Bonding changes in compressed, superhard graphite

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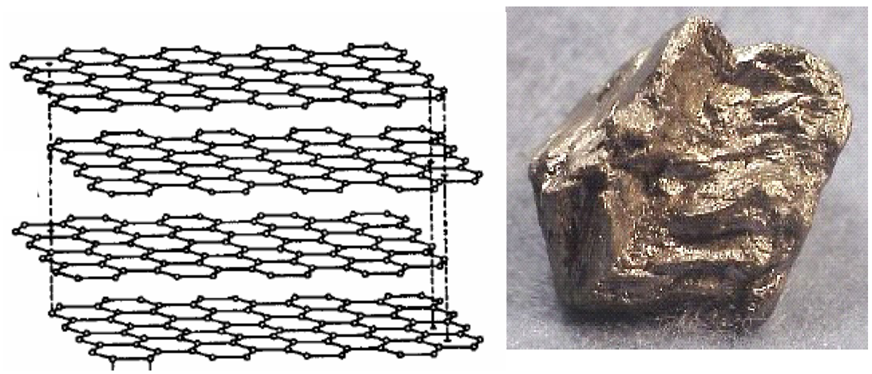
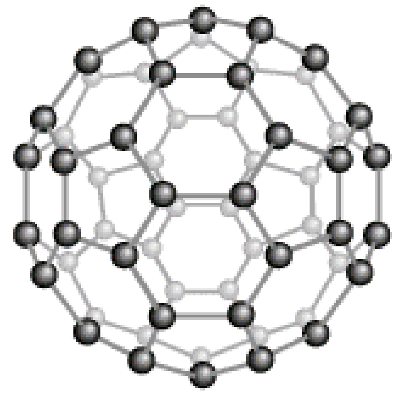
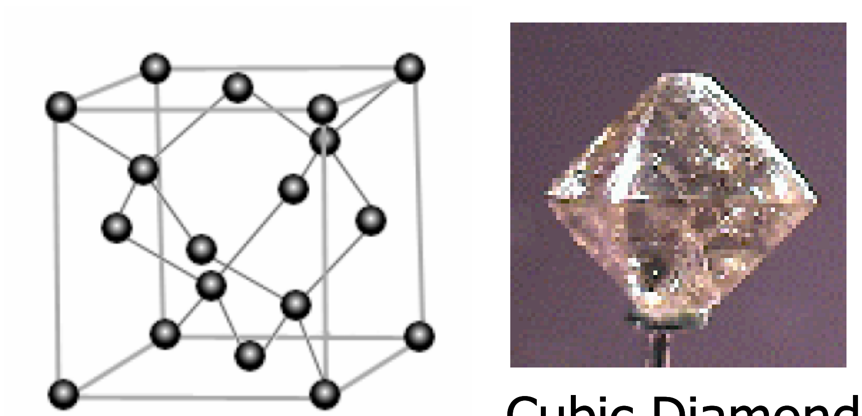
Studying Materials at High Pressure



