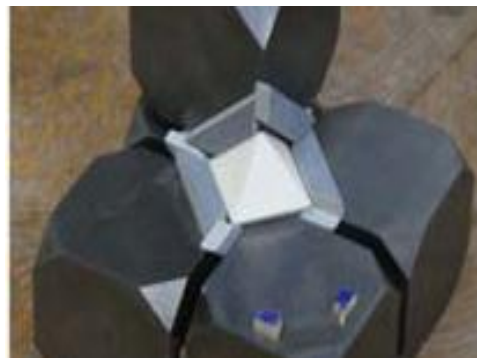
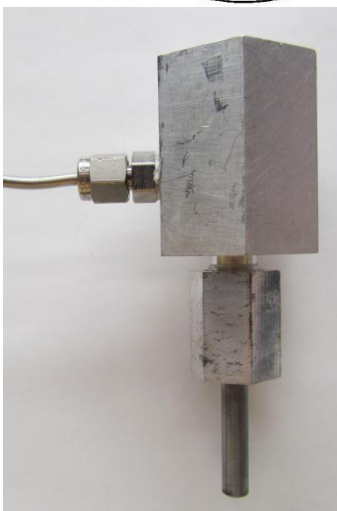
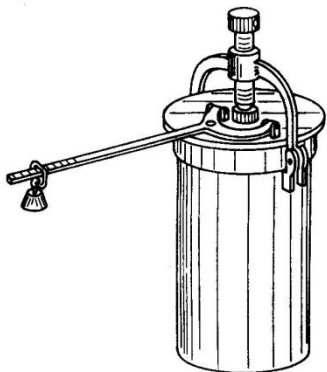
- **5) Acknowledgment**

# Pressure in Universe: 64 order



Pressure:  
change the distance of atoms

# High pressure technique



- **Gas cell**

~1 GPa

- **Muti Anvil Compression**

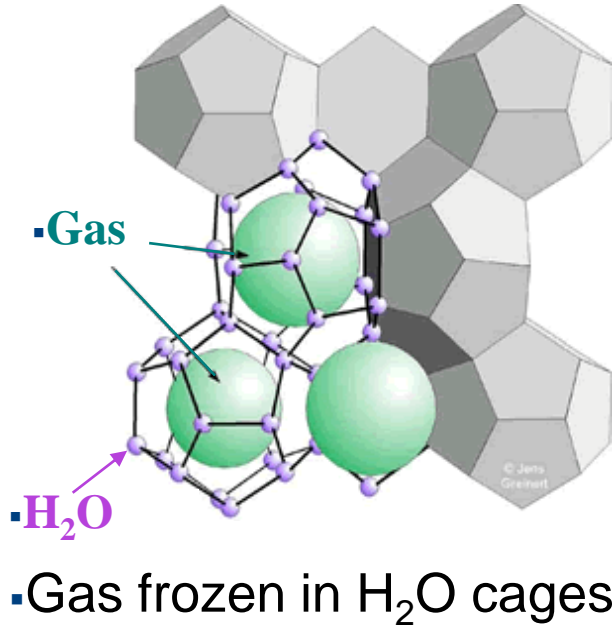
~20 GPa

- **Diamond Anvil cell**

~100 GPa

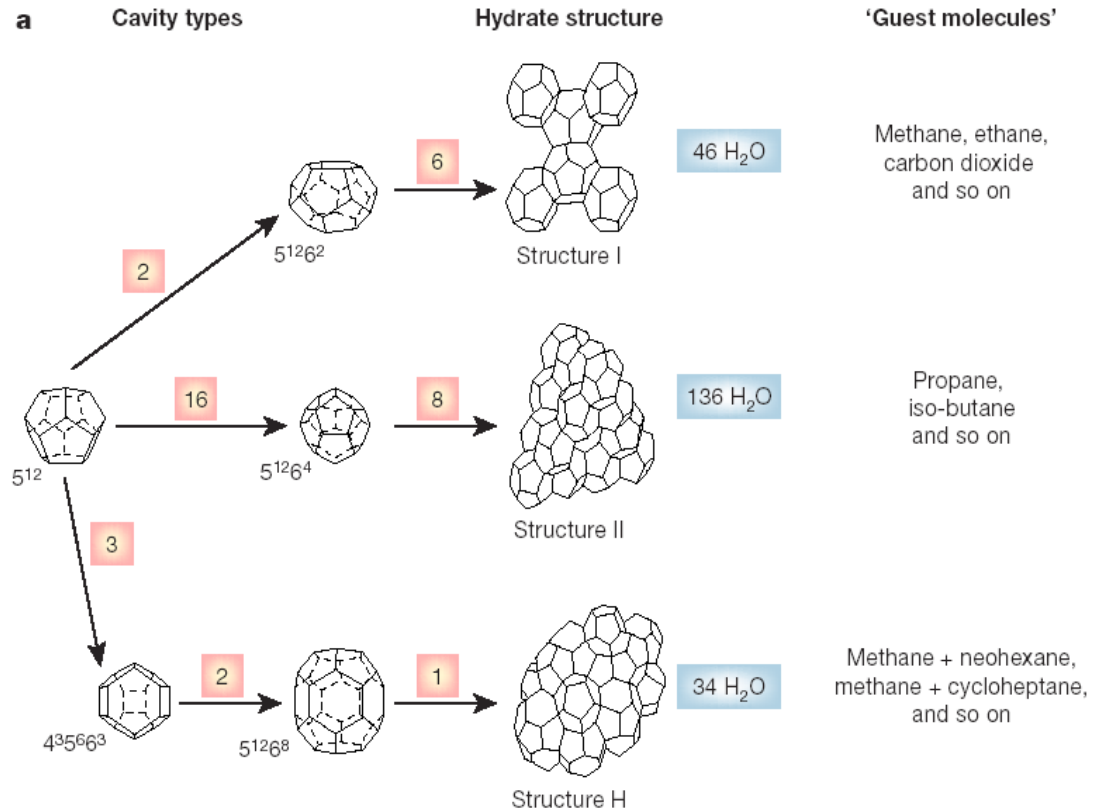
Pressure increased, sample size decreased, gas cell is more related to our environment

# Clathrate Hydrate: study with pressure gas cell



Methane hydrate

SI



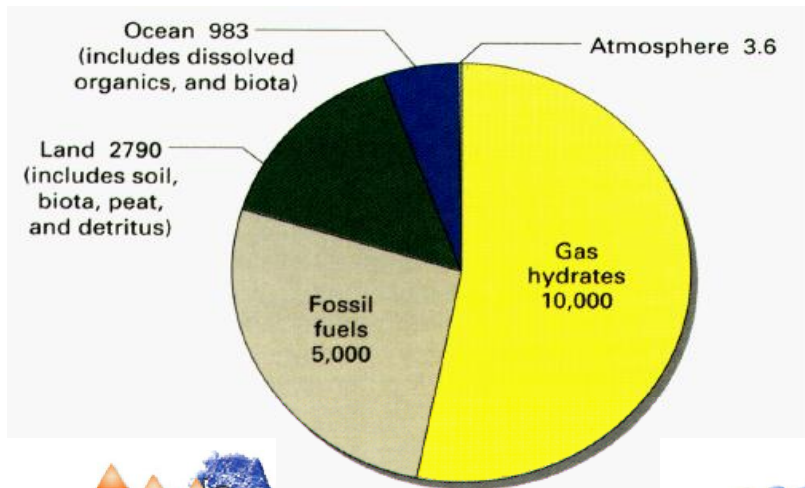
**b**

Hydrate crystal structure	I		II		H		
	Small	Large	Small	Large	Small	Medium	Large
Cavity							
Description	$5^{12}$	$5^{12}6^2$	$5^{12}$	$5^{12}6^4$	$5^{12}$	$4^35^66^3$	$5^{12}6^8$
Number of cavities per unit cell	2	6	16	8	3	2	1
Average cavity radius (Å)	3.95	4.33	3.91	4.73	3.91 <sup>†</sup>	4.06 <sup>†</sup>	5.71 <sup>†</sup>
Coordination number*	20	24	20	28	20	20	36
Number of waters per unit cell	46		136		34		

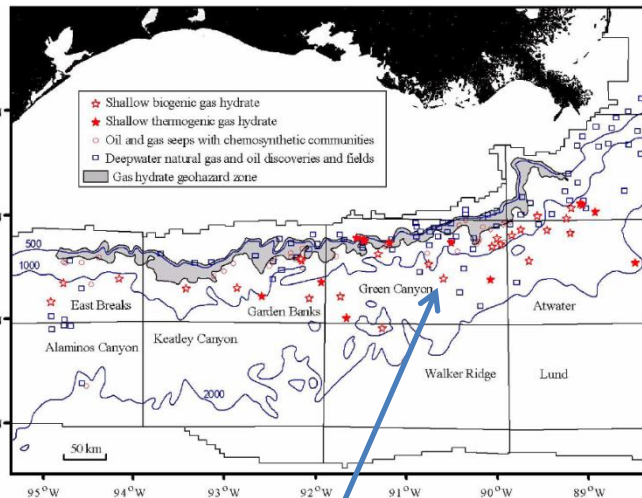
\*Number of oxygens at the periphery of each cavity.

<sup>†</sup>Estimates of structure H cavities from geometric models.

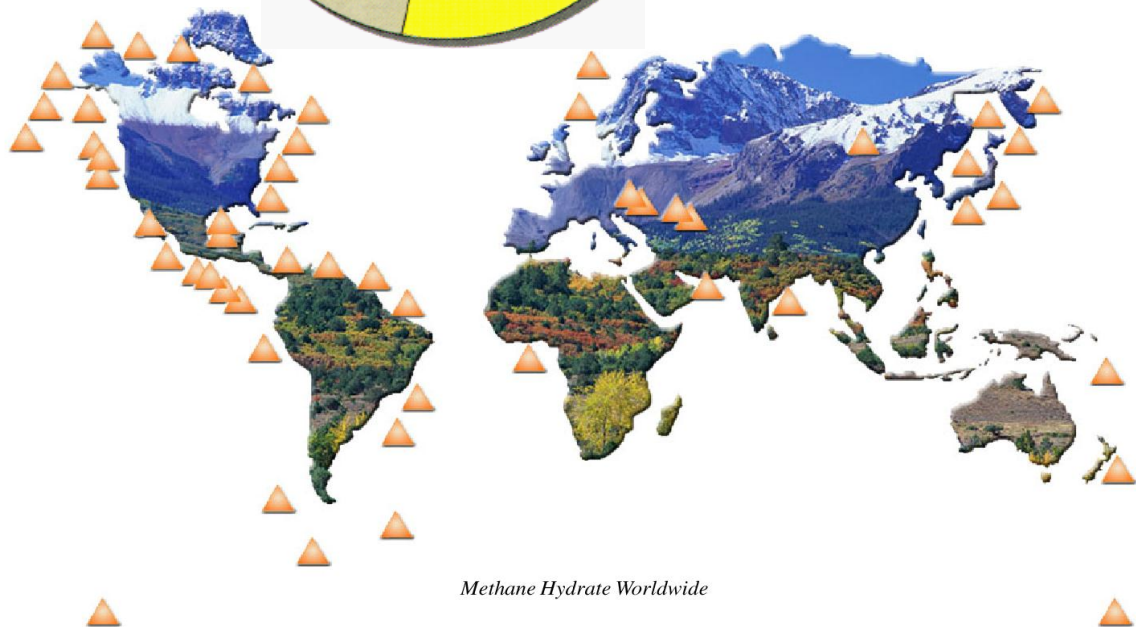
# Clathrate Hydrate: nature gas hydrate



Nature gas hydrate exist worldwide in delicate equilibrium

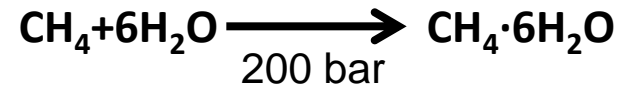
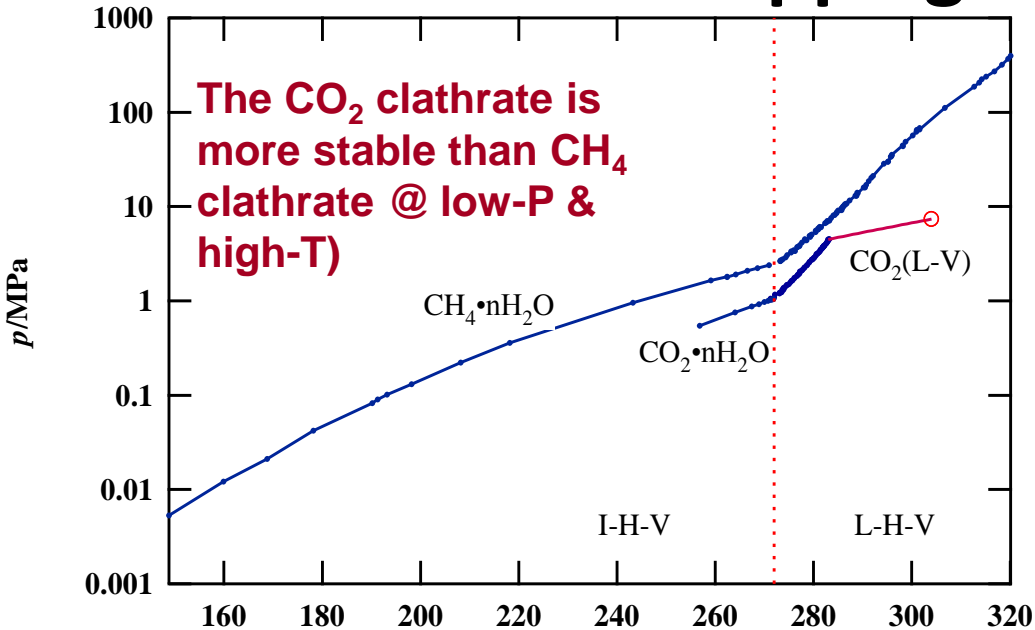


Geohazard: the distribution of clathrate hydrate at Mexico Gulf



rig explosion at Mexico Gulf caused by decomposition of nature gas hydrate

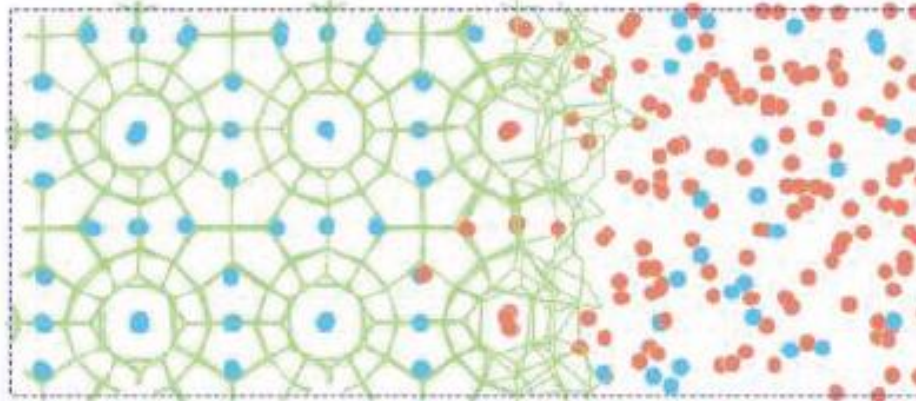
# Swapping CH<sub>4</sub> by CO<sub>2</sub>



Clathrate Hydrate synthesis at Lujan center:

Methane hydrate synthesis:

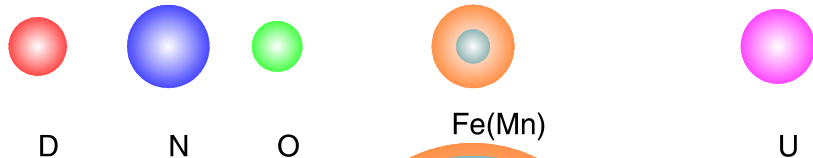
- 1) 270-290K cycling 48h (pure)
- 2) 270K 1 week. (with ice)



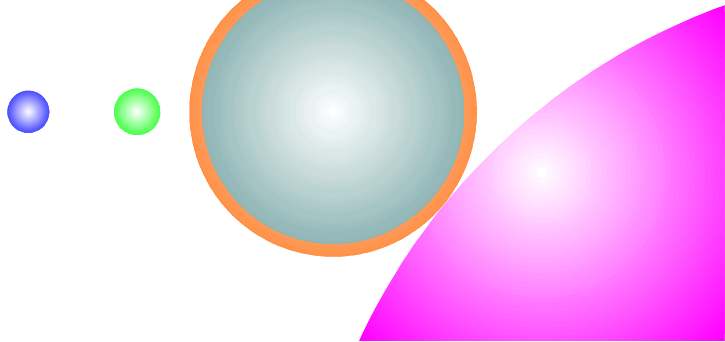
Molecular dynamics simulations show that the replacement can take place without melting of the network of hydrogen-bonded water molecules

# Swapping CH<sub>4</sub> by CO<sub>2</sub>: neutron diffraction

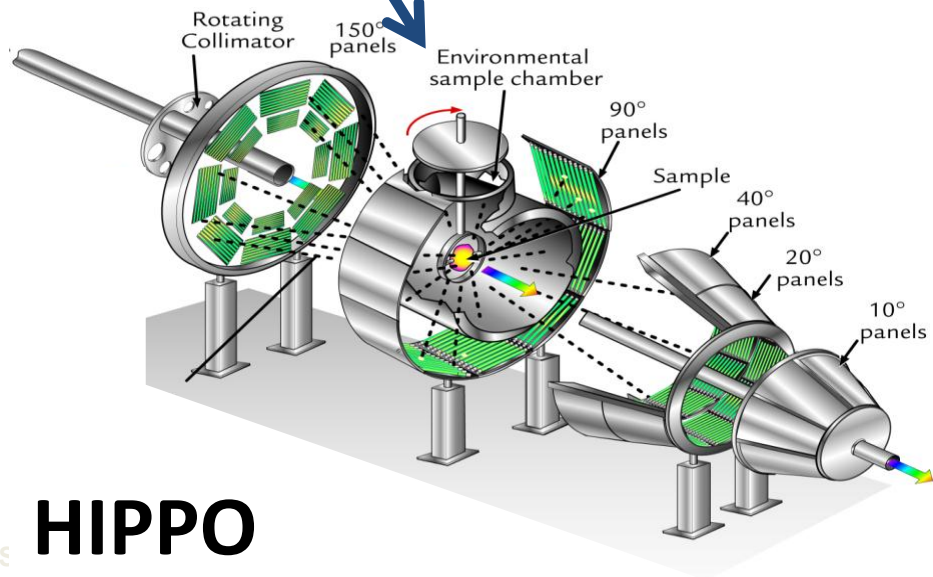
Neutron



X-ray

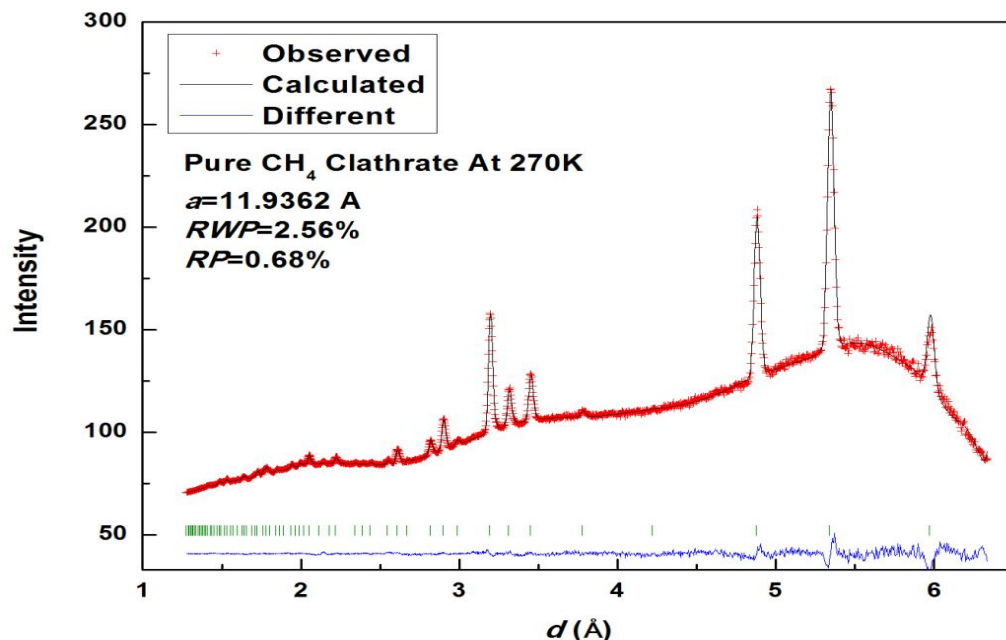


“equal” scattering for light (D, B, C, ...) and heavy (Ta, U, Pu, ...) elements



## HIPPO

# Swapping CH<sub>4</sub> by CO<sub>2</sub>

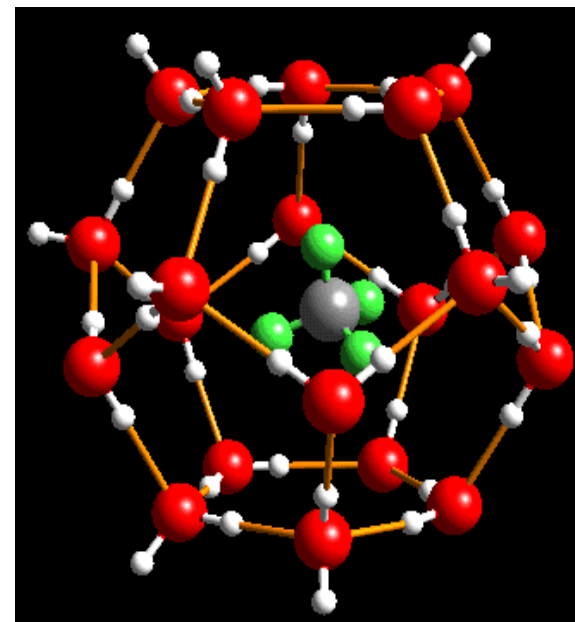


Pure Methane hydrate (SI, cubic) synthesis: 200 Bar.

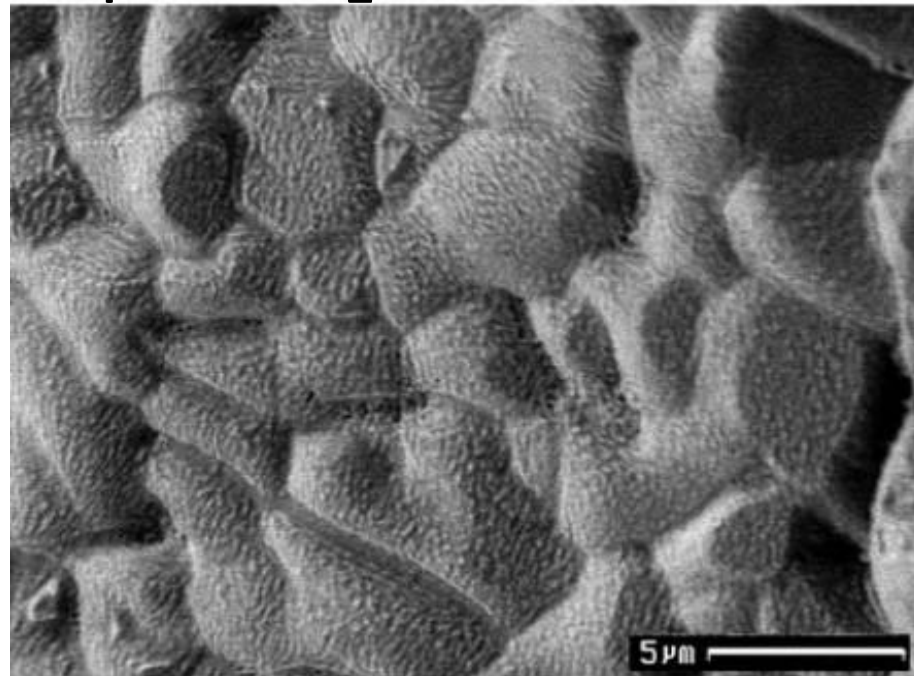
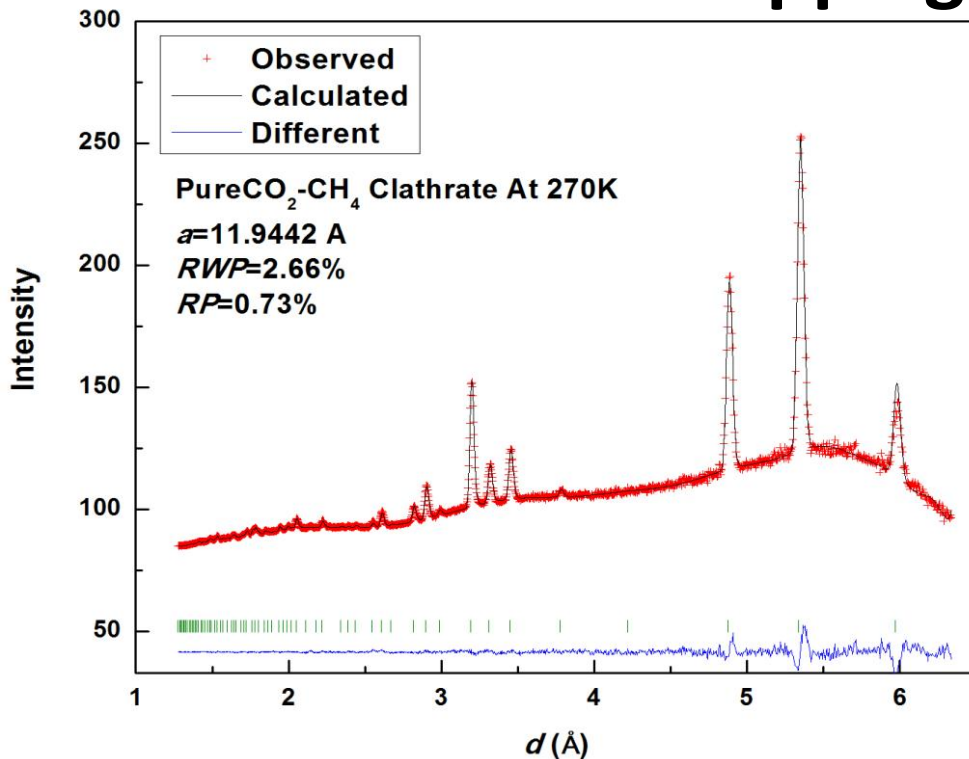
270-290 cycling 48h.