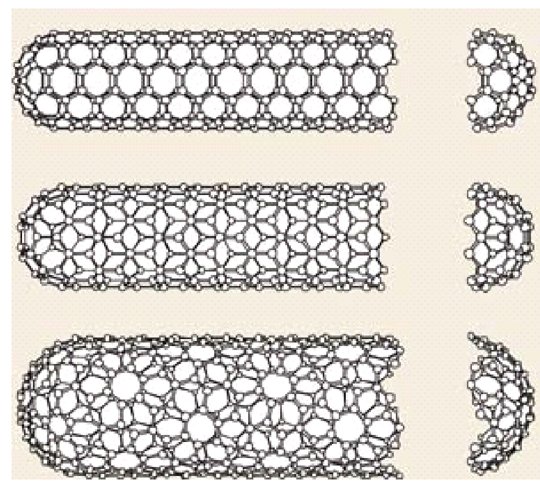
Graphite



Buckminsterfullerene

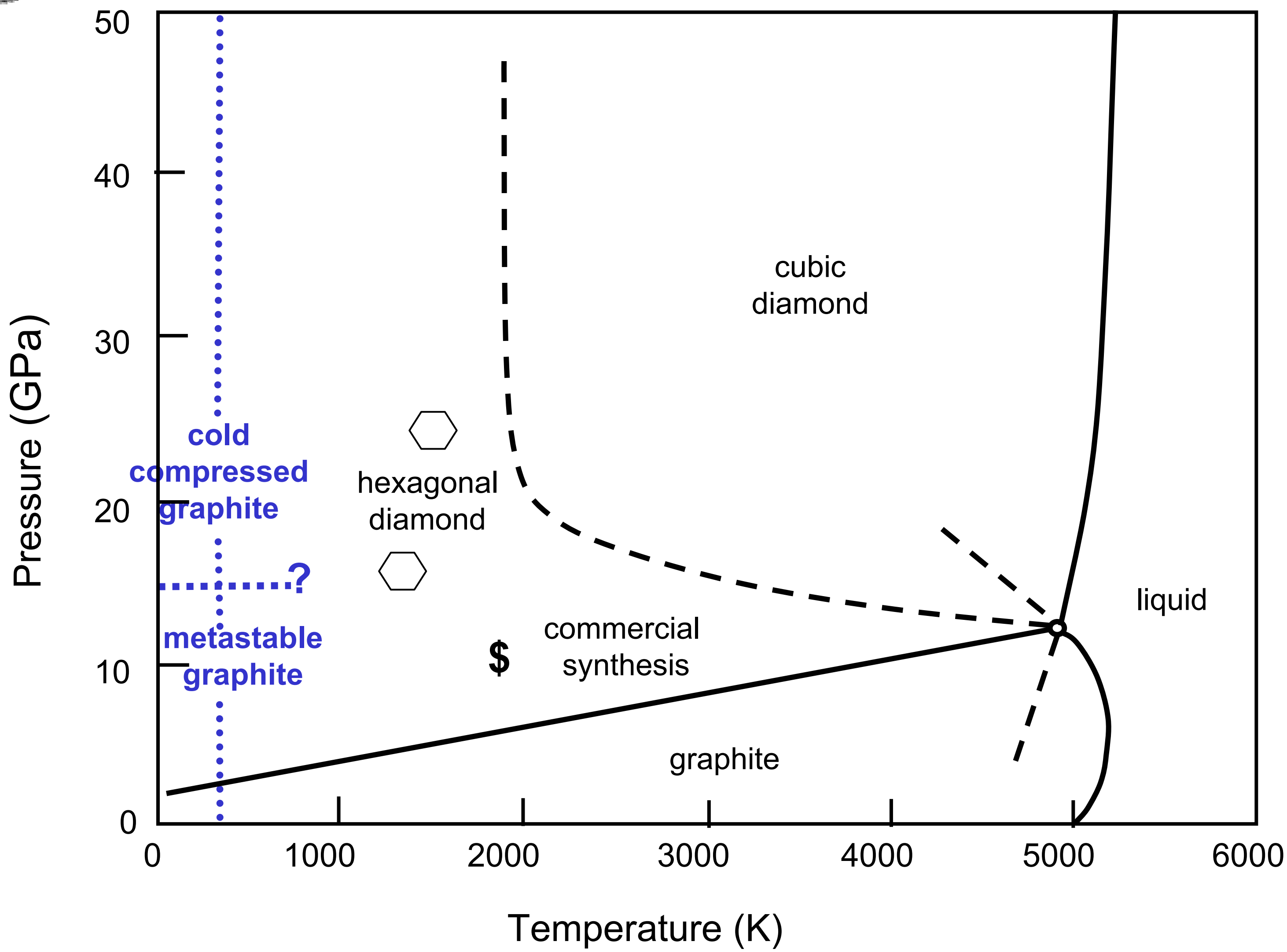


Cubic Diamond



Nanotubes

Carbon phase and reaction diagram



After Bundy *et al*, Carbon 1996

Cold Compression of Graphite

What's the nature of the transition in graphite compressed at ambient temperature?