Both the small cage and the big cage was filled with CH<sub>4</sub>

Atom type	Coordinates of equivalent positions: (000; 0 ½ ½; ½0½; ½½0)+			Occupancy
	x	y	z	
O(1)	0	0.5	0.25	1.00
O(2)	0.1759	0.1759	0.1759	1.00
O(3)	0	-0.3162	0.1068	1.00
D(1)	0.2308	0.2308	0.2308	0.50
D(2)	0	0.4320	0.2046	0.50
D(3)	0	0.3800	0.1677	0.50
D(4)	0	0.3120	0.0565	0.50
D(5)	0.0605	0.2464	0.1428	0.50
D(6)	0.1244	0.2322	0.1329	0.50
C(S)*	0	0	0	1.00
C(L) <sup>-</sup>	0	0.2500	0.5000	1.00



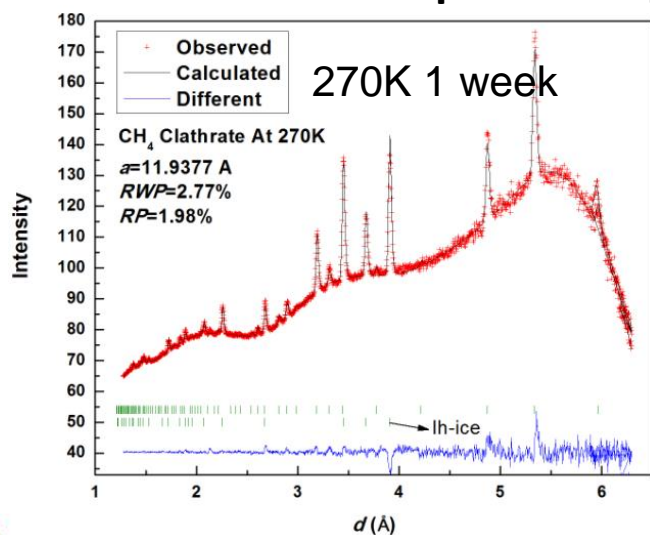
# Swapping CH<sub>4</sub> by CO<sub>2</sub>



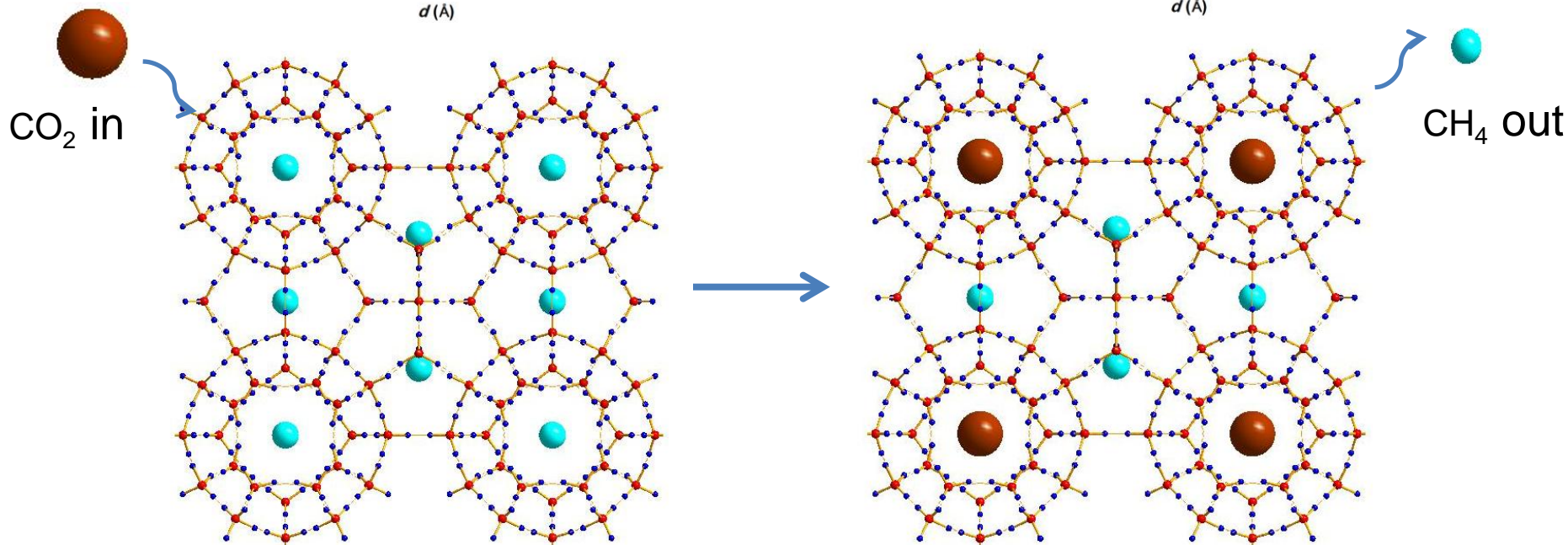
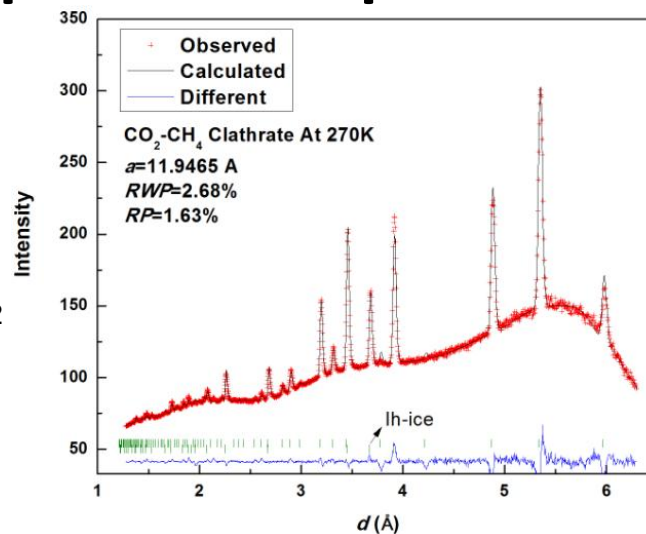
Stern, L. A. *American Mineralogist*, 89, 1162 (2004)

- 1) The swapping experiment condition: 35 bar CO<sub>2</sub>, 270K, 48h;
- 2) Background reduction because of the release of CH<sub>4</sub> in pressure cell;
- 3) Cell parameter enlarged because of the pressure drop;
- 4) <3% CH<sub>4</sub> replaced, Methane hydrate in bulk form, kinetics too slow.

# Swapping CH<sub>4</sub> by CO<sub>2</sub>: From powder ice precursor



270K  
 35 bar CO<sub>2</sub>



~50% CH<sub>4</sub> was replaced by CO<sub>2</sub>, most from big cage, small cage intact. (Helping gas N<sub>2</sub> next step).

# SII structure CO hydrate: Motivations



Molecular size: N<sub>2</sub> < CO < O<sub>2</sub>

However: N<sub>2</sub> (SII), O<sub>2</sub> (SII)

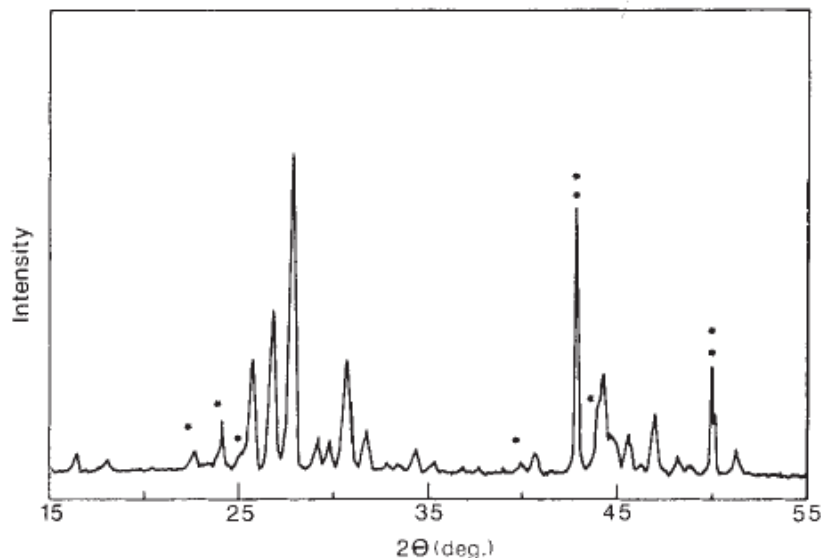
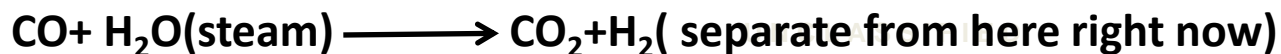


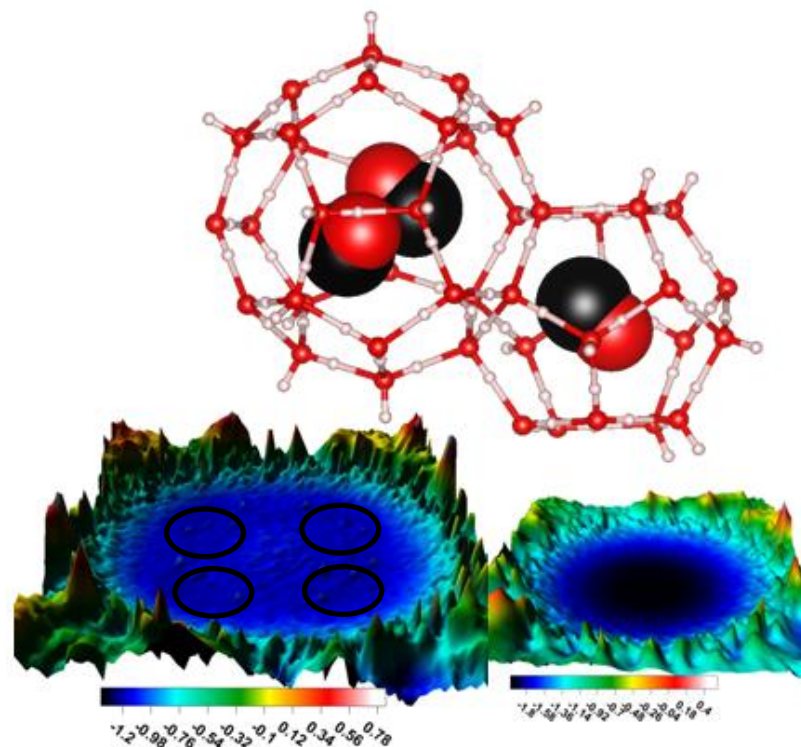
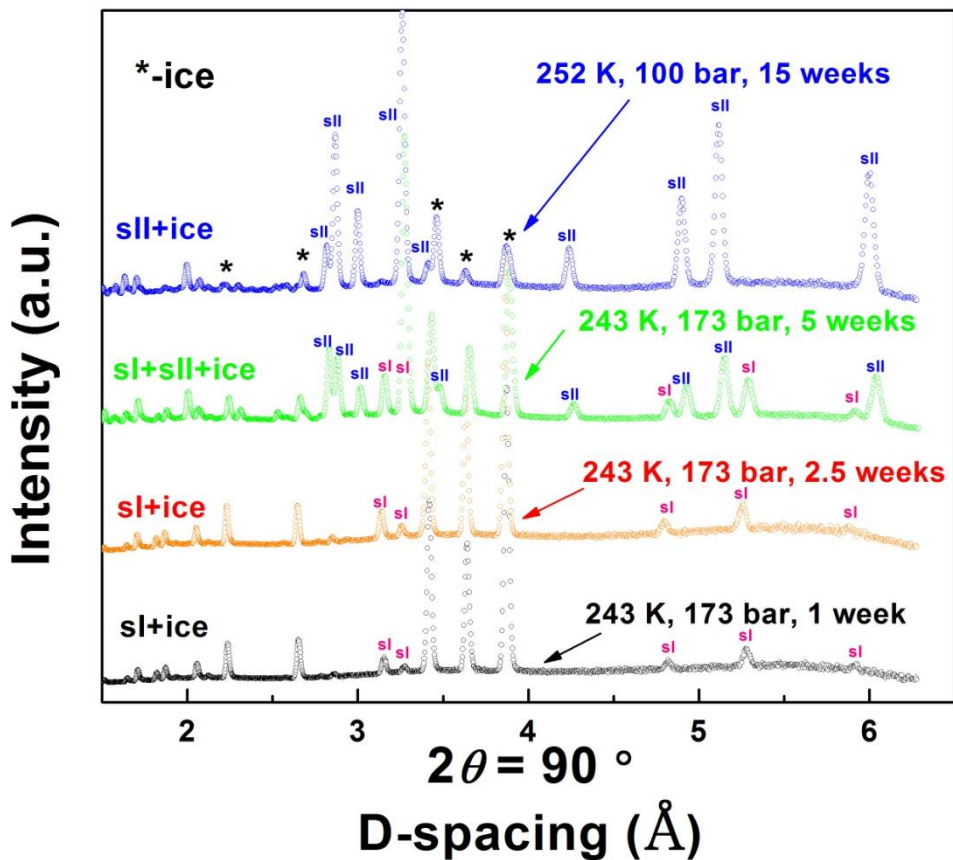
Fig. 2 X-ray powder diffraction pattern of carbon monoxide hydrate. Starred lines are due to ice Ih, double starred lines are due to the sample holder.

Davidson, D. W. et al, Nature 328,418 (1987)

CO hydrate form SI structure clathrate!?



# SII structure CO hydrate: Neutron diffraction



MD simulations:

$$\Delta E = E((\text{CO})_m - (\text{H}_2\text{O})_n) - E((\text{H}_2\text{O})_n) - m \times E(\text{CO})$$

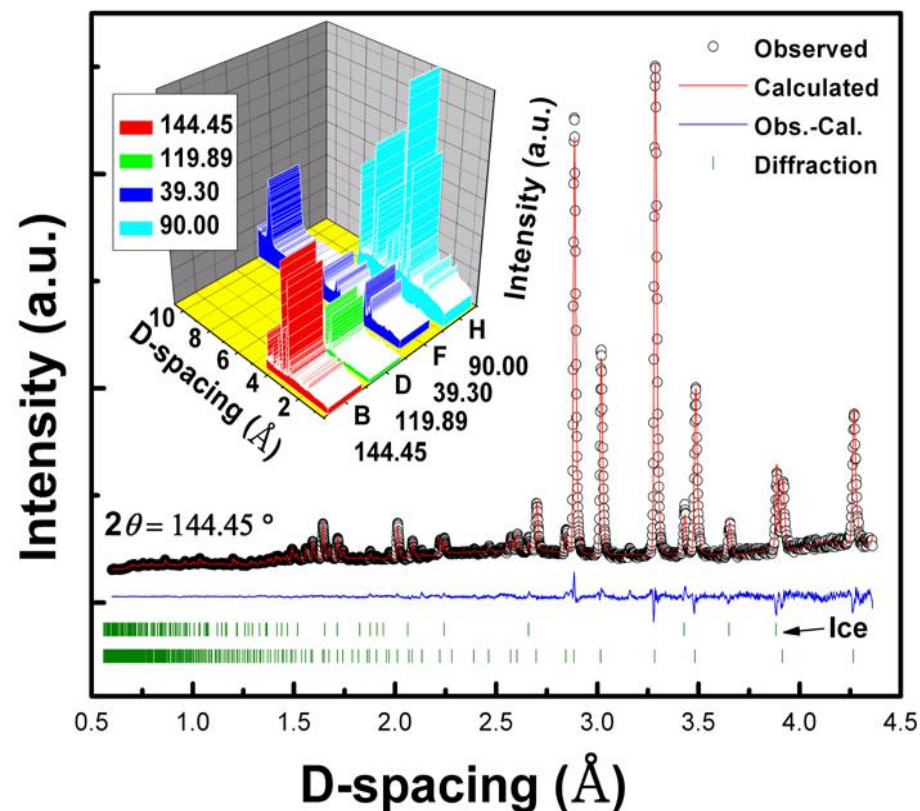
CO interact with all surrounding  $\text{H}_2\text{O}$ , no special point

1 CO in the center of  $5^{12}$ , 0.5  $\text{\AA}$  off.

2 CO in  $5^{12}6^4$  cage is more stable than 1 CO

The CO hydrate formed gradually from (Sl+ice) to (Sl+Sll+ice) to (Sll+ice).

# SII structure CO hydrate: structure refinement



Atom type	Coordinates of equivalent positions: (000; 0 ½ ½; ½0½; ½½0)+			Occupancy
	x	y	z	
O(1)	-0.125000	-0.125000	-0.125000	1.00
O(2)	-0.217562	-0.217562	-0.217562	1.00
O(3)	-0.182699	-0.182699	-0.369759	1.00
D(1)	-0.157596	-0.157596	-0.157596	0.50
D(2)	-0.185507	-0.185507	-0.185507	0.50
D(3)	-0.195966	-0.195966	-0.315926	0.50
D(4)	-0.203384	-0.203384	-0.272634	0.50
D(5)	-0.142002	-0.142002	-0.371704	0.50
D(6)	-0.088553	-0.228918	0.146786	0.50
O(S)*	0.024985	-0.012822	-0.012822	0.1667
C(S)*	-0.030239	-0.005751	-0.005751	0.1667
O(L) <sup>-</sup>	0.304209	0.348103	0.348103	0.1667
C(L) <sup>-</sup>	0.324843	0.401434	0.324843	0.1667

Rietveld refinement of diffraction pattern of All diffraction bank at HIPPO.

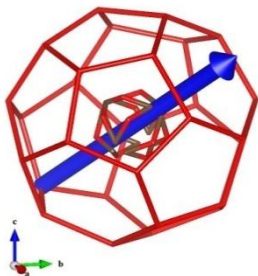
Rwp=2.8%, RP=1.6%

1 CO in small cage and 2 CO in big cage.

The first atoms positions of CO hydrate from experiment.

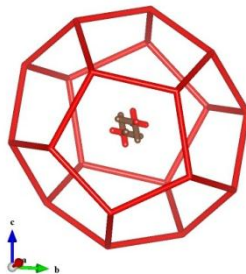
# SII structure CO hydrate: structure refinement

$5^{12}6^4$  cage

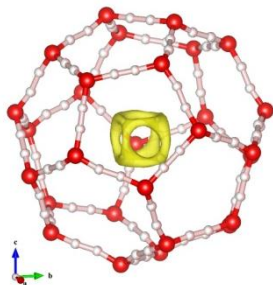


In big cage (left) C (Brown) atoms point toward the 4 hexagons and O (red) atoms point toward the 4 co-vertexes of the three pentagons.

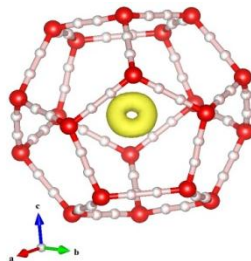
$5^{12}$  cage



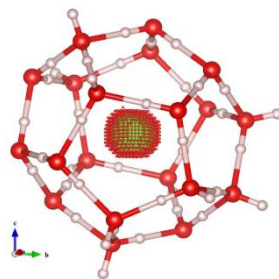
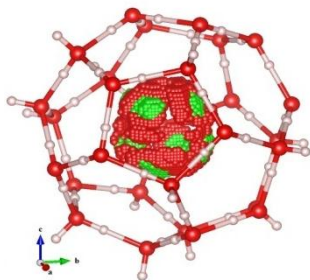
**(a) Retiveld refinement**



In small cage (right), carbon positions forming a donut shape ring lie in between the oxygen positions

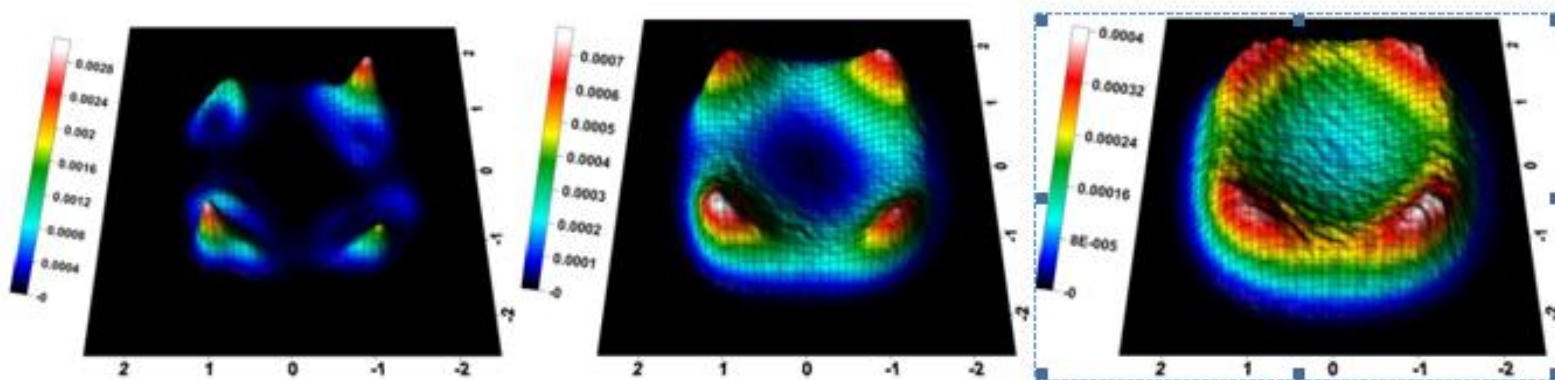


**(b) MEM analysis**

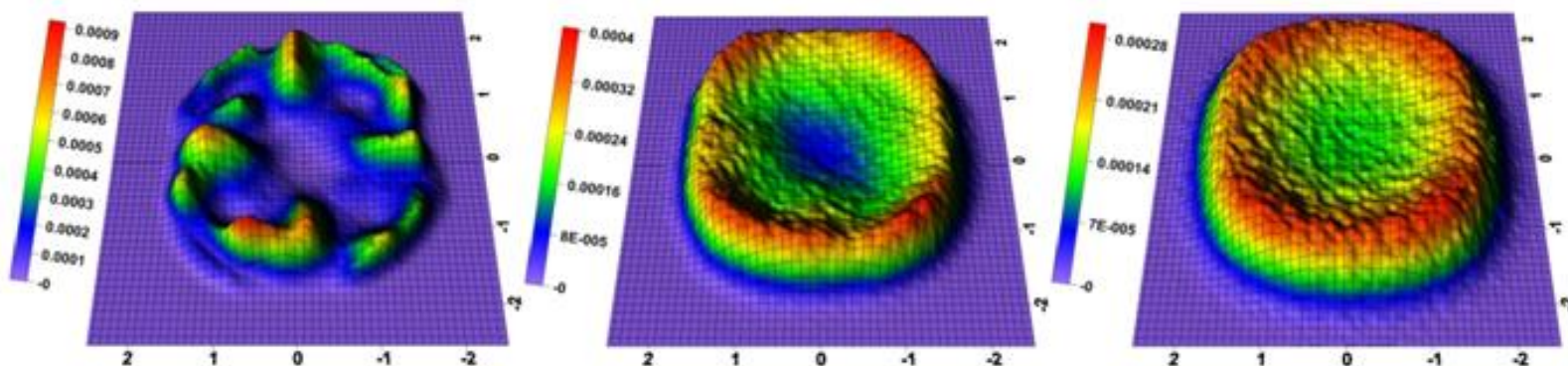


**(c) MD calculation**

# CO molecule density distribution, MD simulation



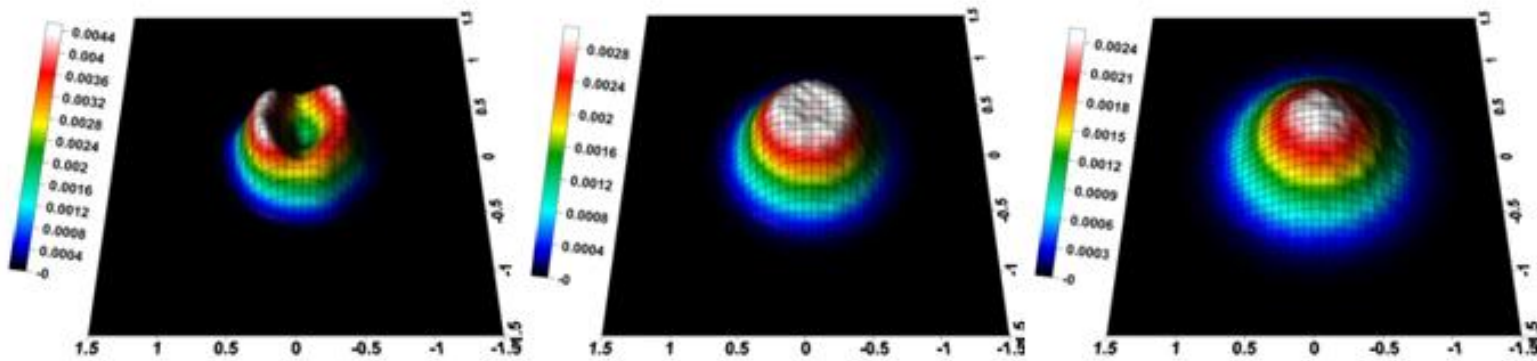
C of CO in  $5^{12}6^4$  cage Left to right: 25 K, 100 K, 260 K



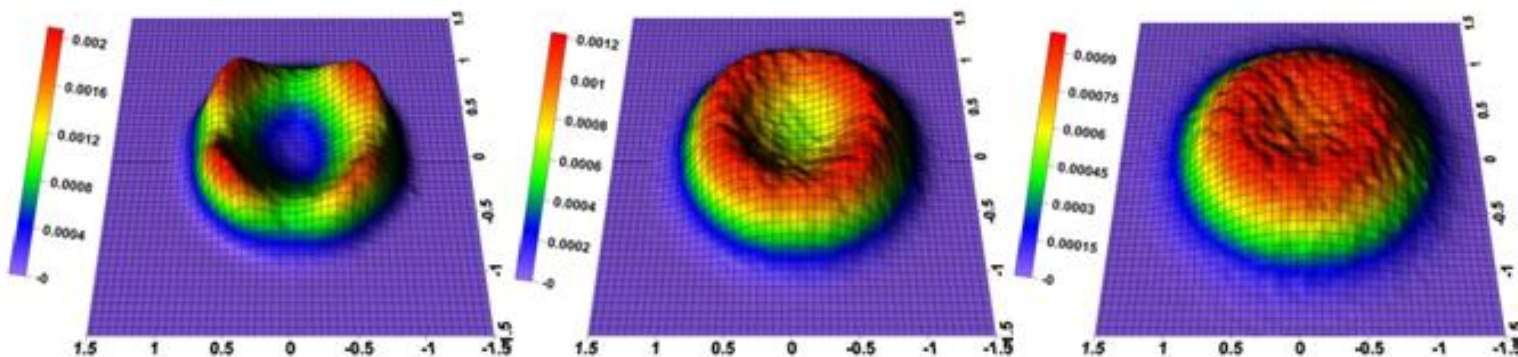
O of CO in  $5^{12}6^4$  cage Left to right: 25 K, 100 K, 260 K

Both C and O atoms in CO molecules in the  $5^{12}6^4$  cage are distributed off the cage center. C atoms is localized and the O atoms rotated around C atoms. Interaction with  $H_2O$  cages in average.