Previous *in-situ* observations of cold compressed graphite:

- Increase in electrical resistivity from semi-metal to insulator at 12 GPa (Aust and Drickamer, 1963; Bundy and Kasper, 1967)
- Optical transmittance above 18 GPa (Utsumi and Yagi, 1991); Drop in optical reflectivity 19 GPa (Hanfland et al, 1989)
- Broadening of higher frequency E_{2g} line (9 GPa by Hanfland et al, 1989; 15–35 GPa by Goncharov et al, 1989); Transition at 18 GPa, but no first order diamond peak (Xu et al, 2002)
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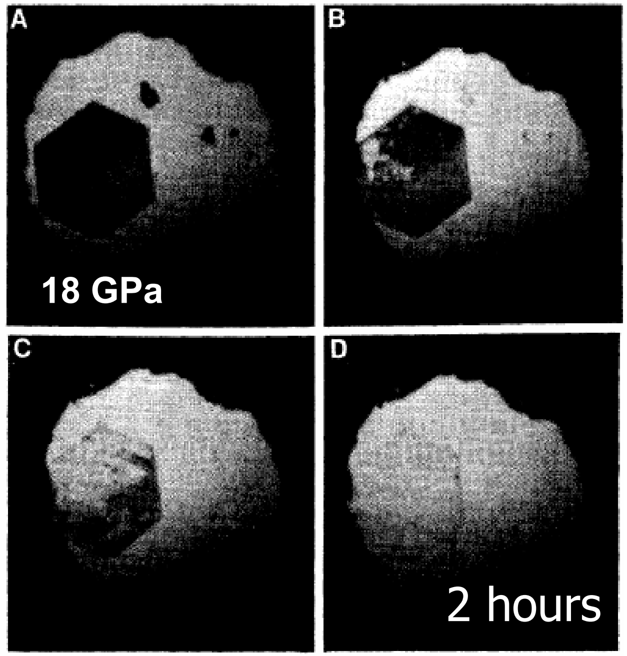
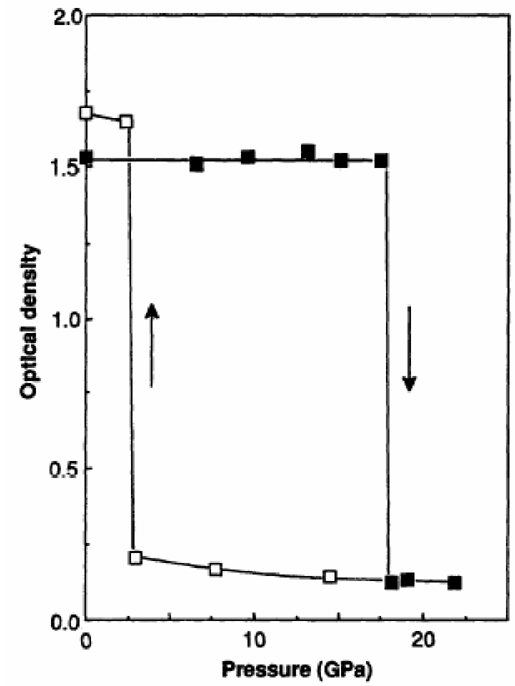
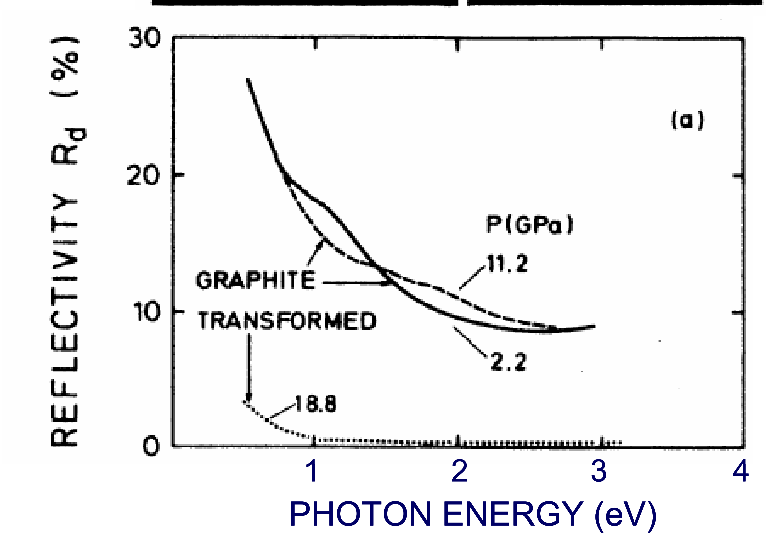
Optical transmission and reflectivity





Utsumi and Yagi, Science 1991



Hanfland *et al*, PRB 1989

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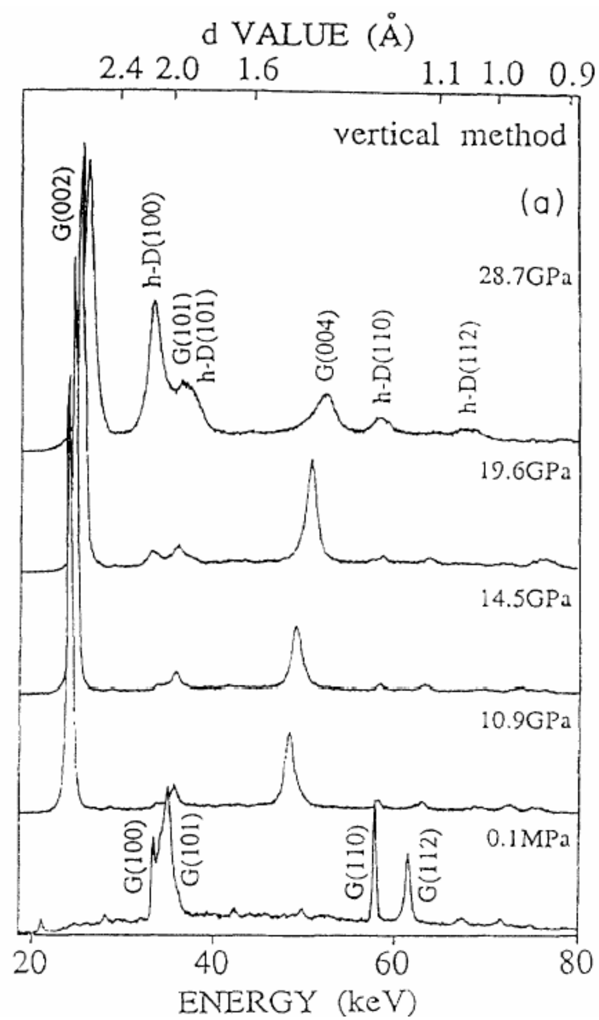
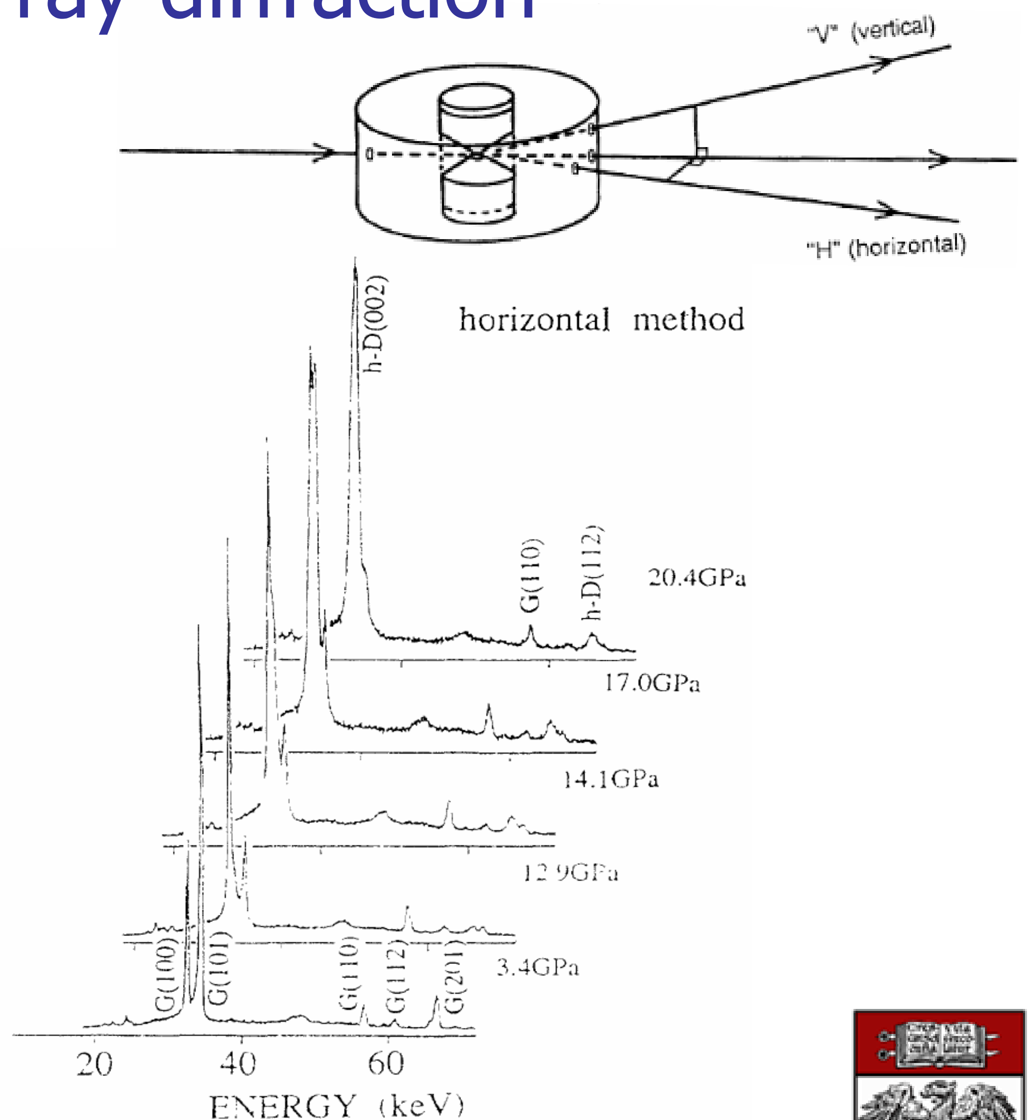
Synchrotron X-ray diffraction