# CO molecule density distribution, MD simulation



C of CO in  $5^{12}$  cage Left to right: 25 K, 100 K, 260 K



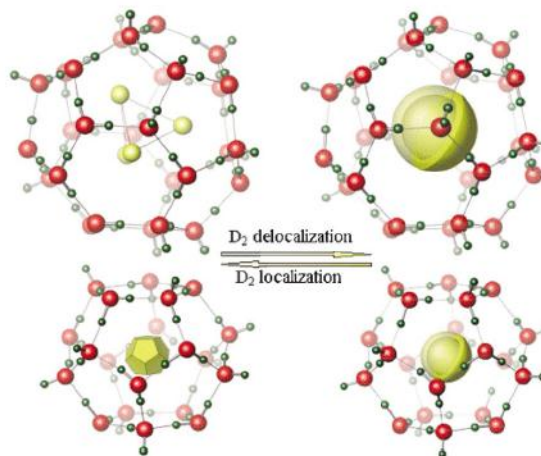
O of CO in  $5^{12}$  cage Left to right: 25 K, 100 K, 260 K

Conclusion: the dipolar of CO interact with  $H_2O$  cages in average way, no special points. The dipolar can change the distribution of CO in cages but not the structure. CO hydrate structure is the same as  $N_2$  and  $O_2$ .

# Can Neon form Clathrate Hydrate?

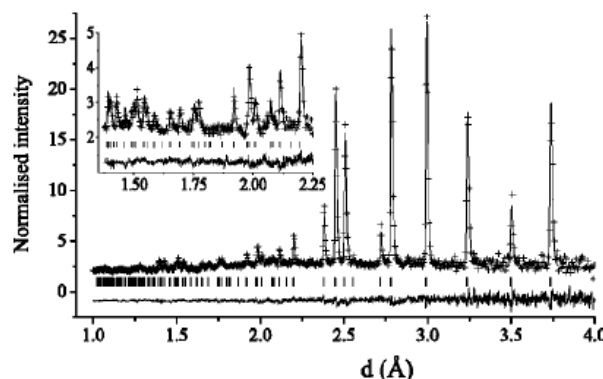
Depending on the shape and size of the included gas molecules, most hydrate clathrates crystallize in crystal structures: SI, SII and SH (all cubic).

For small molecules: H<sub>2</sub>, Ne no hydrate?



D<sub>2</sub> hydrate: SII structure by neutron diffraction, 4D<sub>2</sub> in big cage, 1D<sub>2</sub> in small cage 2K bar. Above 130 K, D<sub>2</sub> were delocalized state, rotating around the centers of the cages. Below 50 K, a complete localization.

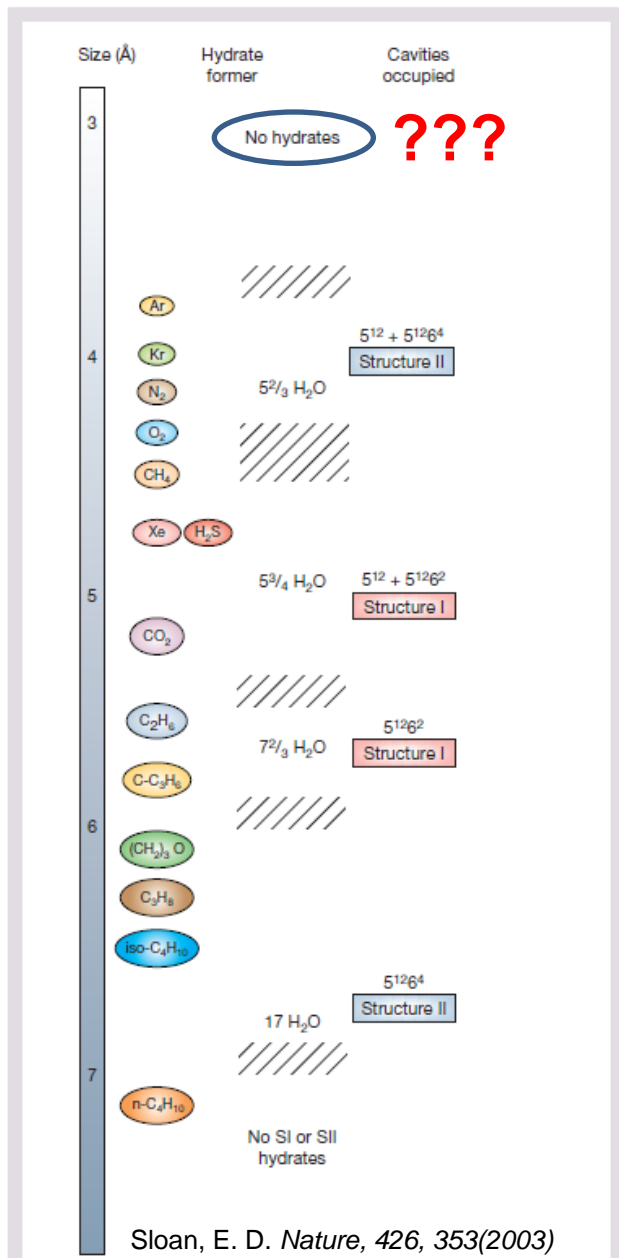
Lokshin, K. et al. *Phys. Rev. Lett.* 93, 125503(2004)



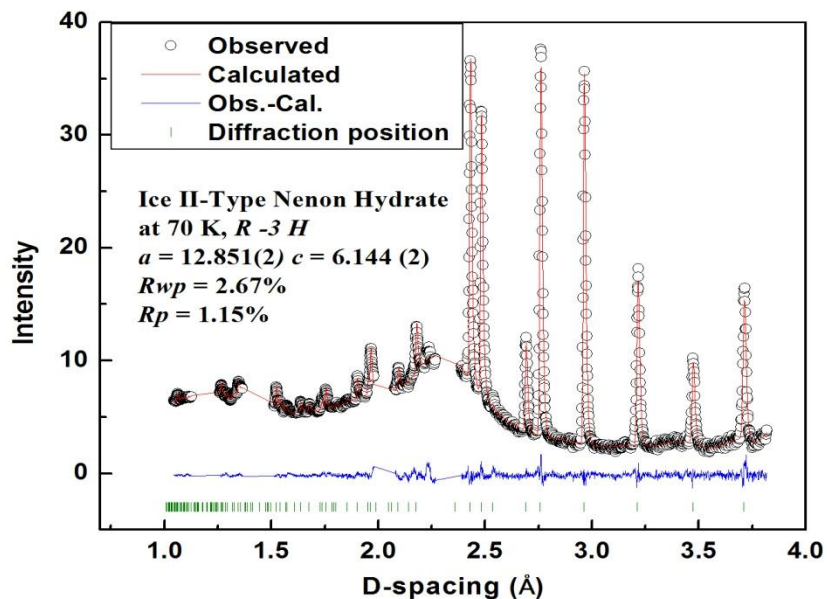
No Ne hydrate at 3.5 Kbar.

Can Ne form hydrate clathrate???

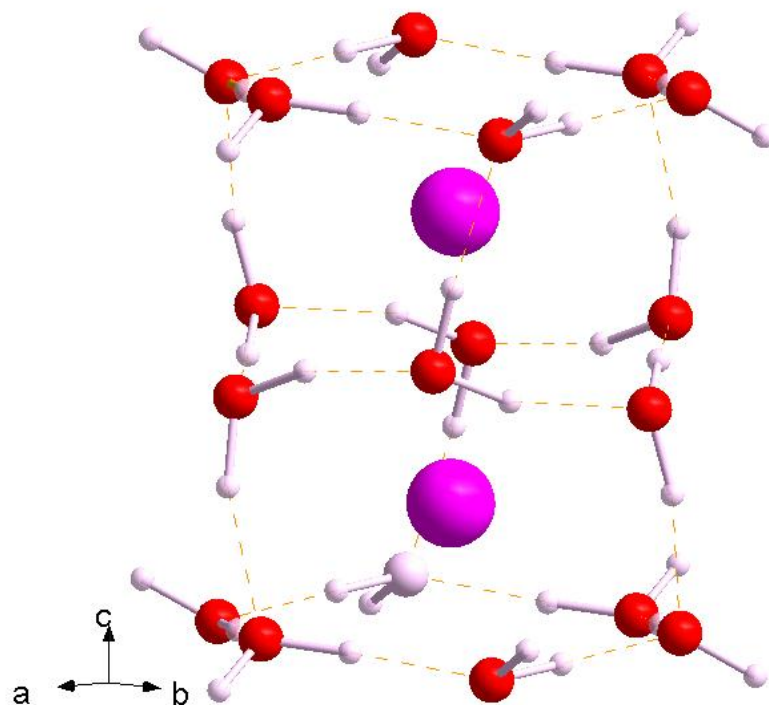
Lokshin, K. et al. *Rev. Sci. Instrum.* 93, 63908 (2005)



# Ice II-Structured Neon Clathrate Hydrate: Al cell

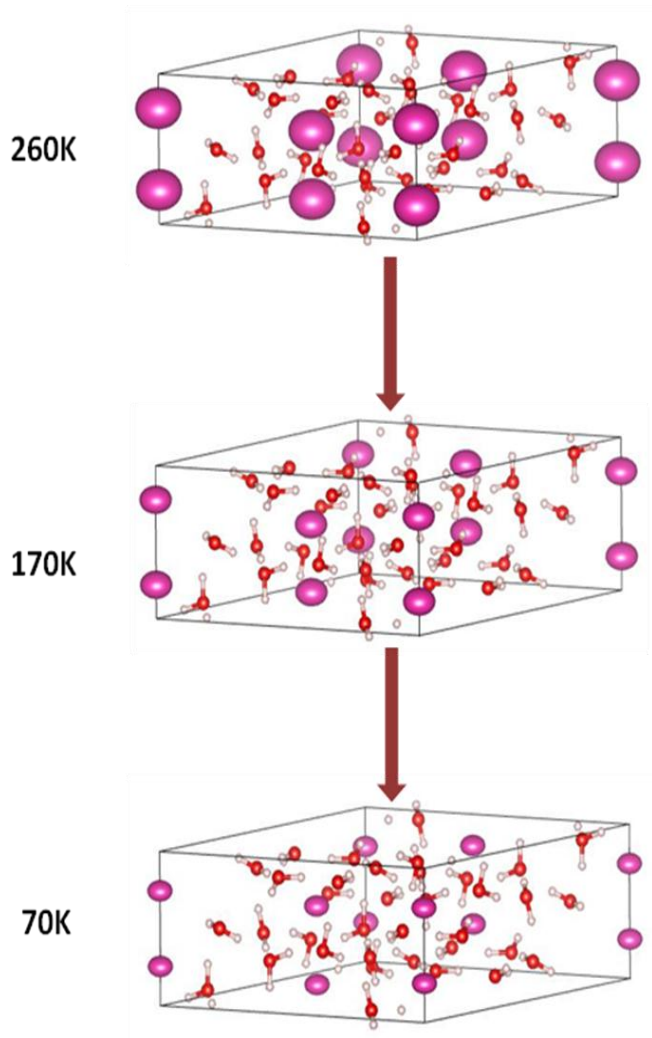


**4.8 Kbar, 70K, the framework ice-II don't need Ne help to be stable**



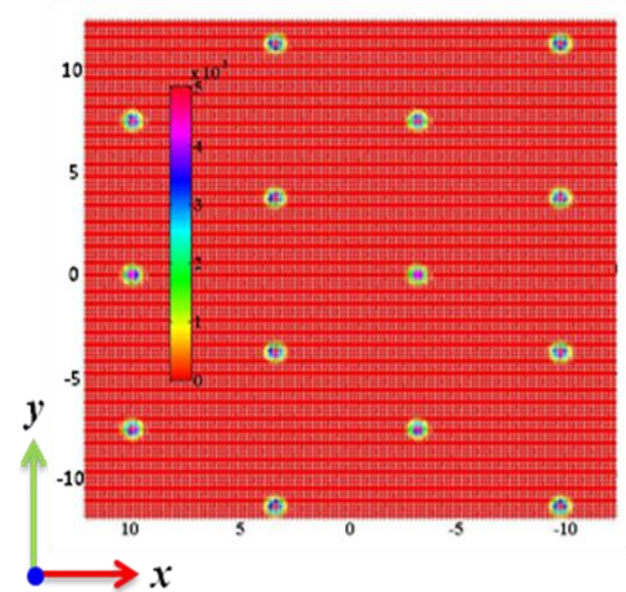
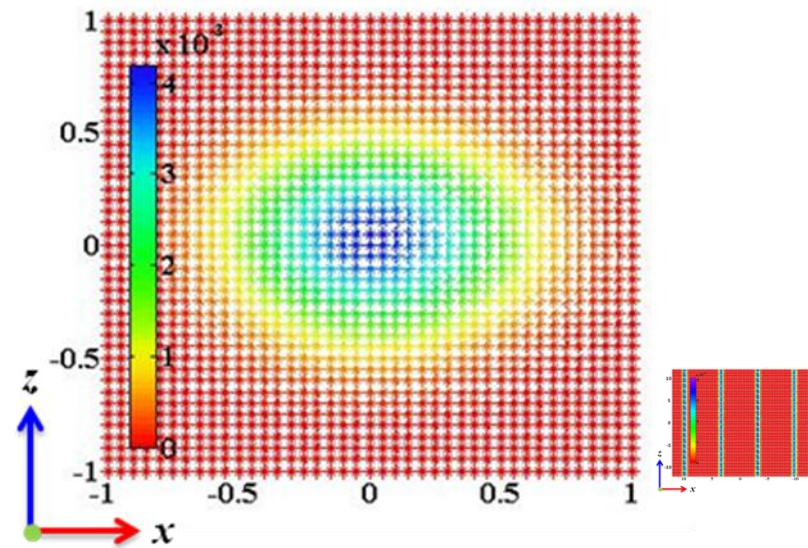
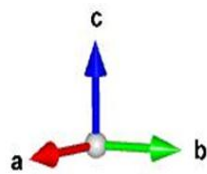
	O1	O2	D1	D2	D3	D4	Ne
x	0.2217(6)	0.1953(8)	0.1513(4)	0.2274(5)	0.1049(6)	0.2363(4)	0
y	0.1955(7)	0.2340(5)	0.2060(5)	0.2186(5)	0.2113(6)	0.3083(7)	0
z	0.0475(10)	0.4887(9)	-0.1480(8)	0.2074(7)	0.4873(10)	0.5582(8)	0.2608(20)

# Encapsulation of Ice II-Structured Neon Clathrate Hydrate



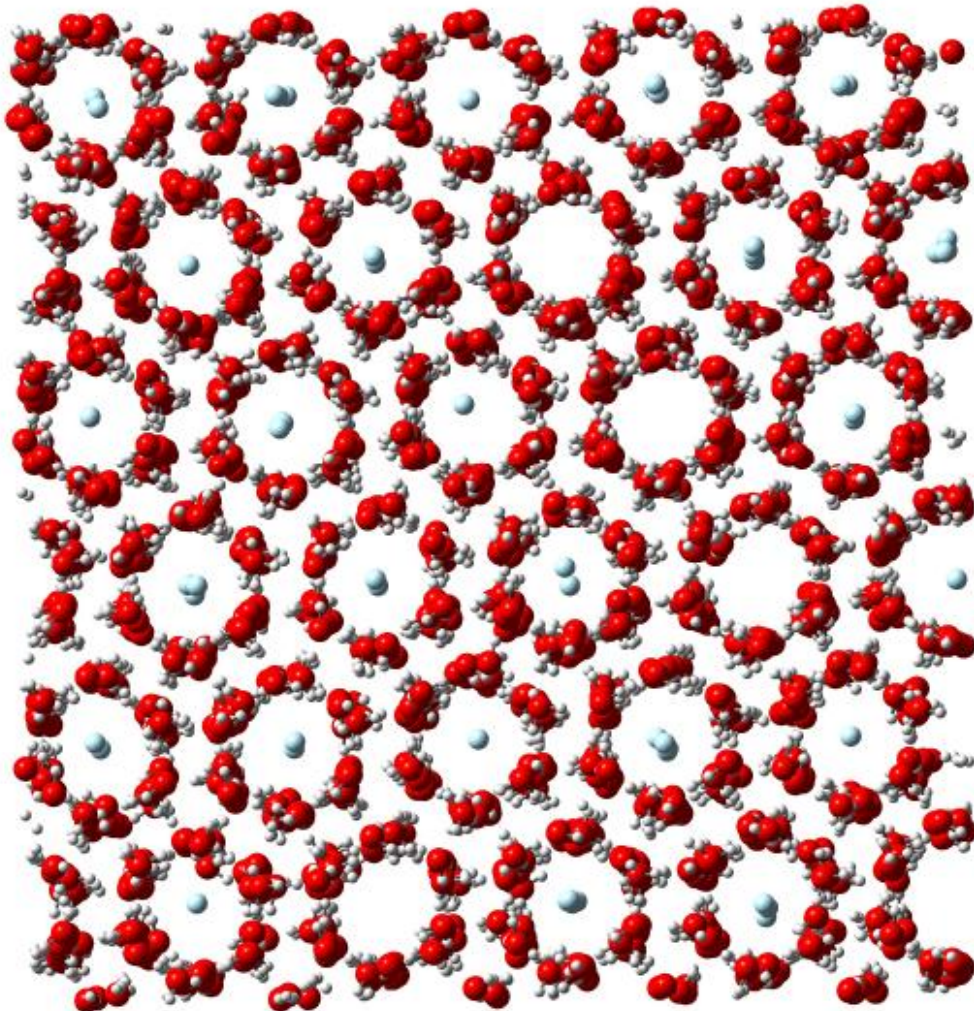
Ne atoms can fill all the space

$U_{iso}$  refinement from diffraction patterns

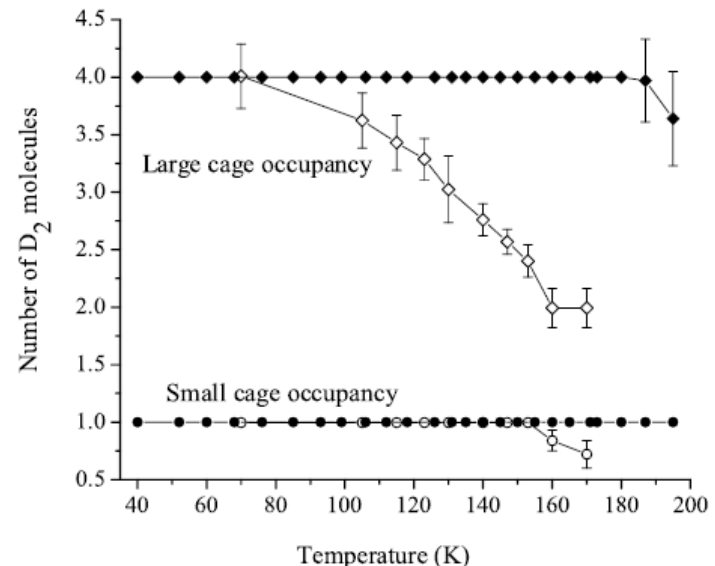


MD simulation

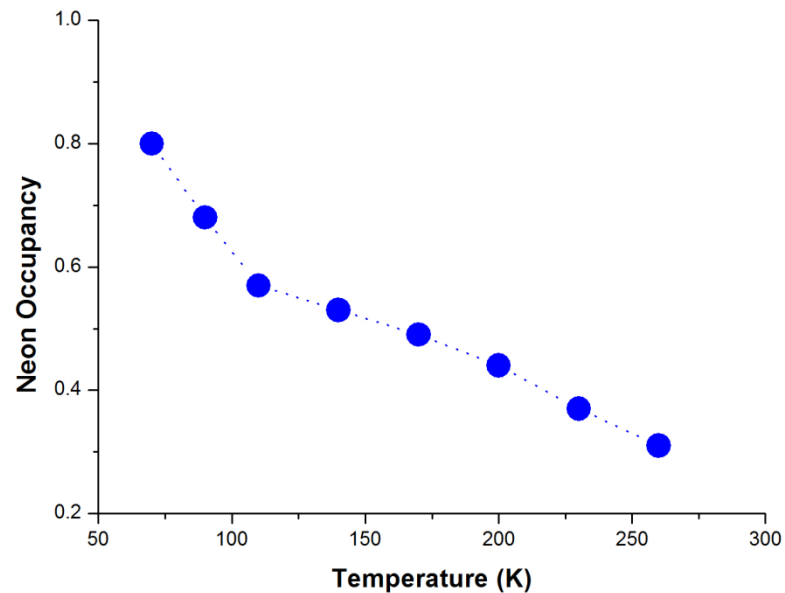
# Encapsulation of Ice II-Structured Neon Clathrate Hydrate



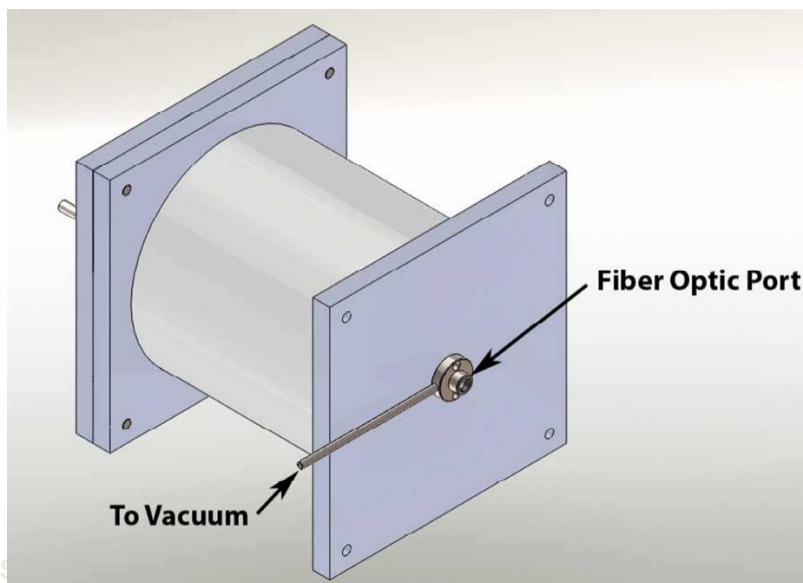
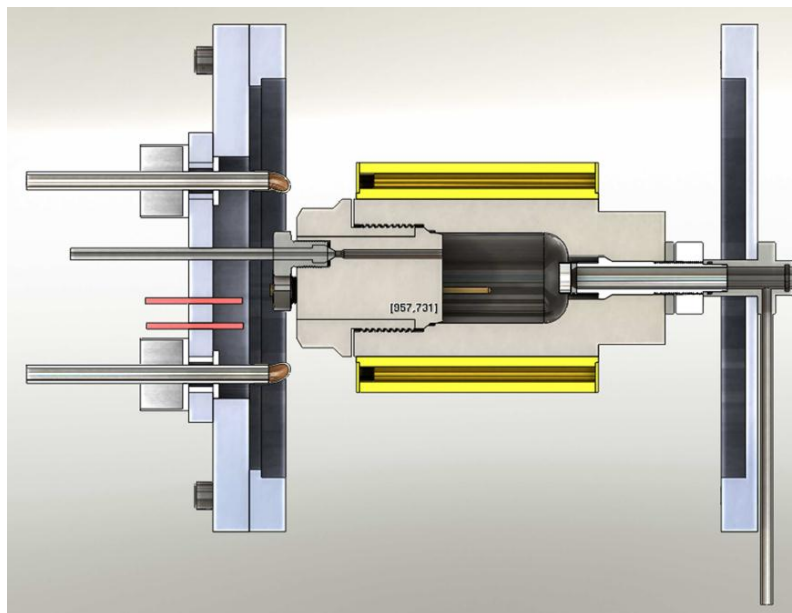
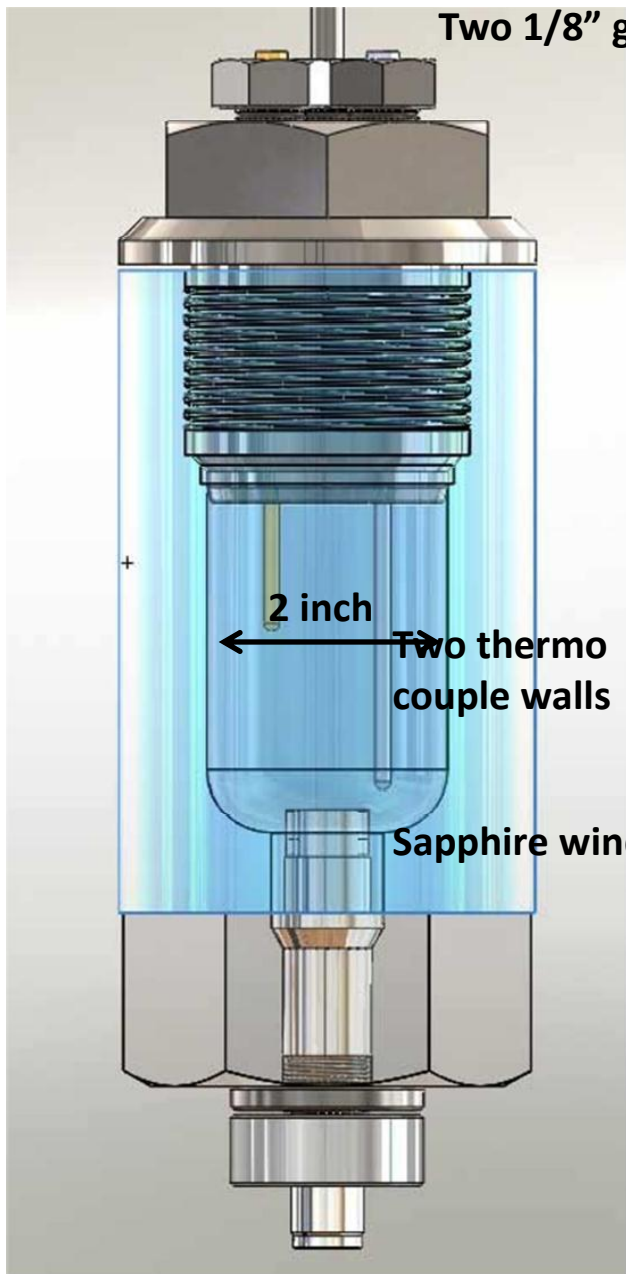
Occupancy of Ne can change with T,  
 $\text{CH}_4$  and CO very stable. Could be  
 corresponding to gas molecule size



Lokshin, K. et al. *Phys. Rev. Lett.* 93, 125503(2004)

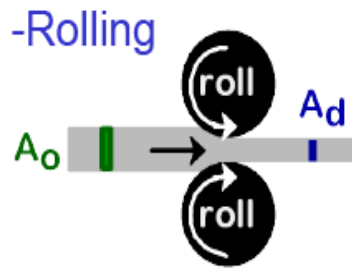
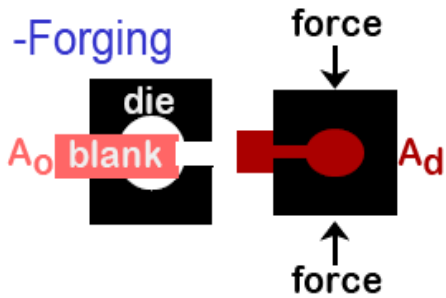
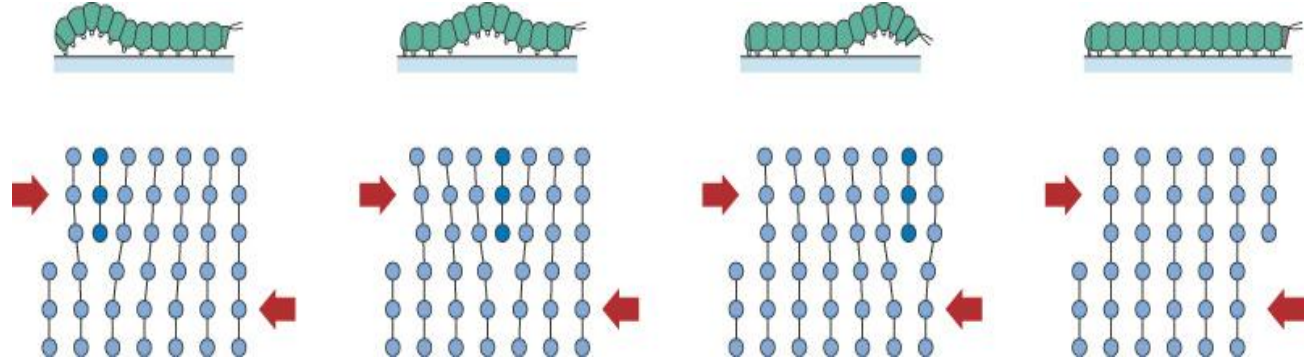
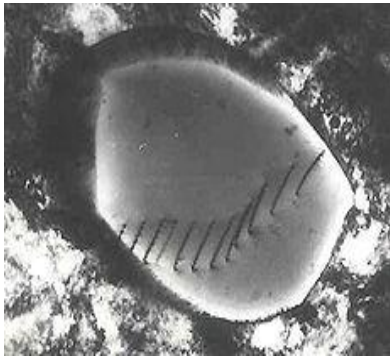


# High pressure Raman cell for hydrate research: for EX5, 2 Kbar

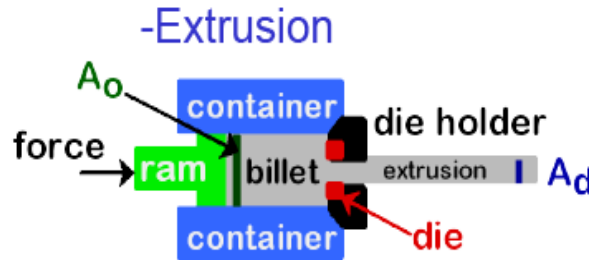
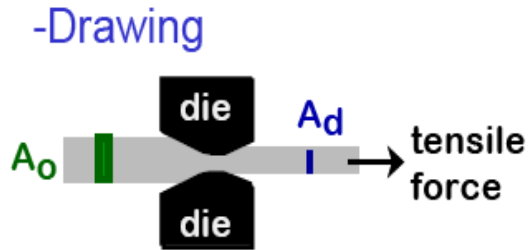
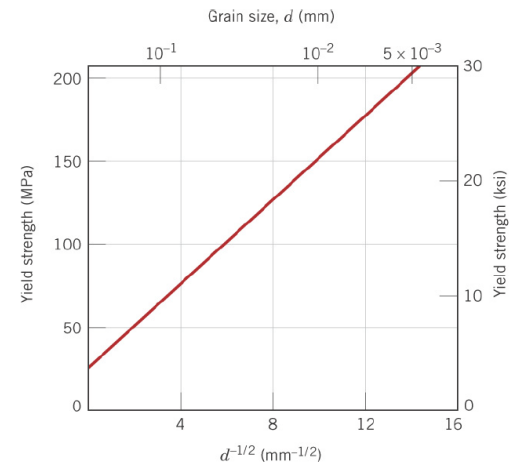


# Nano mechanics: Introduction

The dislocation moment mediates the plastic deformation of the traditional crystals



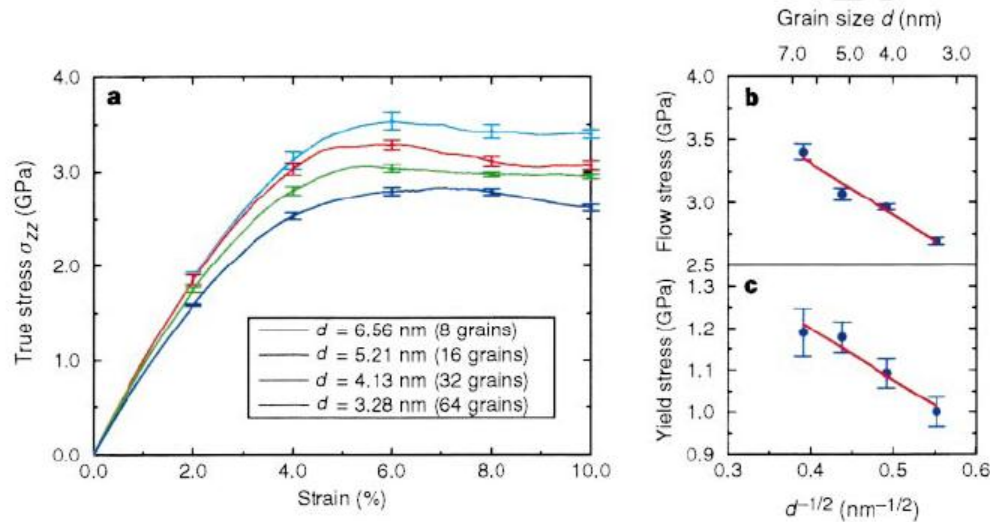
Taylor equation:  $\sigma_{yield} = \sigma_0 + K_y d^{-0.5}$



Hardening of traditional materials: dislocation map improvement

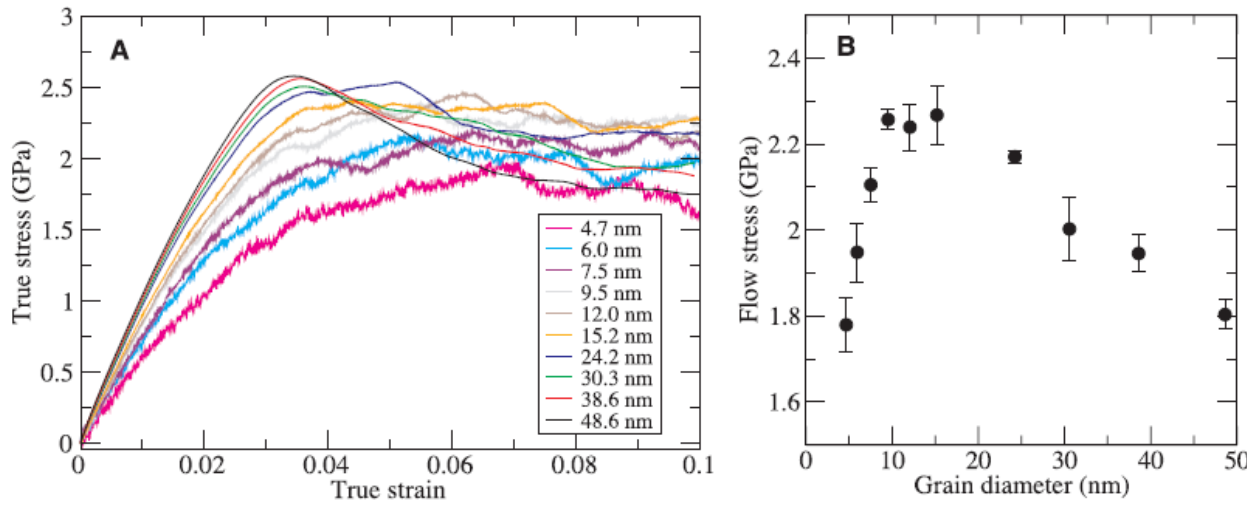
Hall-Patch relation in traditional crystal. **Nano scale, still work???**

# Nano mechanics: Introduction



**Simulation showed that the inversed  $H-P$  relation on Pd, grain boundary behavior.**

• Schiotz J., Tolla, D.D.T., Jacobsen, K. W., 1998, Nature 391:561



**Simulation showed that there should be a critical size when the dislocations no longer work (Cu).**

**How to prove this from experiments?**

• Swygenhoven H., 2002, Science 296:66

# Nano mechanics: Method

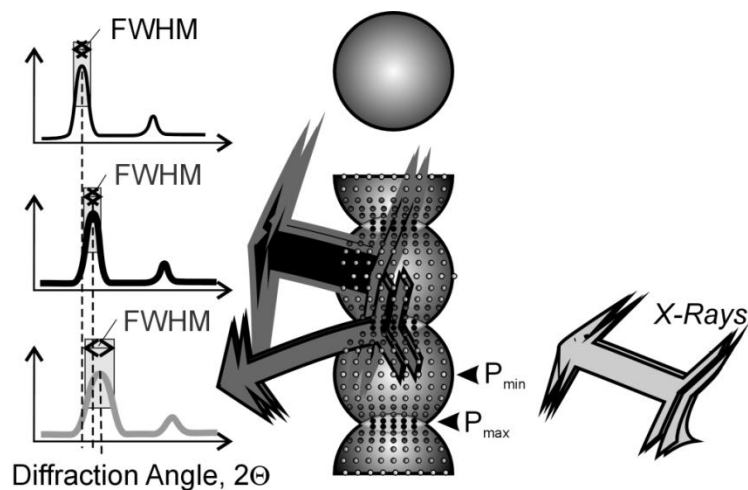


8000D Dual Mixer/Mill

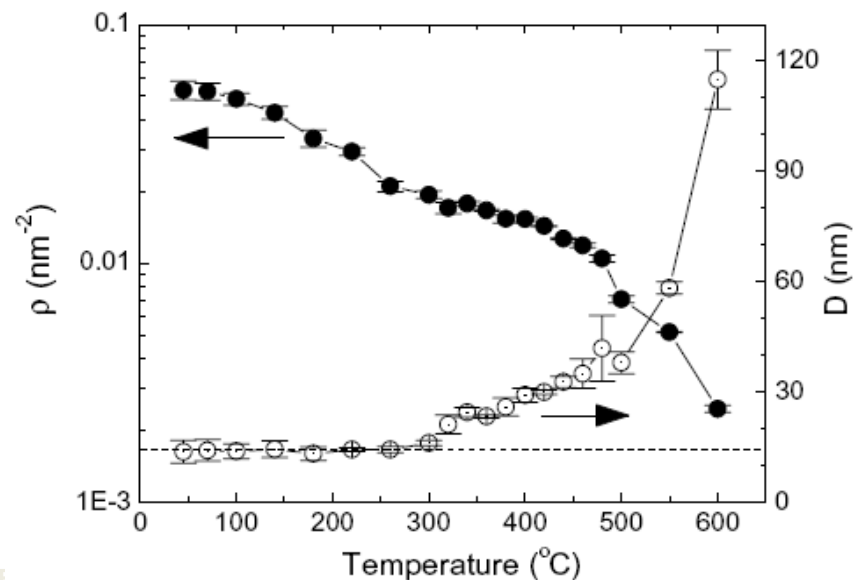
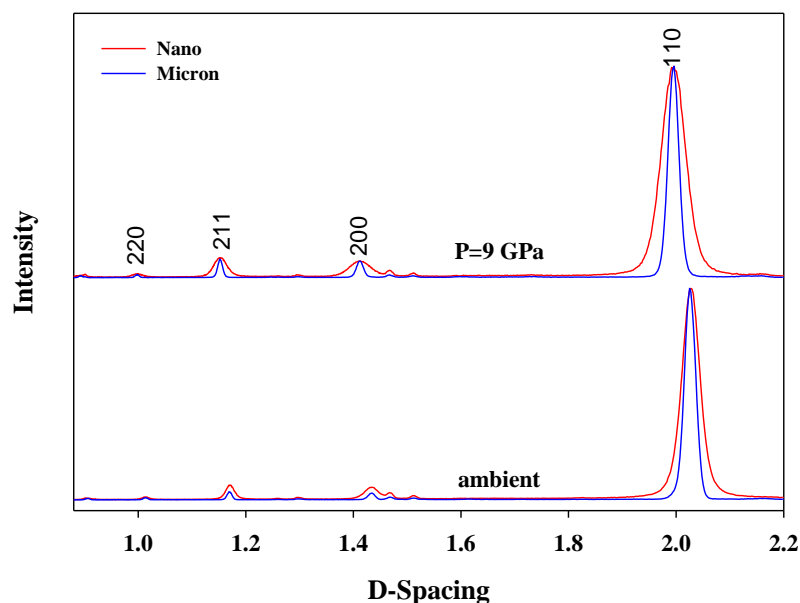
(a), relaxed lattice

(b), macro-strains

(c), micro-strains

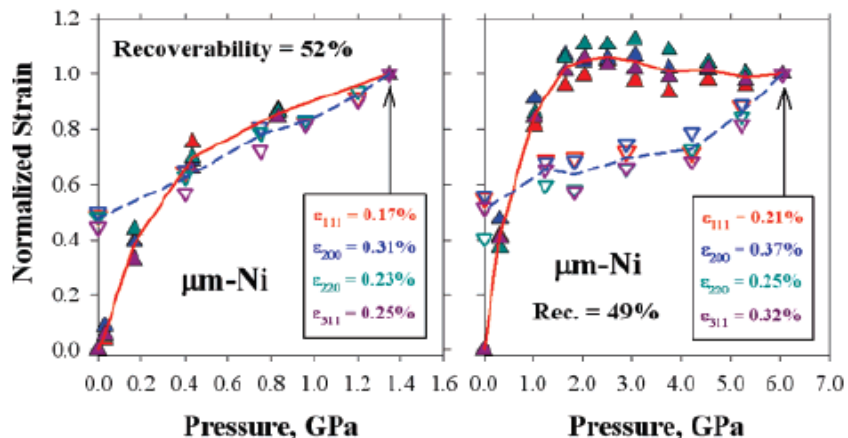


$$\Delta d_{obs.}^2 = \Delta d_{ins.}^2 + \Delta d_{size}^2 + \Delta d_{\varepsilon}^2(P, T)$$

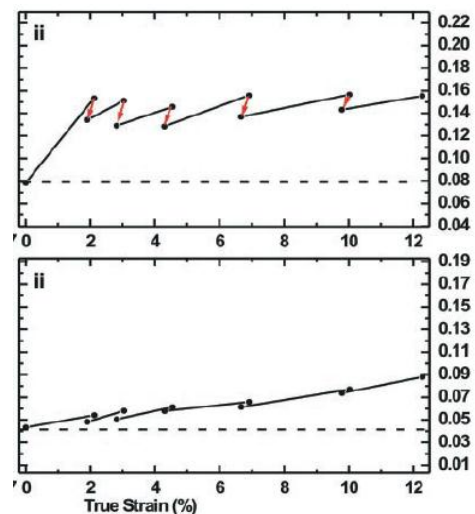


Shen, T., Acta Mater. 55, 5007. 2007

# Nano mechanics: Tri-axial deformation of Fe, Co, under high-P

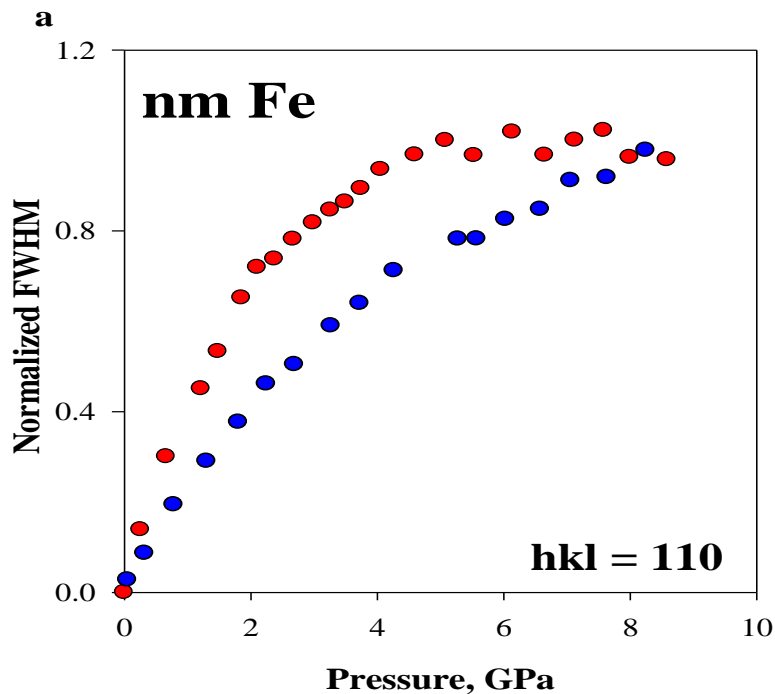


Ni, Zhao Y., Zhang J., Clausen, Shen T. D., Gray G. T. and Wang L., 2007, Nano Lett. 7:426



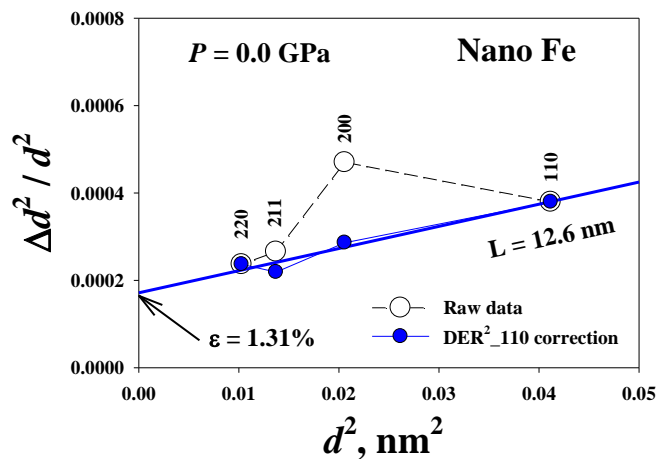
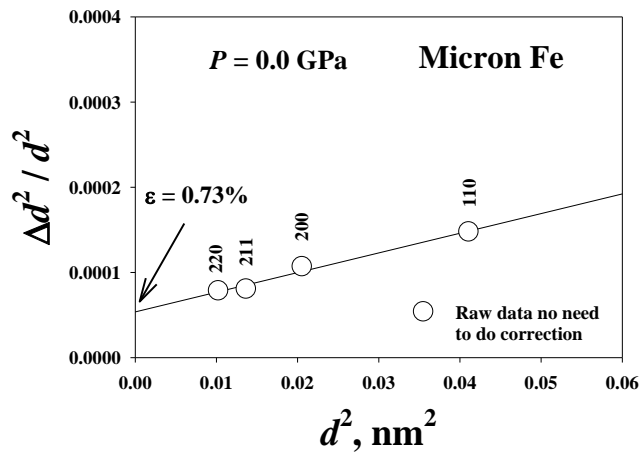
**Residual dislocation network built up after plastic deformation**

-Cu, Budrovic Z., Swygenhoven H. V., Derlet P. M., Petegem S. V., Schmitt B., 2004, Science 304, 273



**Fe (10-20 nm) exhibits 100% peak width recovery after pressure unloading, indicating no additional dislocation network built up in plastic deformation. dislocation behaviors no longer work. (consistent with simulation)**

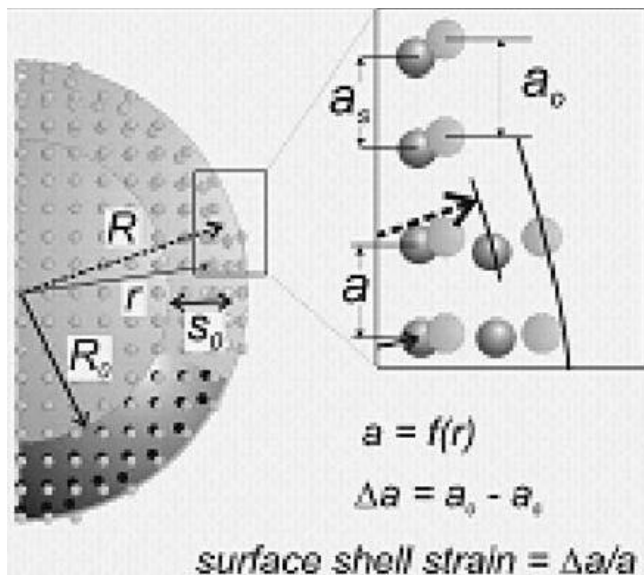
# Nano mechanics: Tri-axial deformation of Fe, Co, under high-P



$$\Delta d_{obs}^2 = \Delta d_{ins.}^2 + \Delta d_{size}^2 + \Delta d_{\varepsilon}^2(P, T)$$

$$\varepsilon = \Delta d_{\varepsilon} / d = \sqrt{\Delta d_{obs}^2 - \Delta d_{ins.}^2} / d(P, T)$$

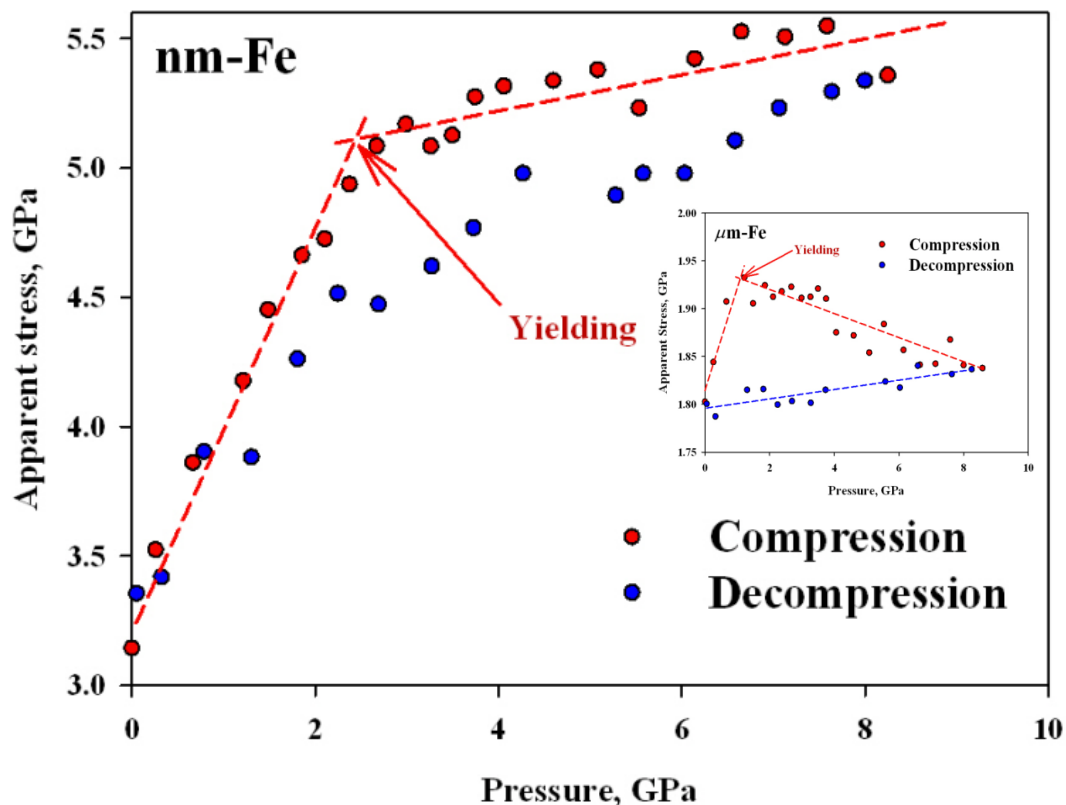
$$\Delta d_{obs}^2 / d^2 = (\varepsilon^2 + \Delta d_{ins}^2 / d^2) + (K/L)^2 d^2(P, T)$$



The raw data for micron Fe line up very nicely in a linear fashion for least-squares fit, and also other micron materials.

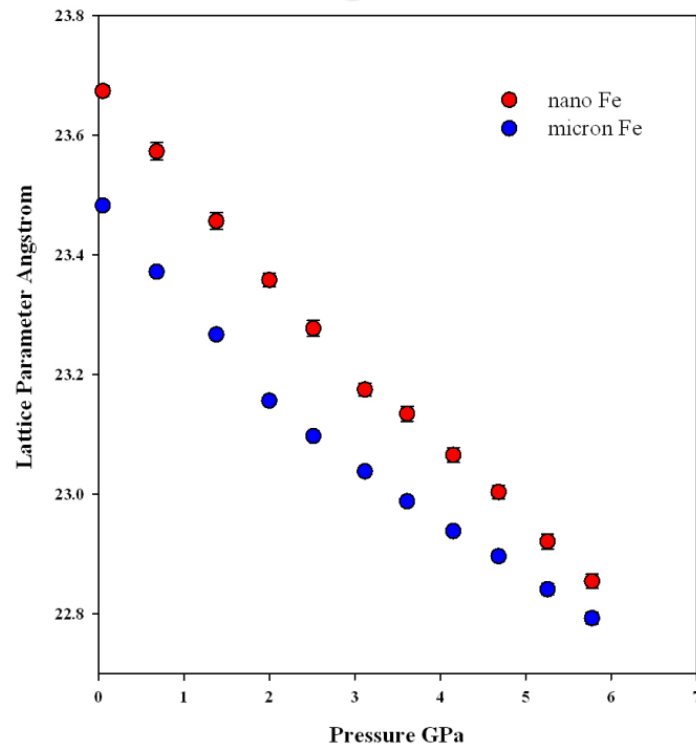
$DER^2 = (E_{hkl}/E_{200})^2$  needs to be applied to nano Fe (10-20nm) to correct the strain differences on individual lattice planes. This is attributed to the internal strain stored in the surface layers of Fe nanocrystals. (also true in nano Ni, during pressure loading/unloading)

# Nano mechanics: Tri-axial deformation of Fe, Co, under high-P



The strength of nano-Fe (2.0 GPa) is 15 times as large as that of micron-Fe (0.13 GPa). The nano scale grain-size reduction is more effective strengthening mechanism.

For micron-Fe, work pressure-induced dislocation annihilation (Taylor equation).



▪ Second order B-M equation of state.

▪  $K_{\text{micron}} = 184.1 \pm 8.2 \text{ GPa}$

▪  $V_{0\text{micron}} = 23.4439 \pm 0,0187 \text{ angstrom}^3$ ,

▪  $K_{\text{nm}} = 152.2 \pm 2.8 \text{ GPa}$

▪  $V_{0\text{nm}} = 23.6665 \pm 0.0094 \text{ angstrom}^3$

▪ **Extension shell**

# Nano Mechanics: Tri-axial deformation of Fe, Co, under high-P

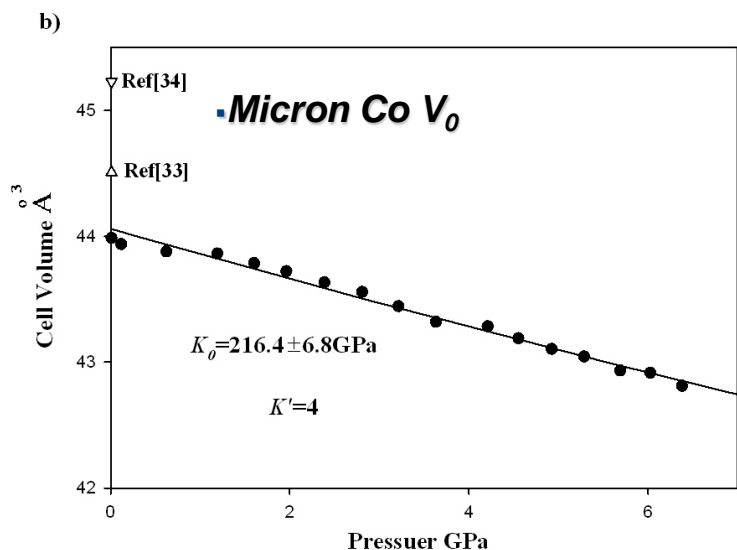
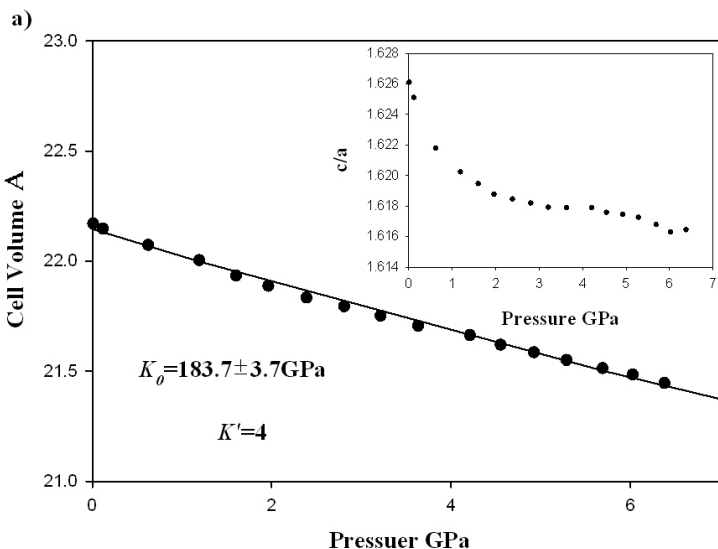


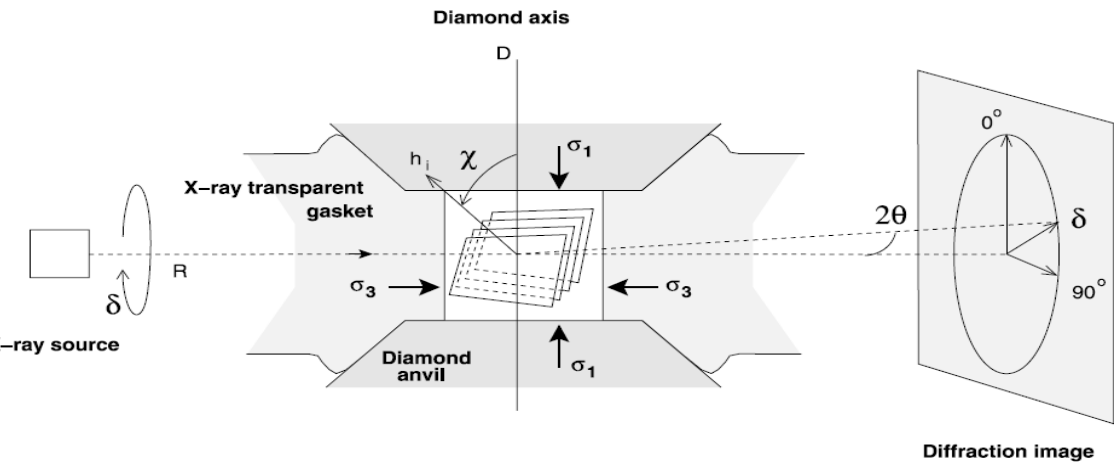
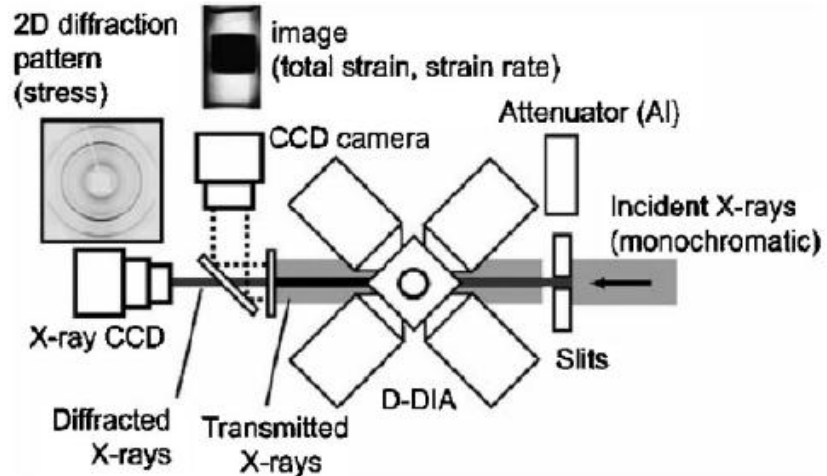
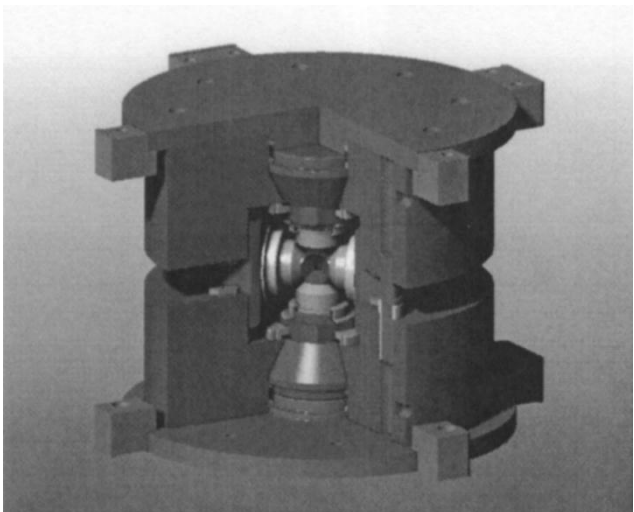
Table I: Summary of bulk moduli for micron and nano Co.

	K (GPa)	K'	ref
Micron Hcp Co	$203 \pm 2$	$3.6 \pm 0.1$	Experiment <sup>27</sup>
	199	$3.6 \pm 0.2$	Experiment <sup>28</sup>
	194	4.6	Theory <sup>29</sup>
	190	3.6	Experiment <sup>30</sup>
	$184.8 \pm 3.8$	4	This work
	$183.7 \pm 3.7$	4.6	This work
	$182.0 \pm 3.5$		This work
Micron Fcc Co	199		Experiment <sup>30</sup>
	185		Experiment <sup>31</sup>
	182		Experiment <sup>32</sup>
Nano Fcc Co	$216.4 \pm 6.8$	4	This work

**The bulk modulus for nano Co is 216 GPa, ~17% higher than that of micron Co (185 GPa). This finding supports a generalized model of nanocrystals with pre-compressed surface layers and indicates that the grain-size induced elastic strengthening and weakening are primarily determined by the nature of internal stress (compressed vs. tensile) present in the surface layer of a nanocrystal. However, no strain-stress curve, technique limit!**

# Nano Mechanics: uni-axial deformation of Ni, under high-P

Deformation-dia  
press  
Since 2004  
By Wang, Yanbin



$$\sigma = \begin{pmatrix} \sigma_1 & & \\ & \sigma_3 & \\ & & \sigma_3 \end{pmatrix} = \begin{pmatrix} \sigma_p & & \\ & \sigma_p & \\ & & \sigma_p \end{pmatrix} + \begin{pmatrix} 2\sigma_t/3 & & \\ & -\sigma_t/3 & \\ & & -\sigma_t/3 \end{pmatrix}$$

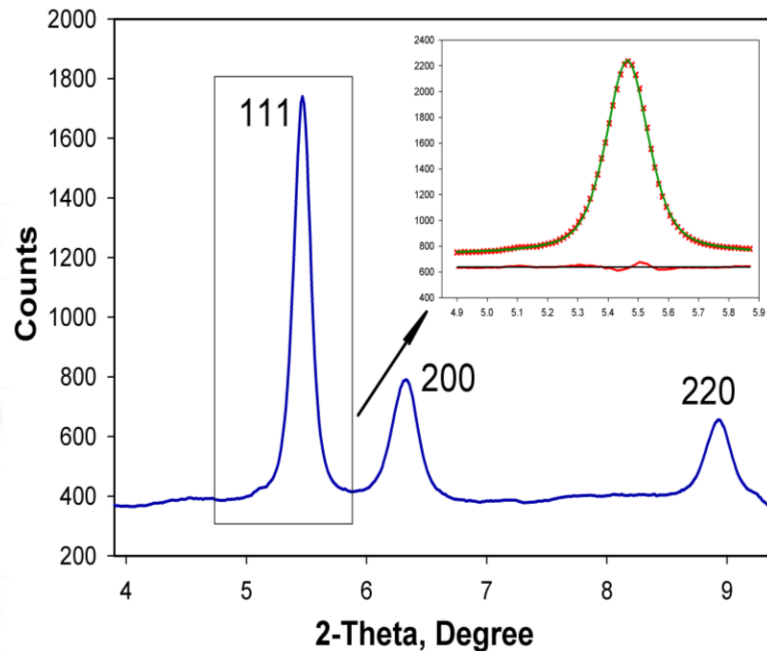
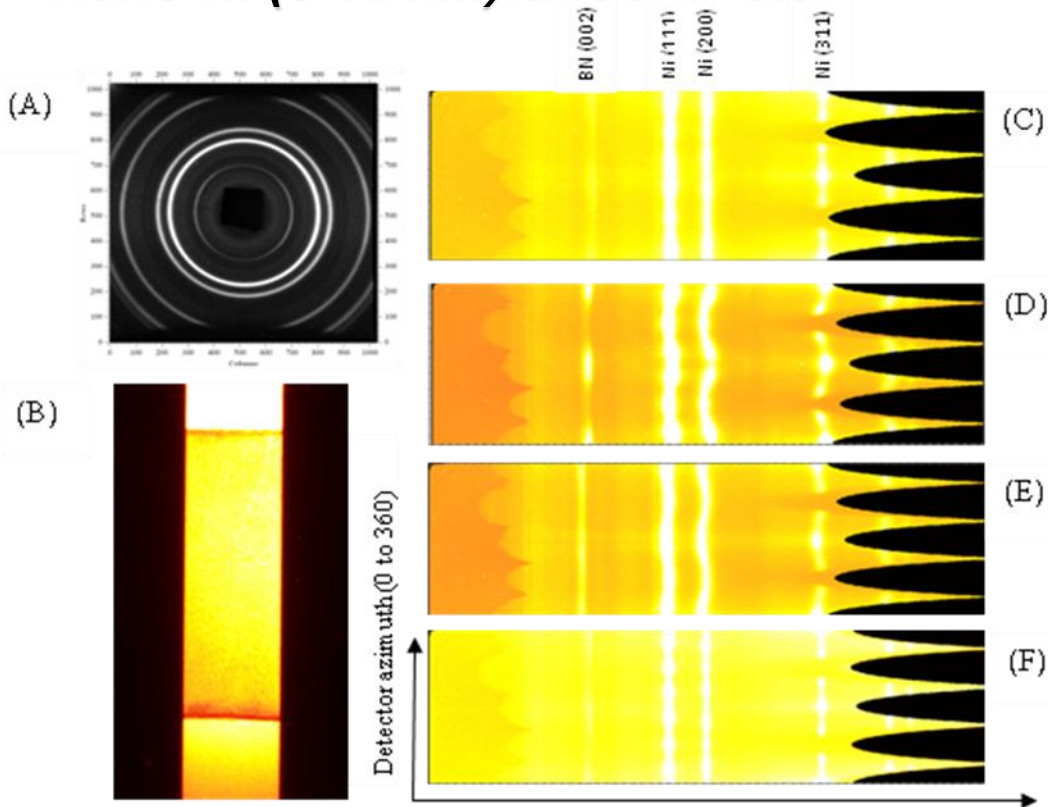
$$\epsilon'_3 = \epsilon^R(l_1 l_2 l_3) = \epsilon_p^R(l_1 l_2 l_3) + \epsilon_d^R(l_1 l_2 l_3)$$

$$\epsilon_d^R(l_1 l_2 l_3) = -\left(\frac{t}{3}\right)(1 - 3 \cos^2 \psi) \times \left[0.5 \times \left(\frac{3}{E(l_1 l_2 l_3)} - \beta(l_1 l_2 l_3)\right)\right]$$

$$\epsilon(l_1 l_2 l_3) = \epsilon_p(l_1 l_2 l_3) + \alpha \epsilon_d^R(l_1 l_2 l_3) + (1 - \alpha) \epsilon_d^V$$

# Nano Mechanics: uni-axial deformation of Ni, under high-P

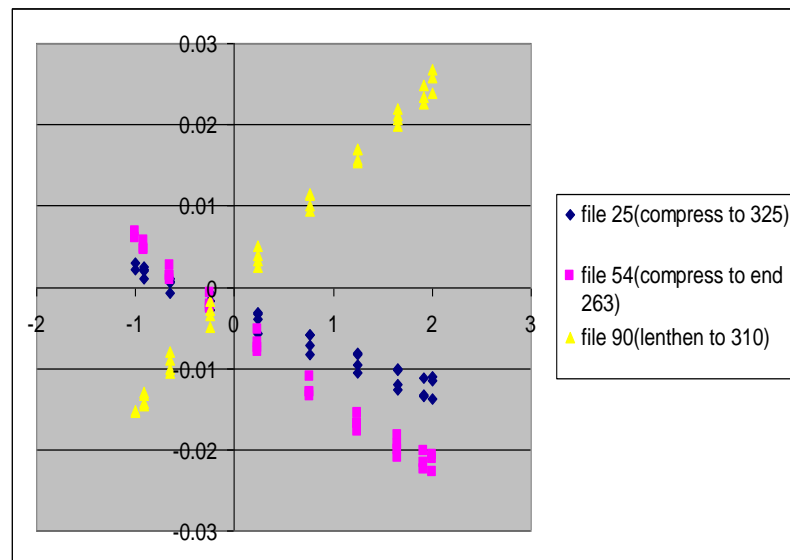
## Nano Ni (8-12 nm): under D-dia



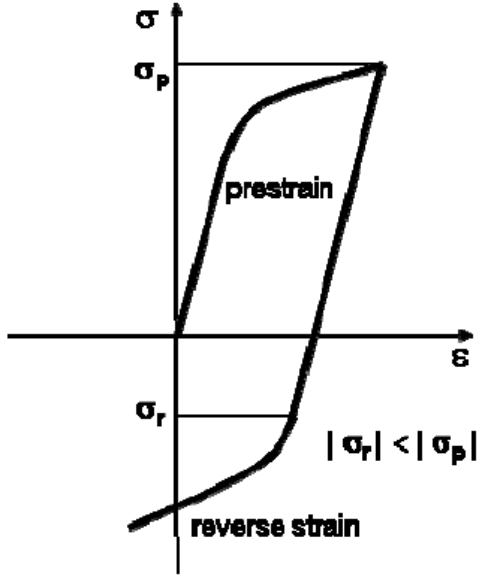
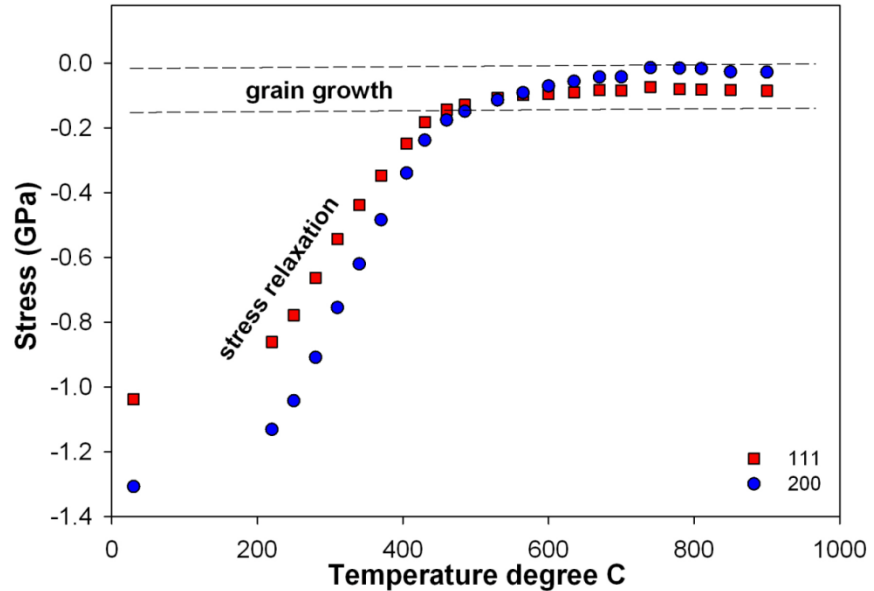
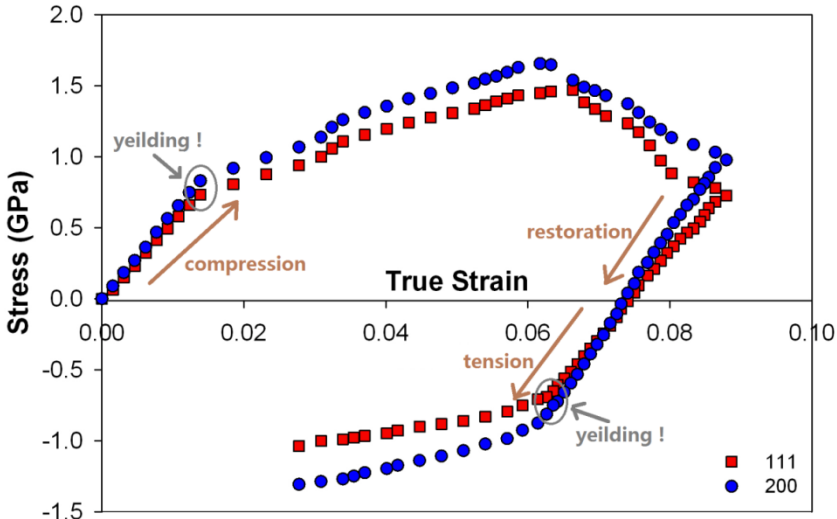
## Diffraction peak refinement with gsas

Fitting to:

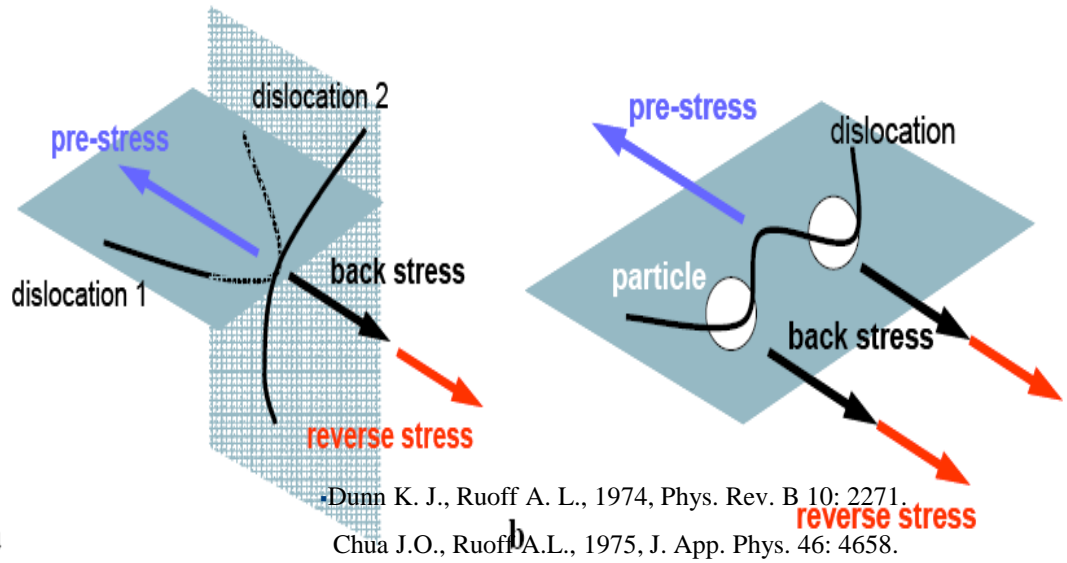
$$\varepsilon(\phi, hkl) = \varepsilon_p - \varepsilon_t(khl)(1 - 3\sin^2 \phi)$$



# Nano Mechanics: Tri-axial deformation of Fe, Co, under high-P



▪ Bauschinger effect

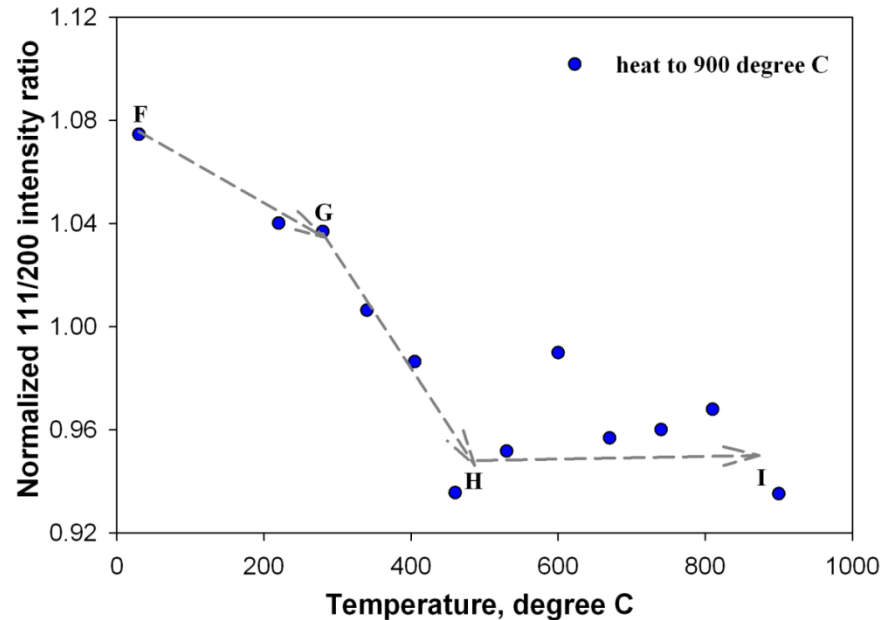
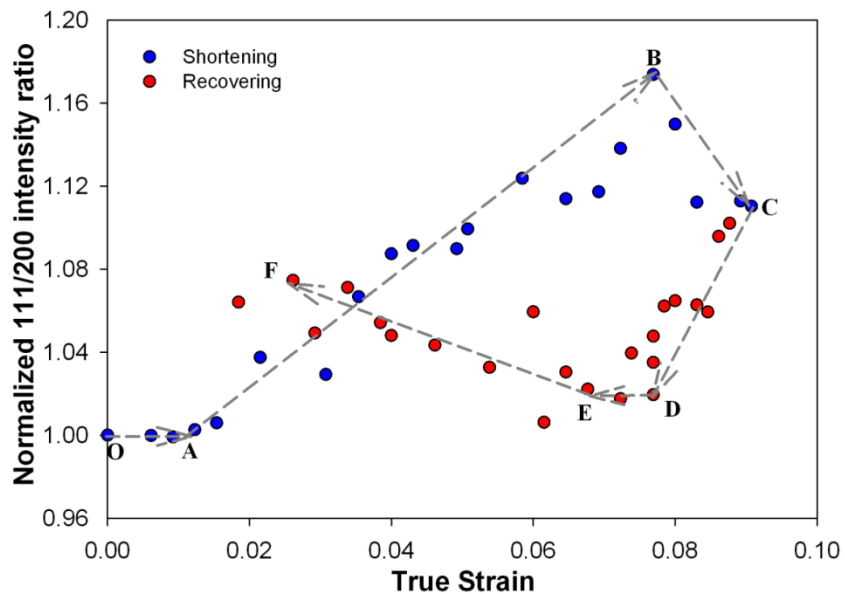


▪ Dunn K. J., Ruoff A. L., 1974, Phys. Rev. B 10: 2271.

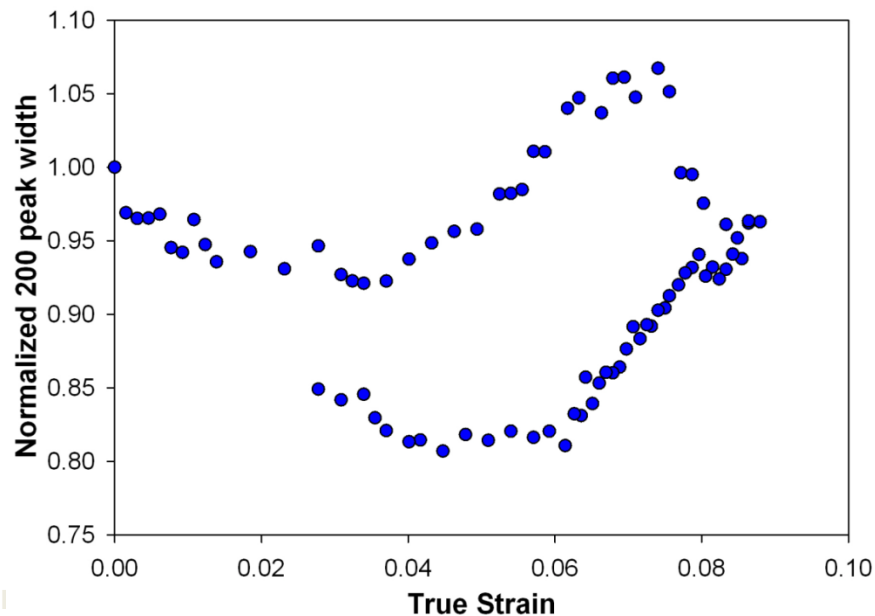
▪ Chua J.O., Ruoff A.L., 1975, J. App. Phys. 46: 4658.

## ▪ Anti-fatigue-how plastic deformation behave?

# Nano Mechanics: Tri-axial deformation of Fe, Co, under high-P

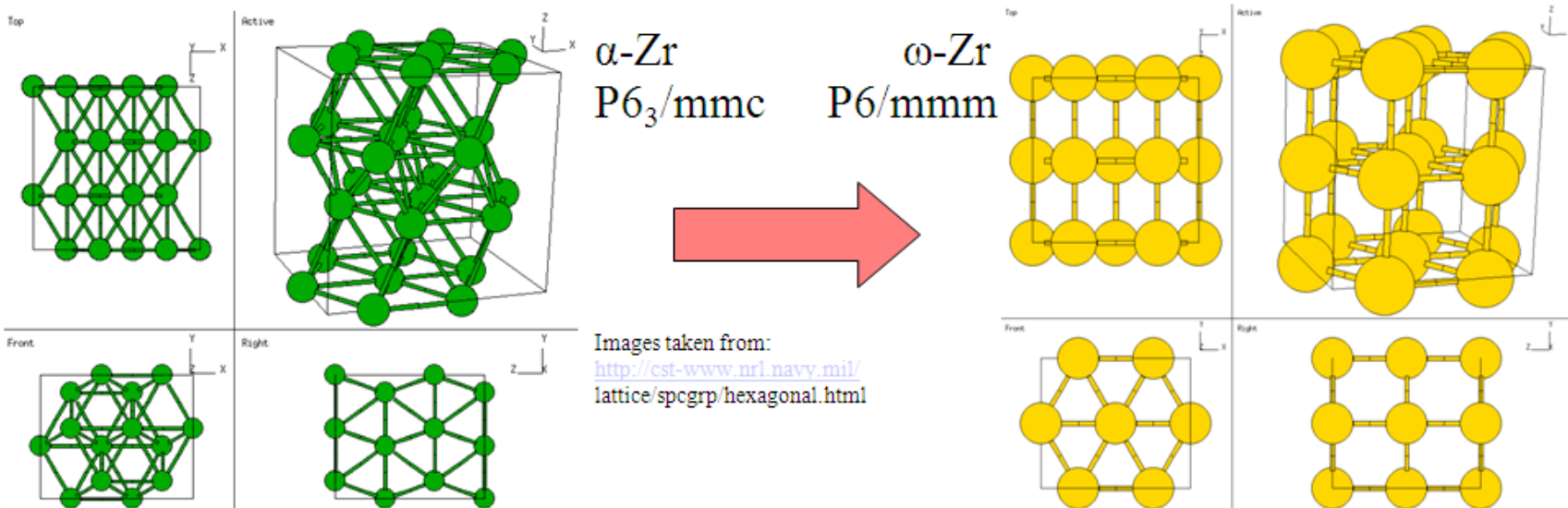


- *plastic deformation behavior:*
- *1) grain rotation*
- *2) grain growth*

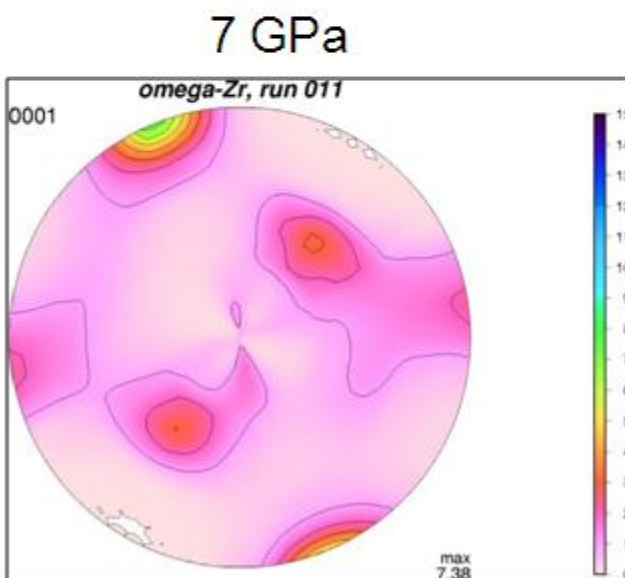
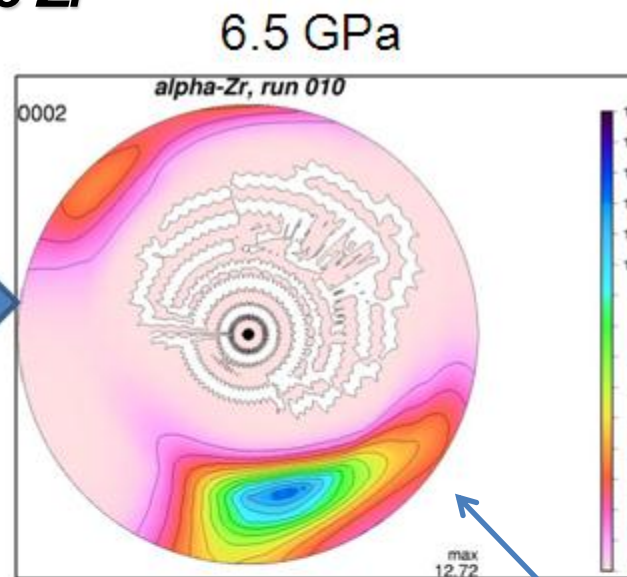
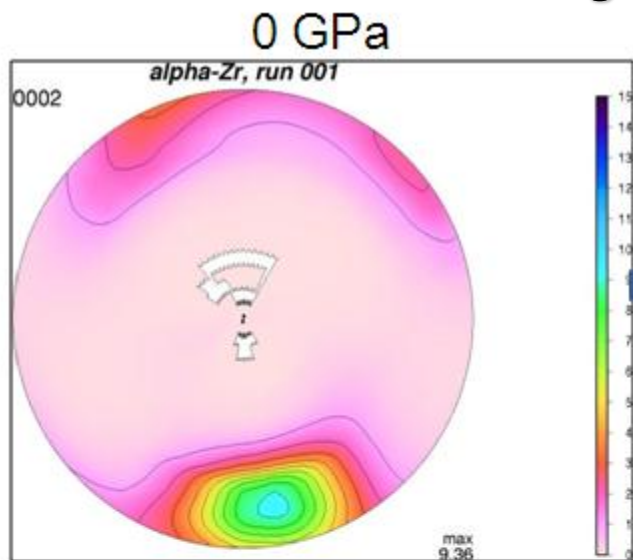


## High pressure mechanics: omega phase Zr

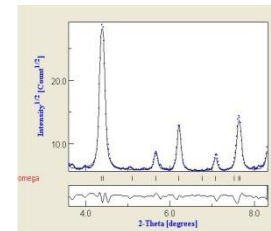
- Zr is widely used in the nuclear, biomedical, and aerospace industries.
- The omega phase was first encountered by Frost *et al.* in 1954 who found that some aged alloys.
- Pure Zr has been well studied, it has low yield strength ~100 MPa.
- The omega phase offers a 2.5% more efficient atomic packing which could lead to higher yield strength



# High pressure mechanics: omega phase Zr



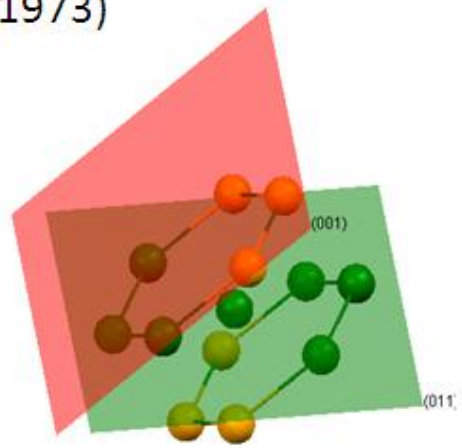
Texture refinement by MAUD



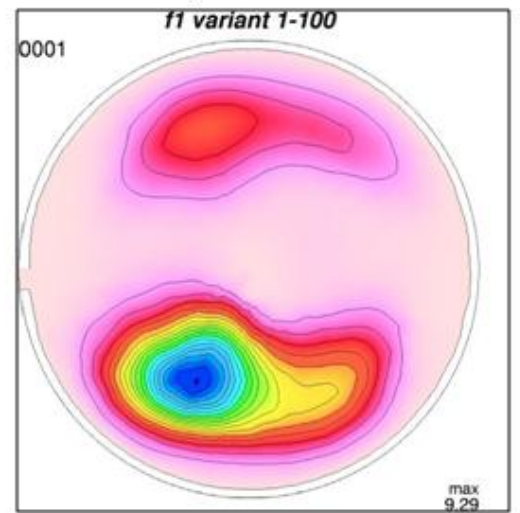
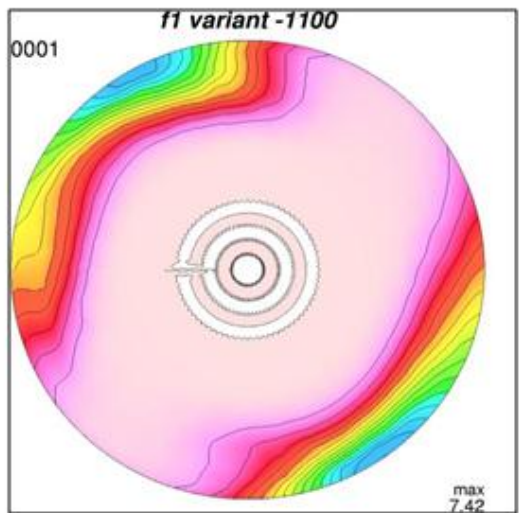
The  $\alpha$ -Zr has a (0001) texture at ambient condition. After the phase transition from  $\alpha$  phase to  $\omega$  phase, the pole figure changes because of the slip of atoms.

# High pressure mechanics: omega phase Zr

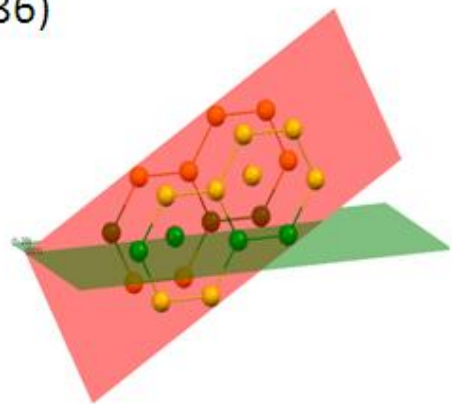
UZ model  
(1973)



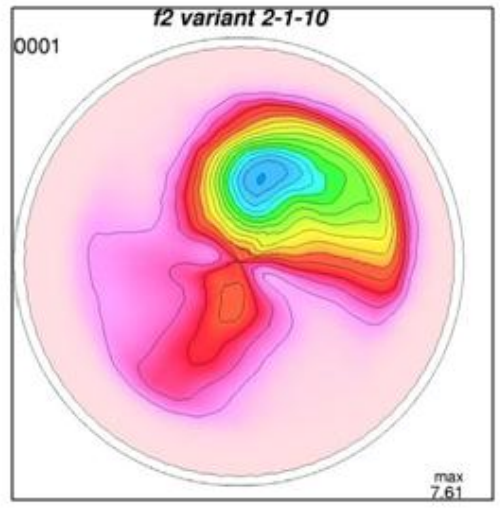
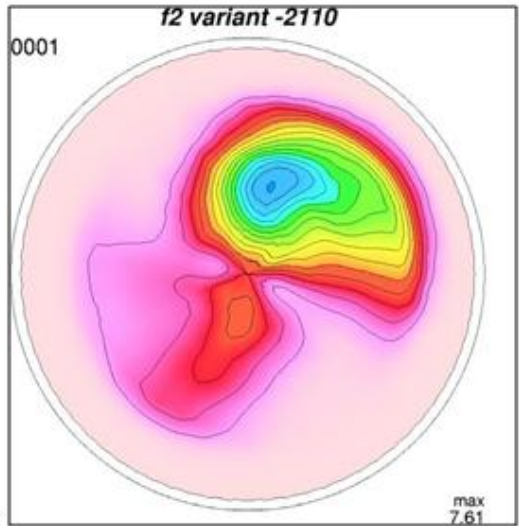
$(0001)_\alpha \parallel (10\bar{1}1)_\omega$  and  $[10\bar{1}1]_\alpha \parallel [11\bar{2}3]_\omega$



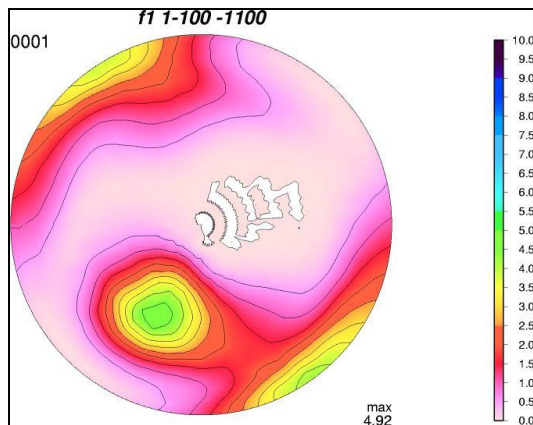
BRT model  
(1986)



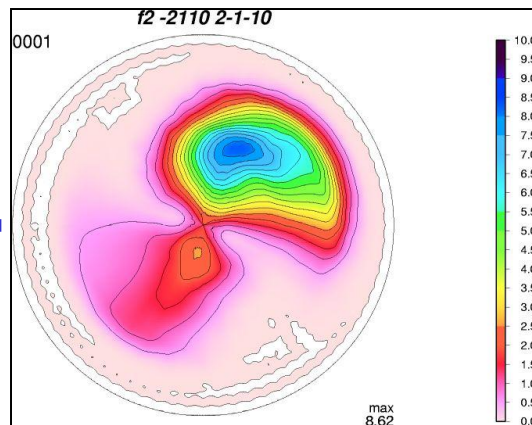
$(0001)_\alpha \parallel (1\bar{2}10)_\omega$  and  $[2\bar{1}\bar{1}0]_\alpha \parallel [0001]_\omega$



# High pressure mechanics: omega phase Zr

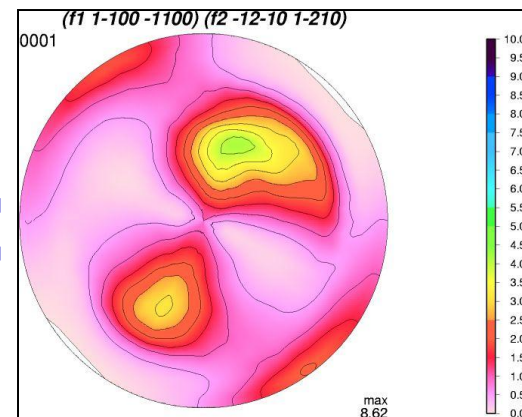


+



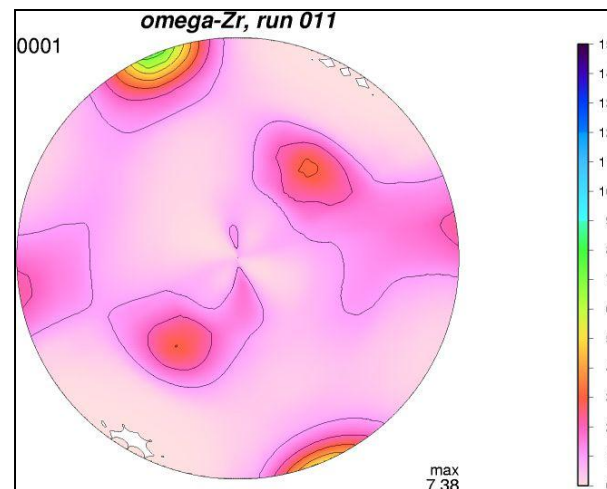
=

theoretical

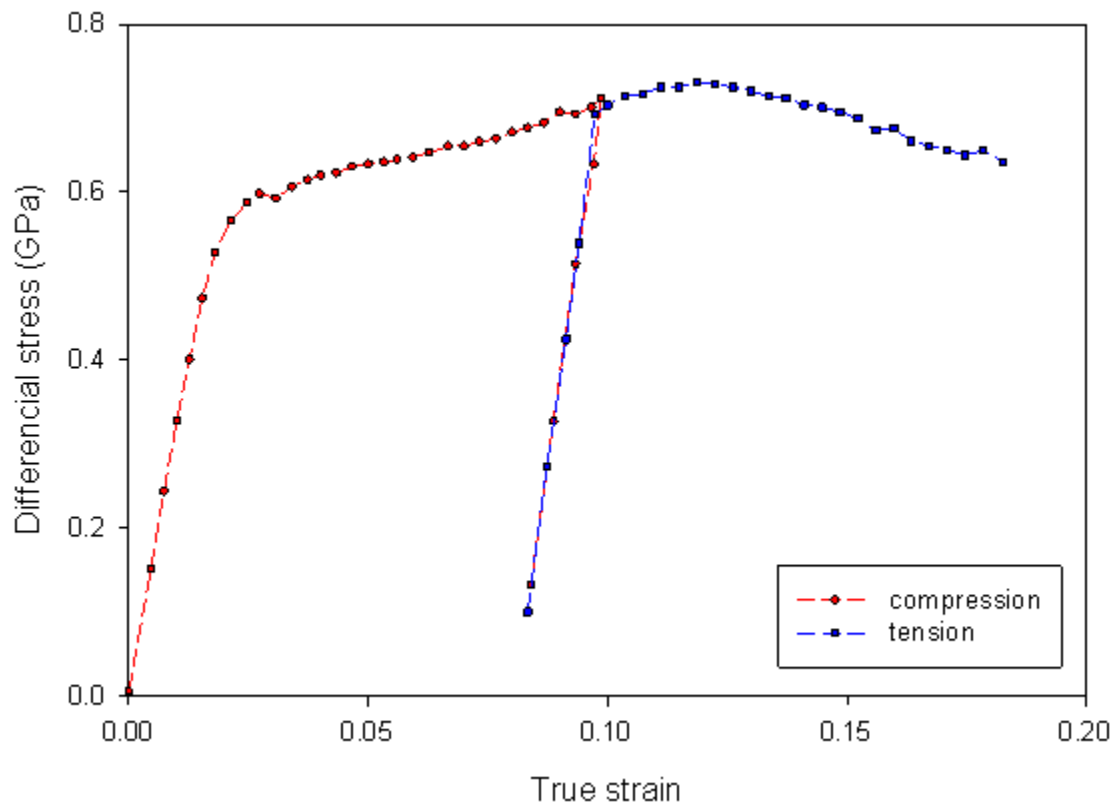


?

- Both the UZ model (1973) and the BRT model(1986) should work during the phase transition from  $\alpha$  to  $\omega$  phase at 7 GPa ambient temperature condition.



# High pressure mechanics: omega phase Zr



Significant hardening of  $\omega$  phase Zr compared to the ambient  $\alpha$  phase.

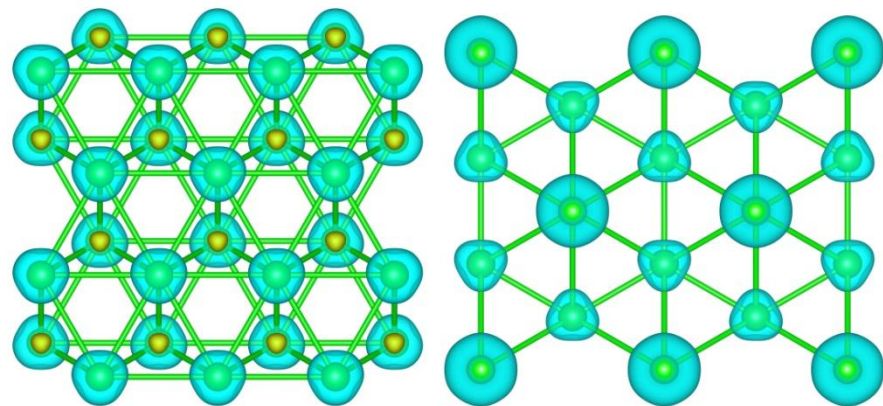
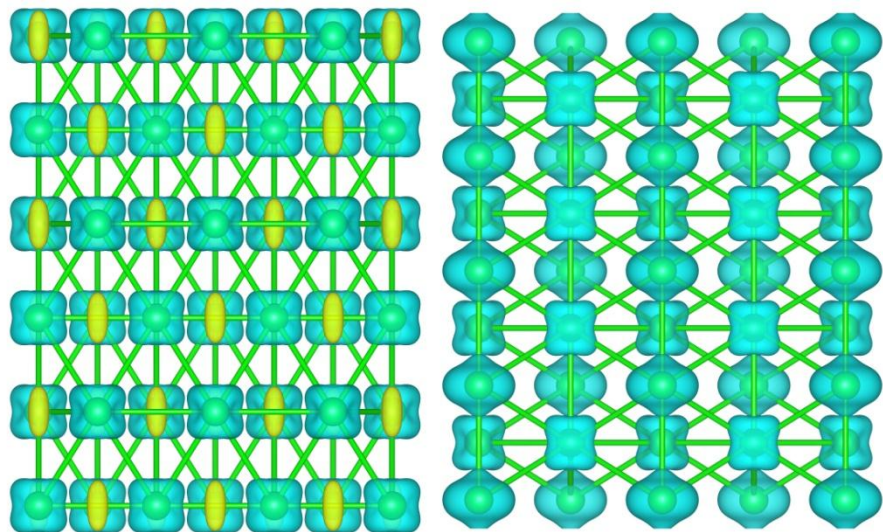
	C11	C12	C13	C33	C44	B	G
$\alpha$	146.7	68.5	71.0	163.3	26.0	97.4	33.8
$\omega$	160.9	73.7	53.6	195.1	33.8	97.6	44.7

**DFT simulations:**

**Similar B but higher G for  $\omega$**

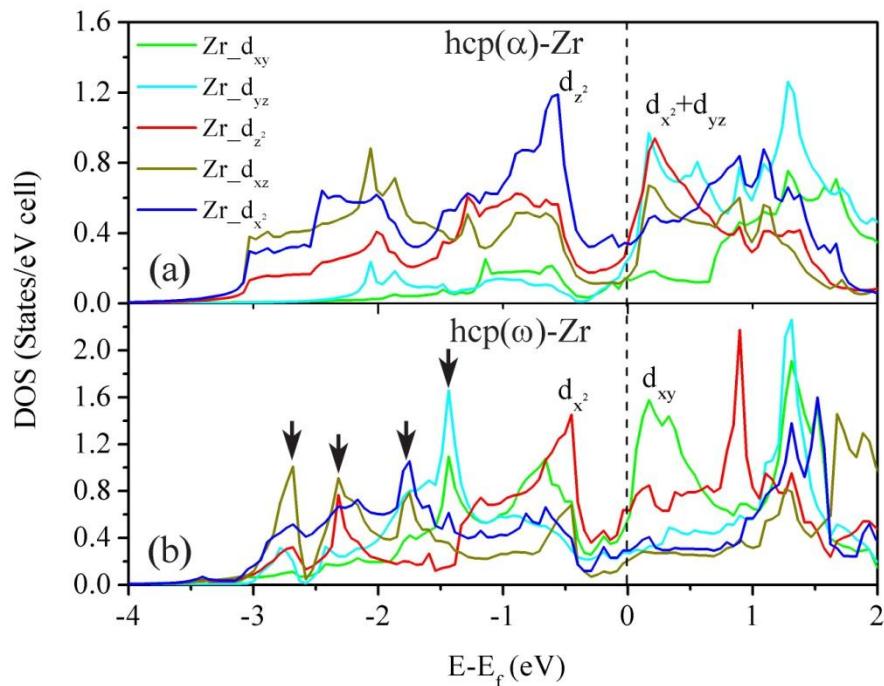
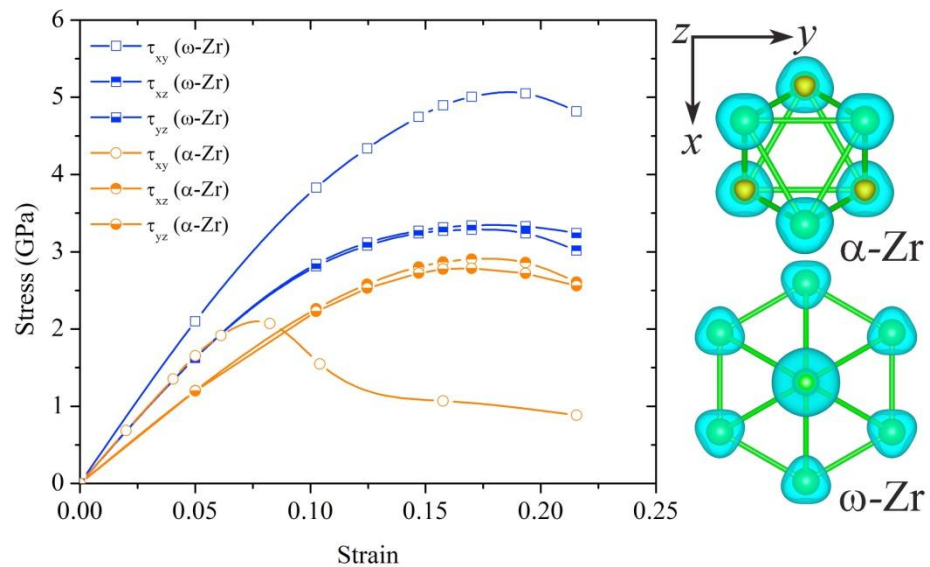
All unit in GPa

# High pressure mechanics: omega phase Zr

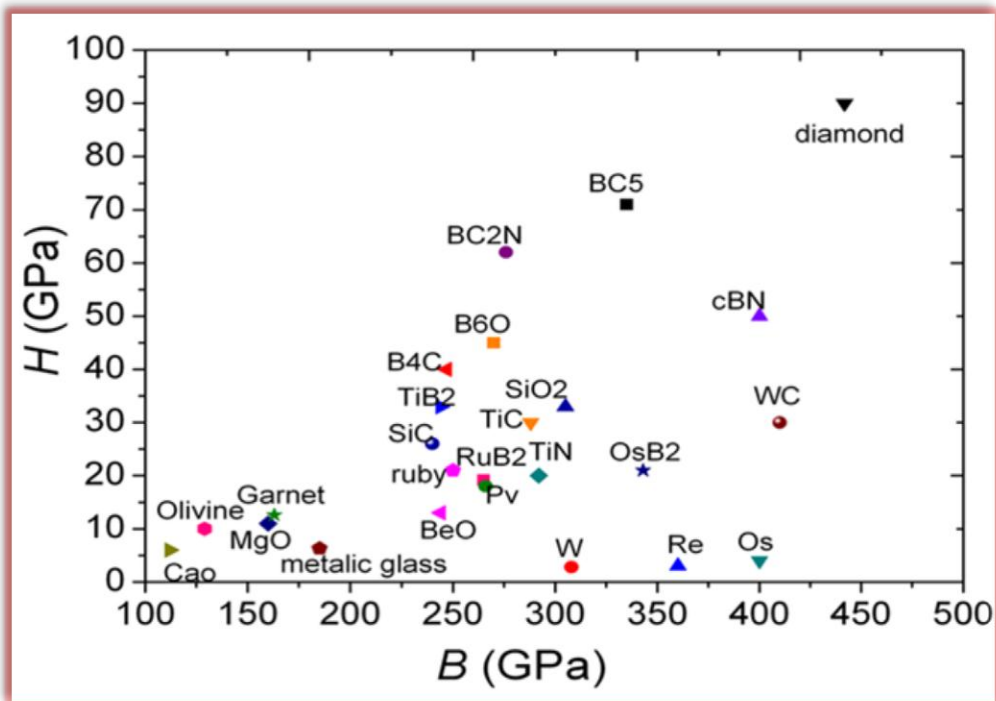


$$\tau_p = K \exp(-\alpha \zeta / b)$$

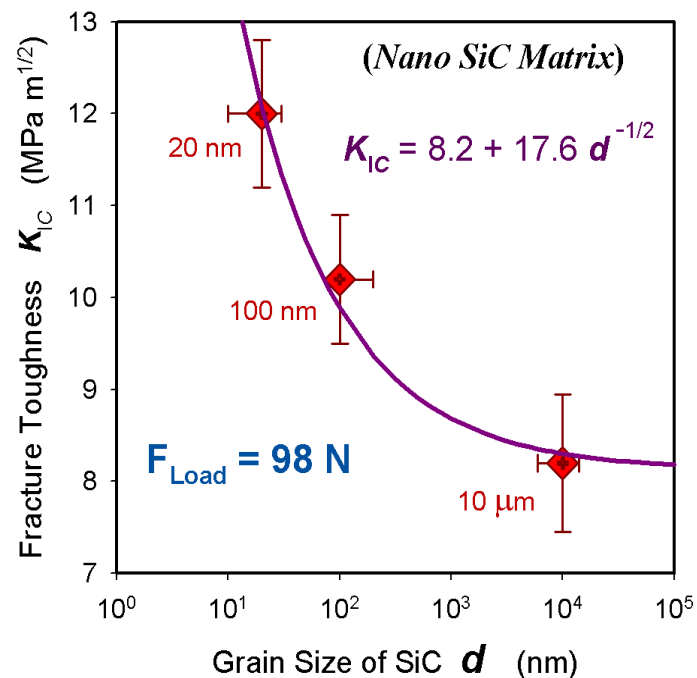
$$\zeta = Kb / 4\pi\tau_{\max}$$



# High pressure mechanics: Diamond



## Nanostructured Diamond-SiC Composites

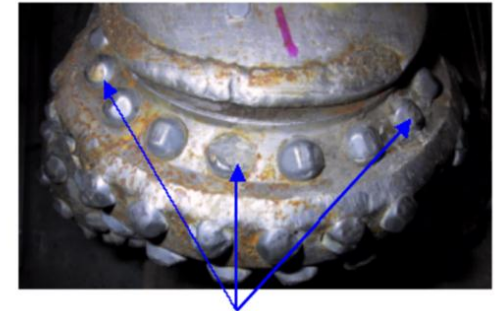
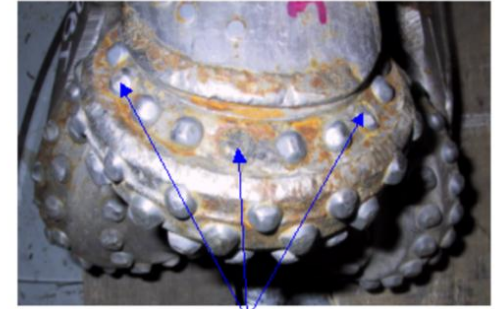
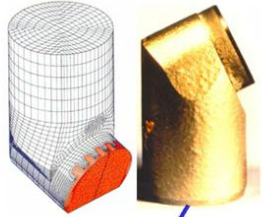
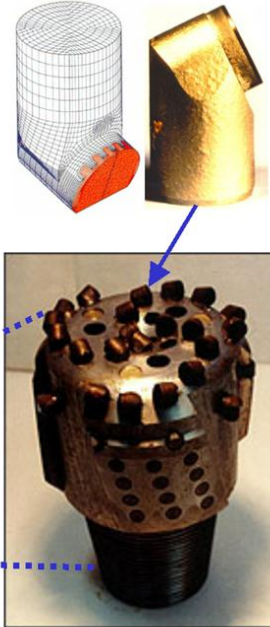
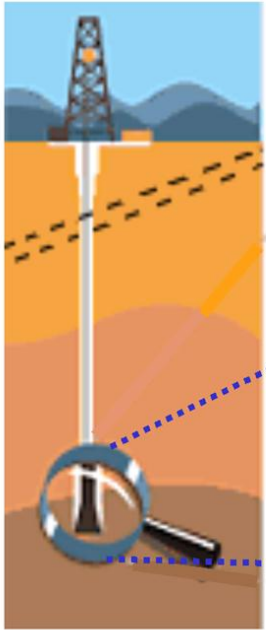


Diamond is the hardest material to mankind, but with low toughness

**No experimental study on the yield strength of diamond**

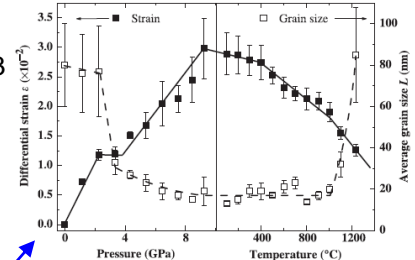
## High pressure mechanics: Diamond

- **Materials selected to be studied: Fe, Co, Ni, Diamond, TiC (component for Diamond composites).** (Jilin Uni, Sichuan Uni).
- **why high pressure?**

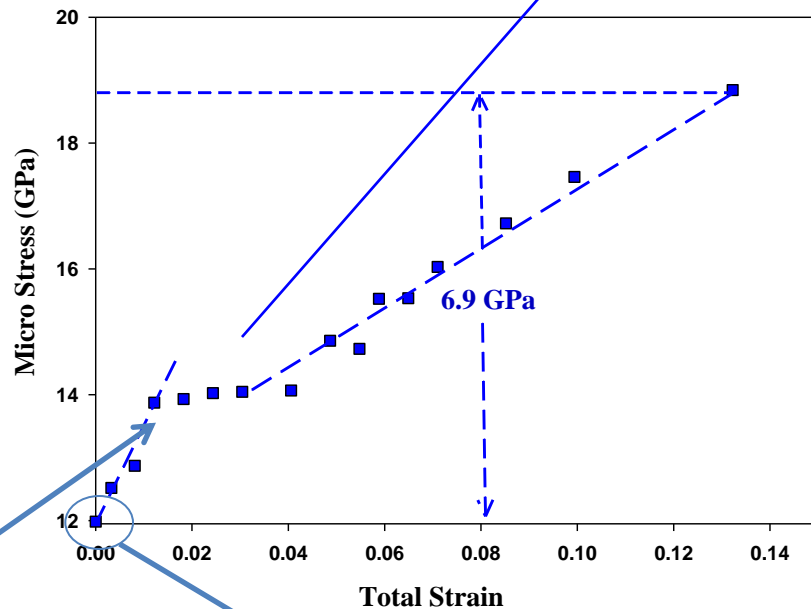
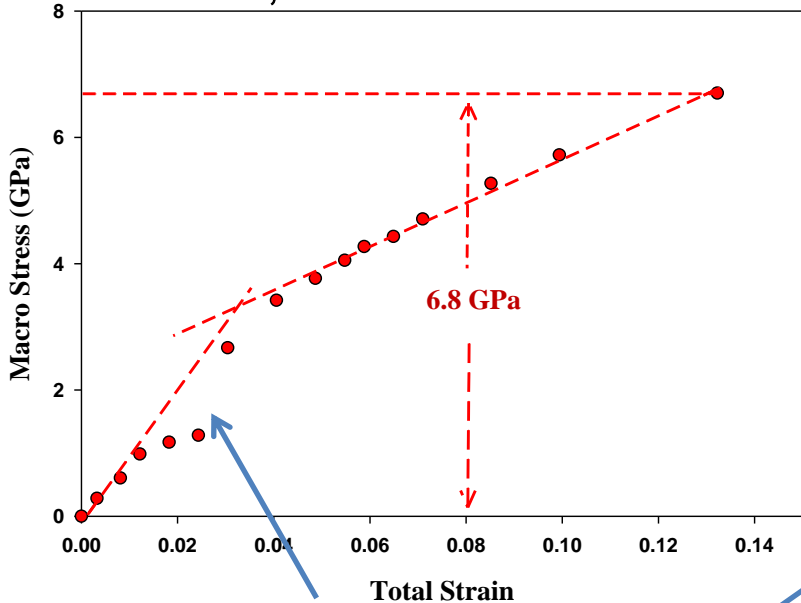


**Few studies on the yield strength of polycrystalline diamond composites component under high-pressure/high-temperature conditions.**

# High pressure mechanics: Diamond



■ Room T, 3-4 GPa

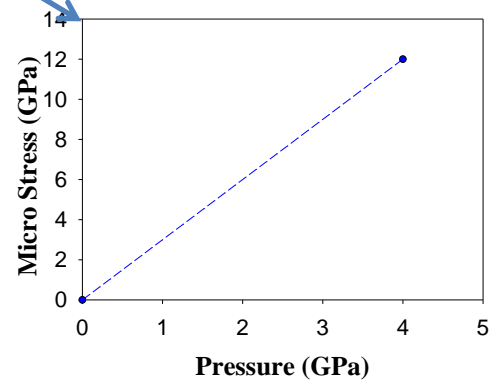


*Diamond grains start cracking*

*Elastic behavior with no yielding*

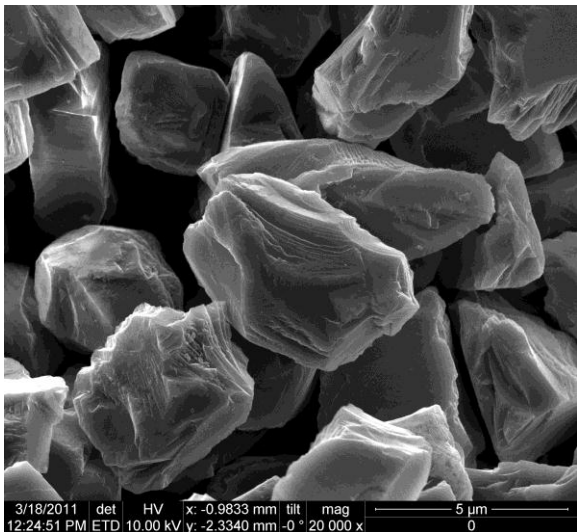
*Micro stress = Macro stress*

*Brittle Fracture!*

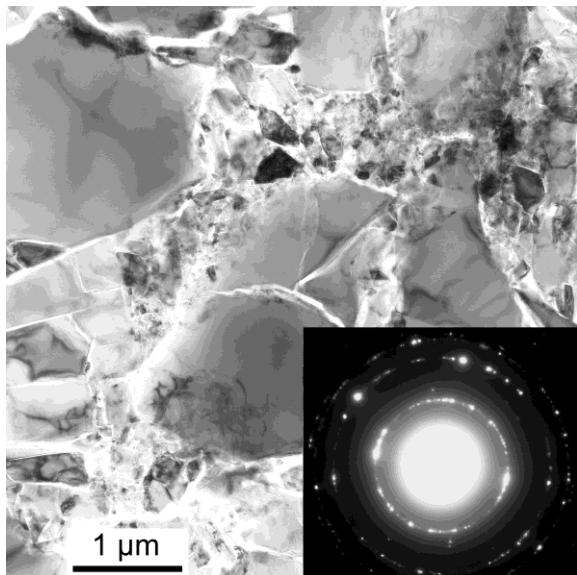
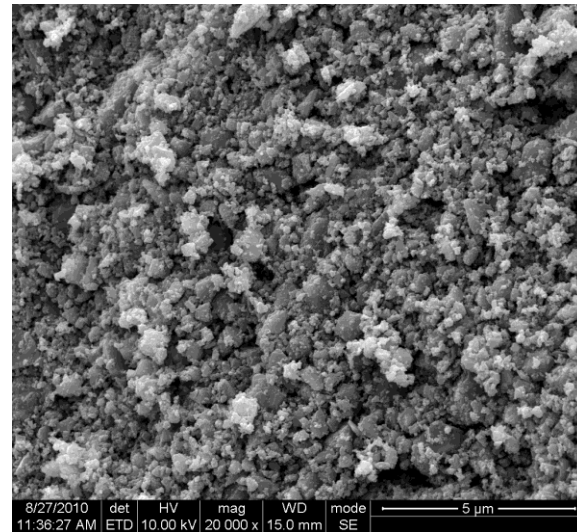


# High pressure mechanics: Diamond

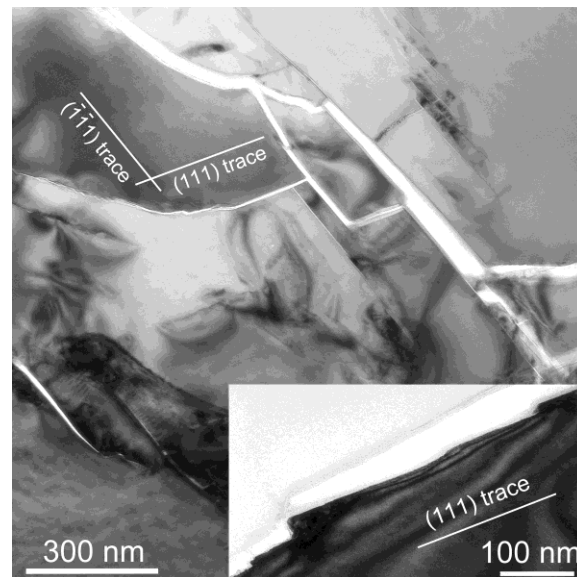
Initial



After  
deformed

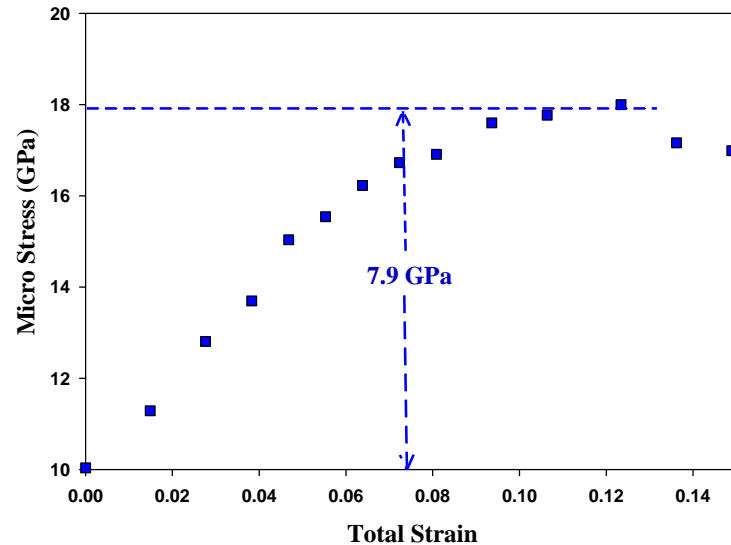
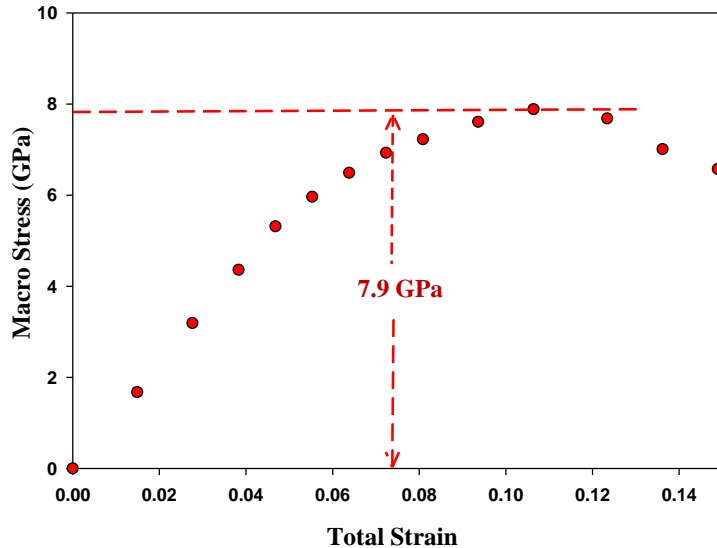


After deformed  
**TEM**  
**<111> cleavage**



# High pressure mechanics: Diamond

▪ 1000 °C, 3-4 GPa



*Plastic deformation with flow stress = 7.9 GPa*

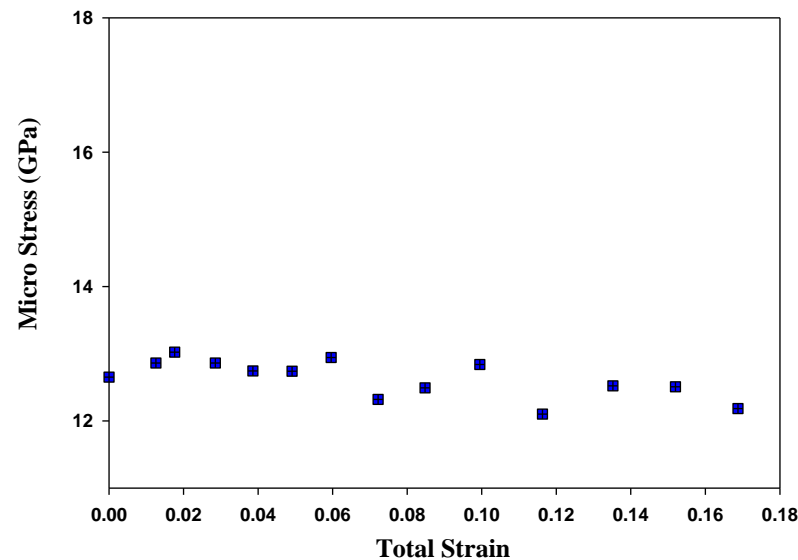
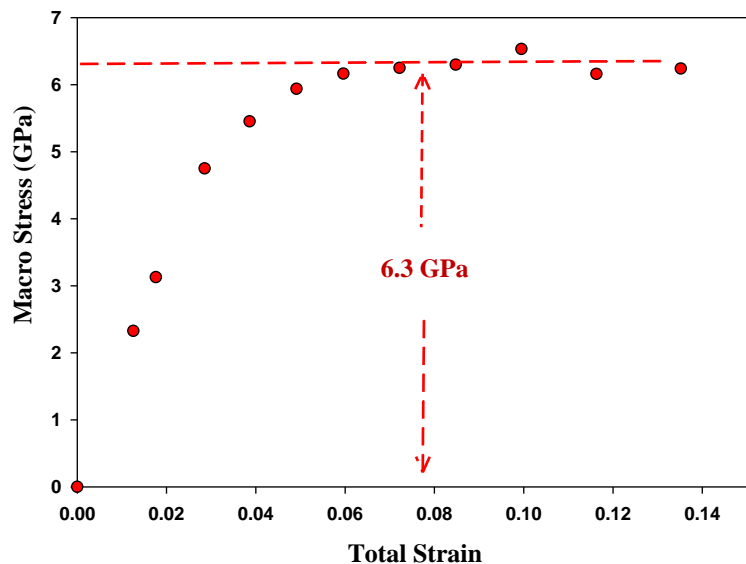
*The brittle fracture behavior at RT was not observed*

*Transition of deformation modes from brittle fracture at RT to dislocation-mediated plasticity at 1000 °C*

*Micro stress = Macro stress*

# Deformation of Diamond under high-*P*: continued

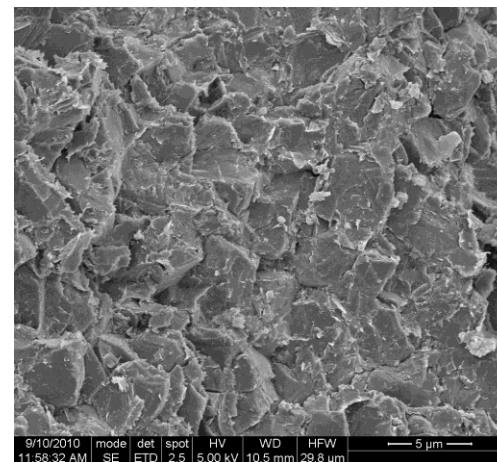
1200 ° C, 3-4 GPa



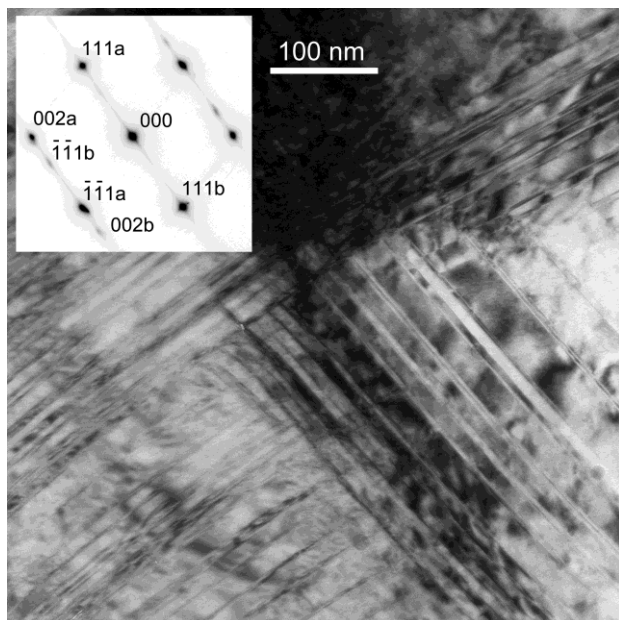
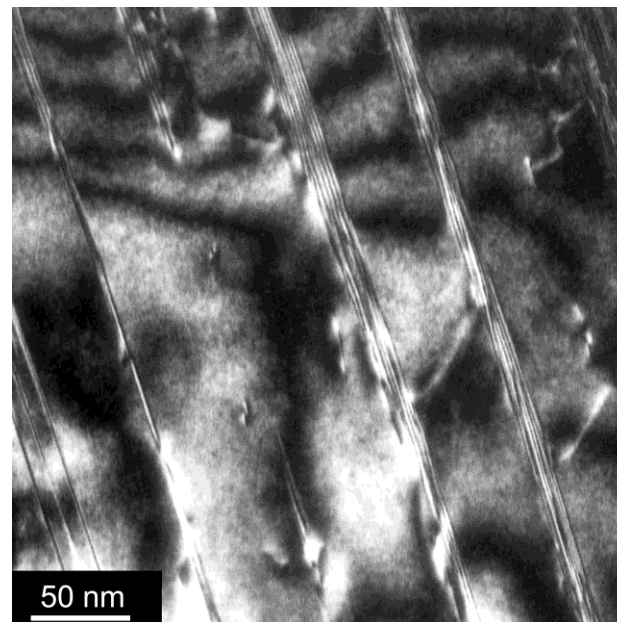
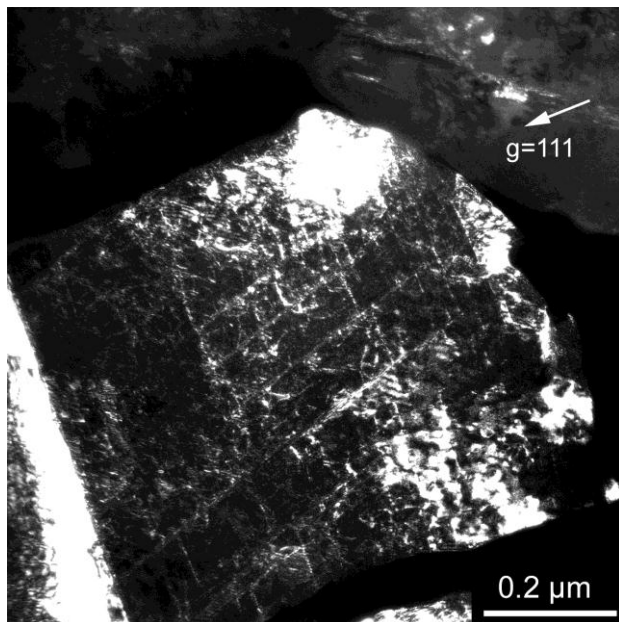
*Ductile yielding with macro flow stress = 6.3 GPa*

*Temperature induced stress relaxation as compared to observations at 1000 °C*

*No obvious grain size reduction in the recovered sample*

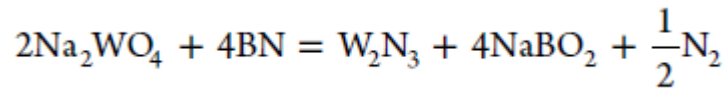
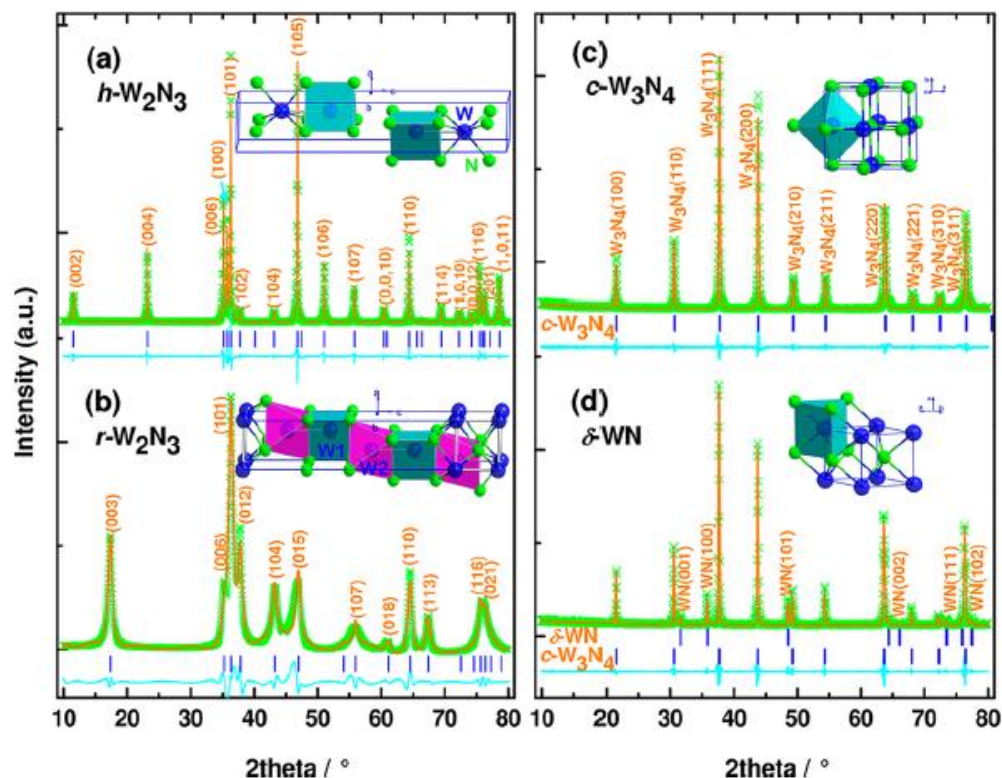


# High pressure mechanics: Diamond



**Both the dislocations  
(111) $\langle$ 110 $\rangle$  and micro twins  
work during the deformation of  
diamond**

# High pressure mechanics: $WN_x$



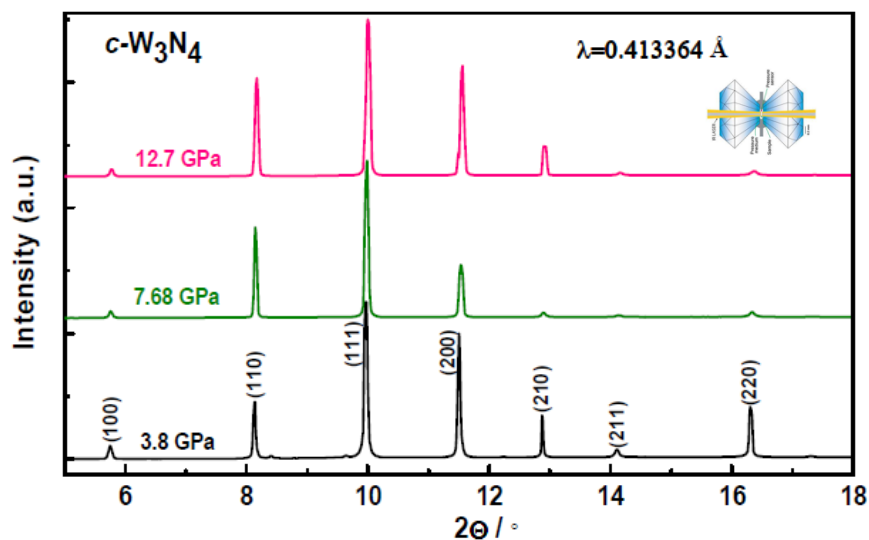
- 1) New approach to provide N to reactions
- 2) Low pressure (5 GPa) which is reality for production

Table 1. Summary of Structural Parameters for  $h\text{-W}_2\text{N}_3$ ,  $r\text{-W}_2\text{N}_3$ ,  $c\text{-W}_3\text{N}_4$ , and  $\delta\text{-WN}$  Determined by XRD Refinements

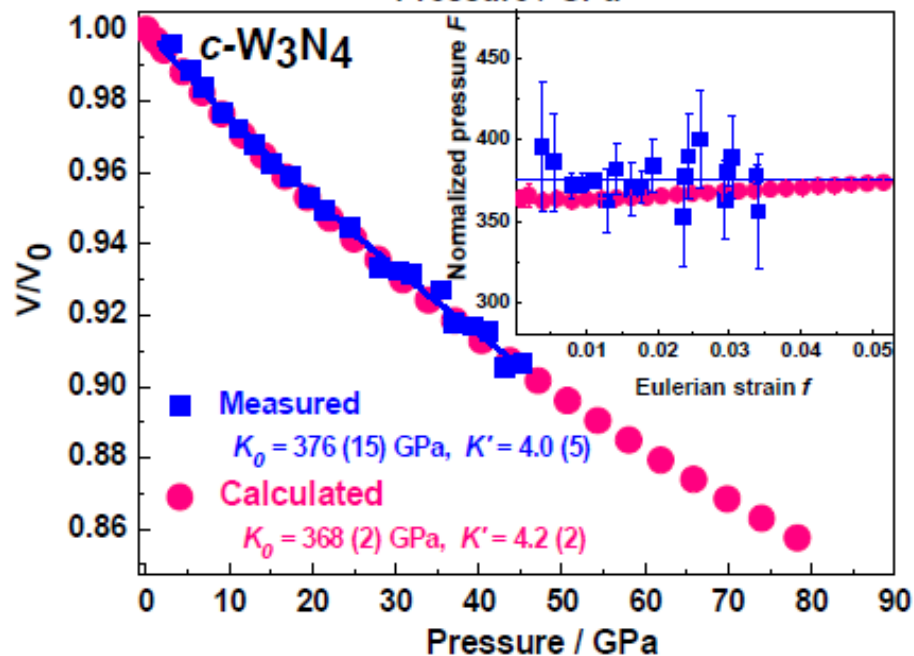
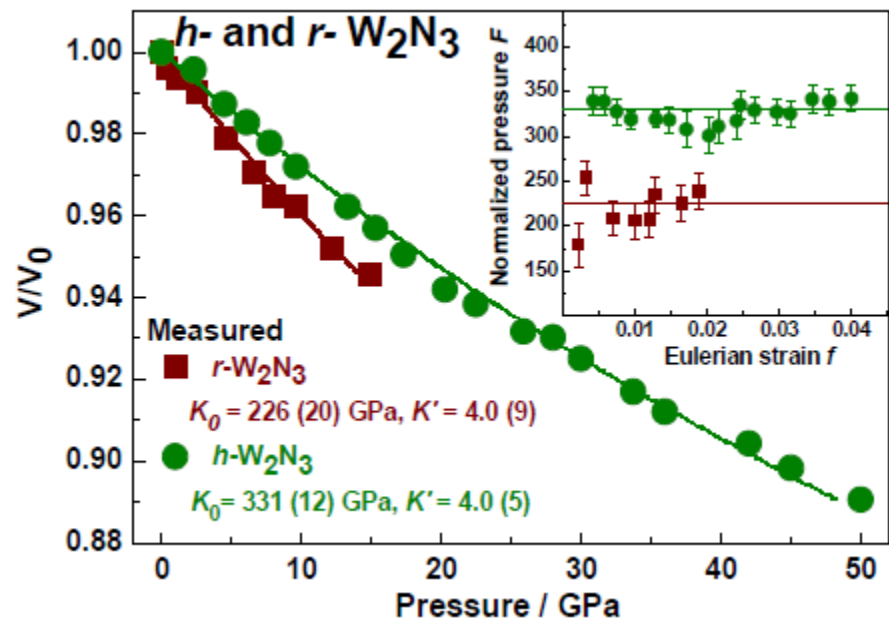
	$h\text{-W}_2\text{N}_3$	$r\text{-W}_2\text{N}_3$	$c\text{-W}_3\text{N}_4$	$\delta\text{-WN}$
space group	$P6_3/mmc$ (No. 194)	R3 (No. 146)	$Pm\bar{3}m$ (No. 221)	$P\bar{6}2m$ (No. 187)
$a_0, c_0$ (Å)	2.890(3), 15.286(2)	2.889(7), 15.291(5)	4.125(6)	2.895(5), 2.830(4)
$\rho$ (g cm <sup>-3</sup> )	12.31	12.29	14.37	16.00
W positions	$4f, (1/3, 2/3, 0.840)$	$3a, (0, 0, 0)$ $3a, (0, 0, 0.831)^a$	$3c, (1/2, 1/2, 0)$	$1a, (0, 0, 0)$
N positions	$4f, (1/3, 2/3, 0.070)$ $2c, (1/3, 2/3, 1/4)$	$3a, (0, 0, 0.249)$ $3a, (0, 0, 0.416)$	$1b, (1/2, 1/2, 1/2)$ $3d, (1/2, 0, 0)$	$1d, (1/3, 2/3, 1/2)$
$d_{W-N}$ (Å)	2.163(3)	2.090(4), 2.104(4), 2.111(5)	2.063(4)	2.190(3)
$R_p$ (%)	8.64	6.82	8.78	7.96

<sup>a</sup>S.O.F. = 0.3333.

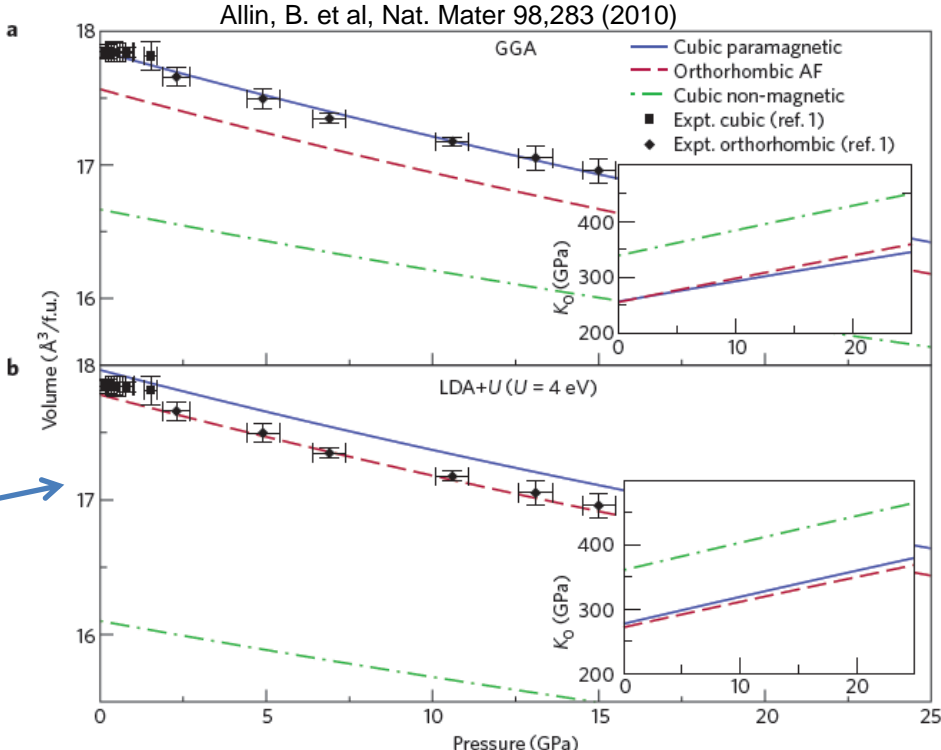
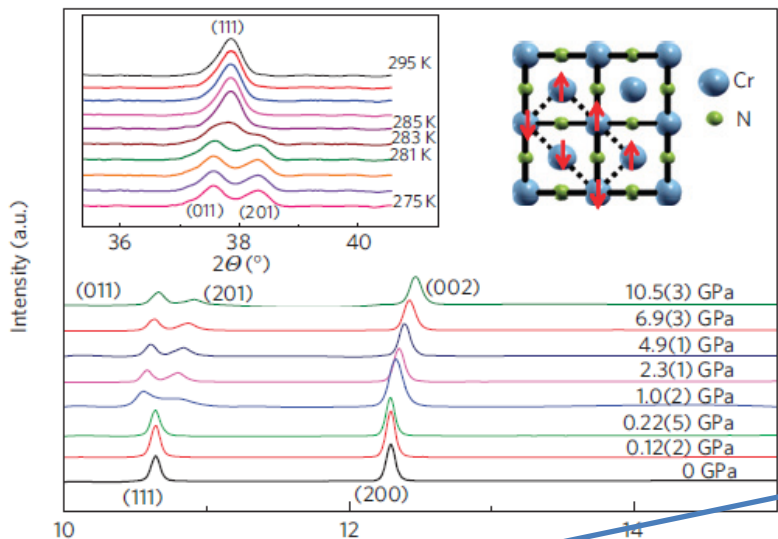
# High pressure mechanics: $WN_x$



- 1) He gas as pressure media, which guarantee good hydrostatic pressure up to 50 GPa.
- 2) High B was found in  $c-W_3N_4$ , comparable to  $c-BN$

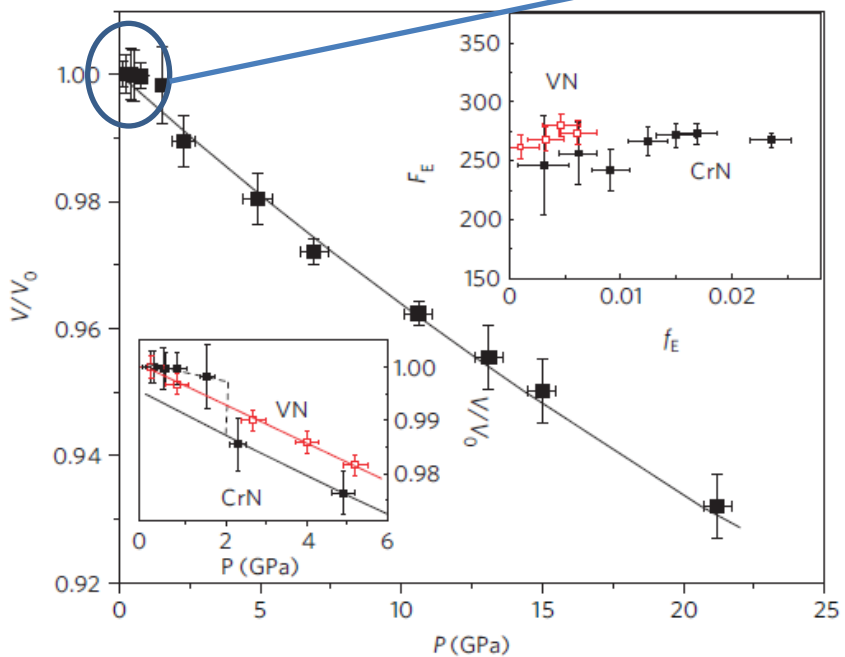


# High pressure mechanics: CrN<sub>x</sub>



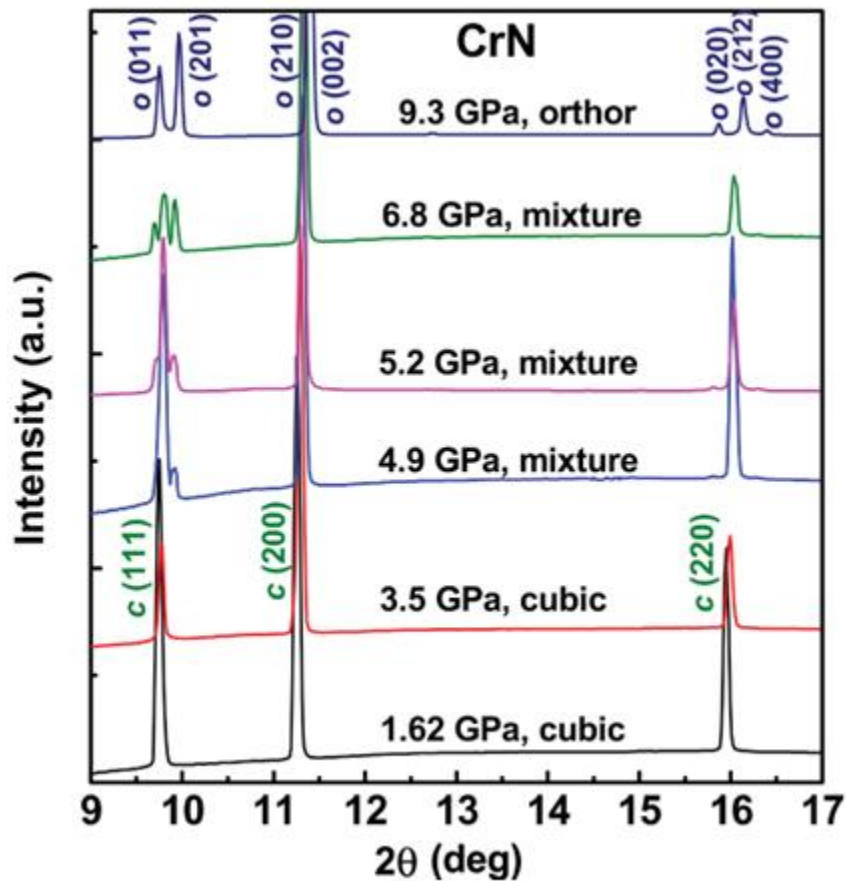
**Questioned by Allin, the simulation didn't count for spin! No Reduction!**

**No experimental data !!!**

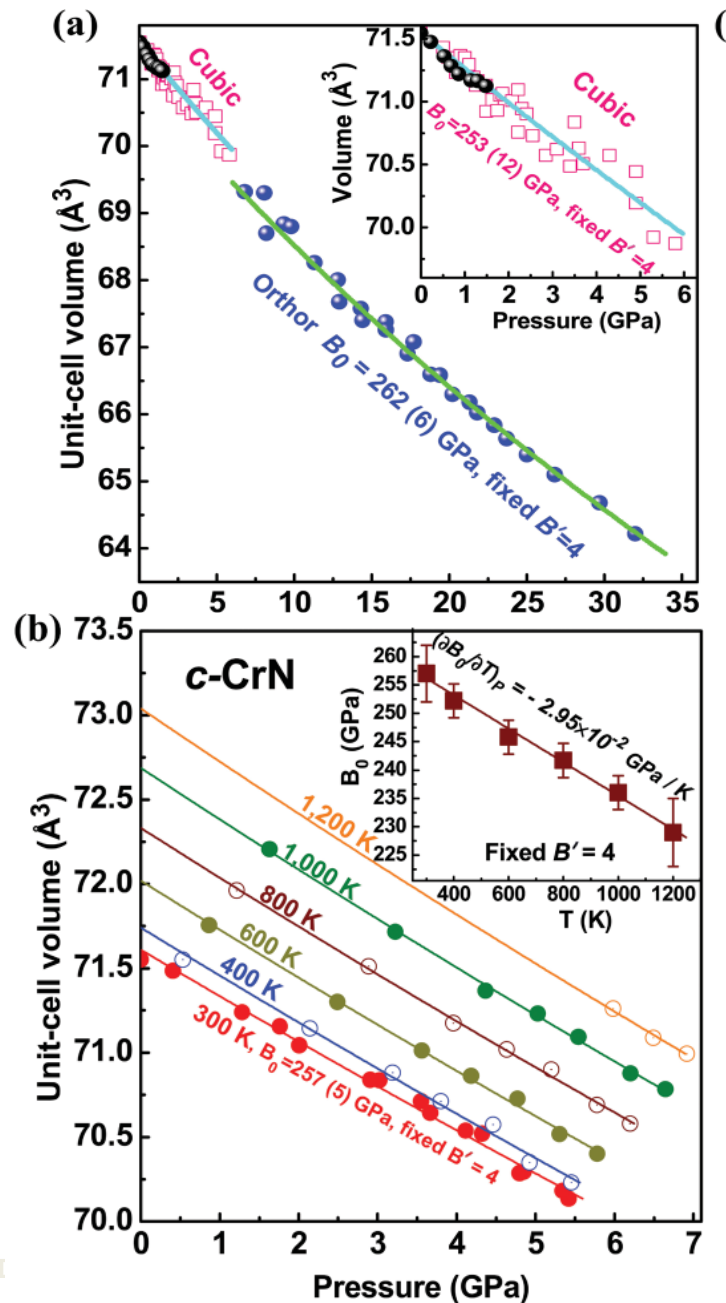


Ravadulla, F. et al, Nat. Mater 8,947 (2009)

# High pressure mechanics: $\text{CrN}_x$



No reduction of the bulk modulus at high pressure phase!



# Acknowledgement

**The work was performed under the supervision of:**

**IOP:**

**Prof. Jin, Changqing**

**LANL:**

**Prof. Yusheng Zhao**

**Experiment was conducted at X17B2 of NSLS, BNL**

**Beam Line Scientist at X17B2: Dr. Liping Wang**

**13-BM-D of APS, ANL**

**Beam Line Scientist at 13-BM-D: Dr. Yanbin Wang**

***Thank You!***