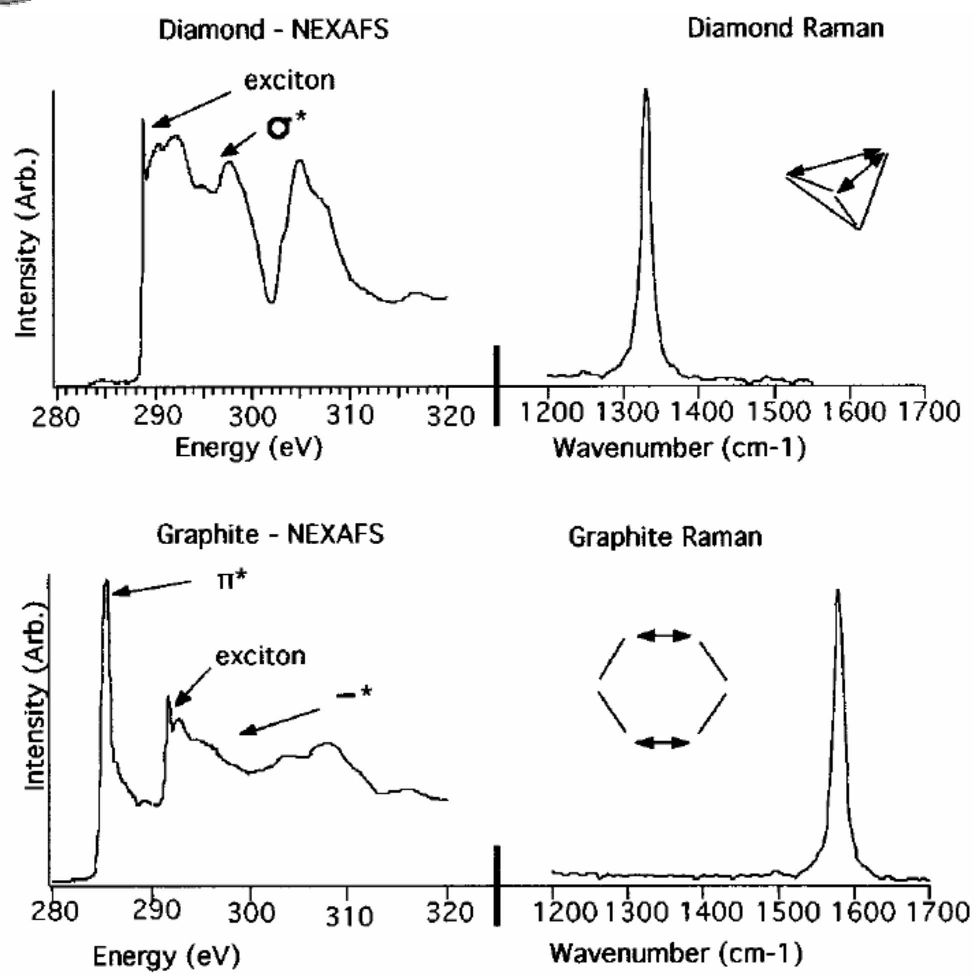
Yagi *et al*, PRB 1992

Cold Compression of Graphite

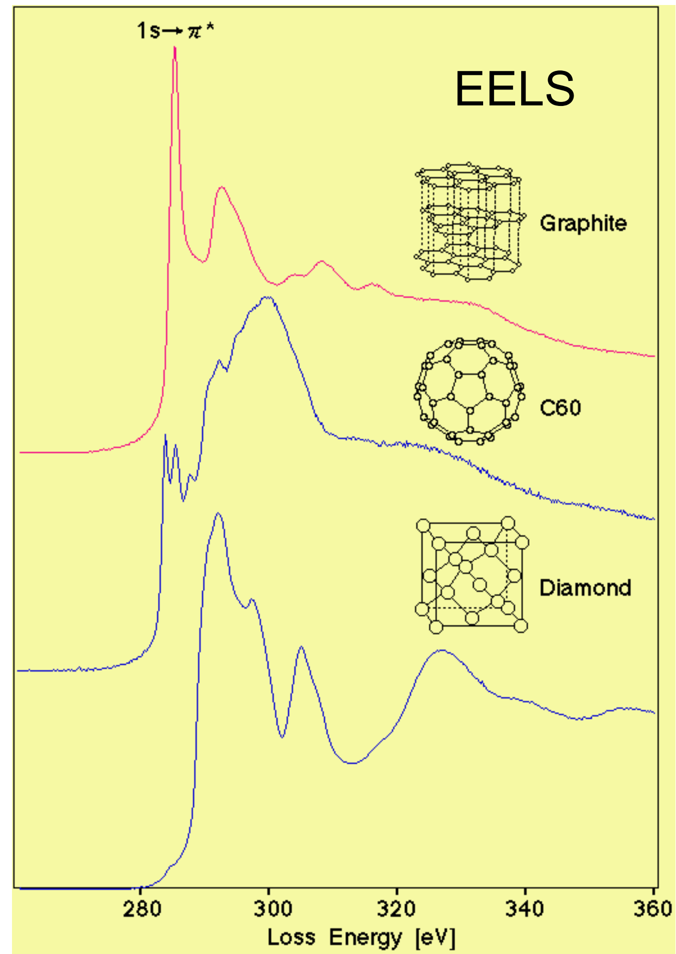
What’s the nature of the transition in graphite compressed at ambient temperature?

- What is the nature of the bonding changes?
  - Use inelastic x-ray scattering spectroscopy (x-ray raman) to directly measure unfilled electronic states, giving the chemical bonding state, which allows characterization of the π- and σ- bonding changes in compressed graphite
- What is the atomic arrangement?.
  - X-ray diffraction (XRD) under hydrostatic conditions to investigate structural changes.
- Is this a new phase of carbon?

Carbon Near Edge Structure



Coffman *et al*, APL 1996



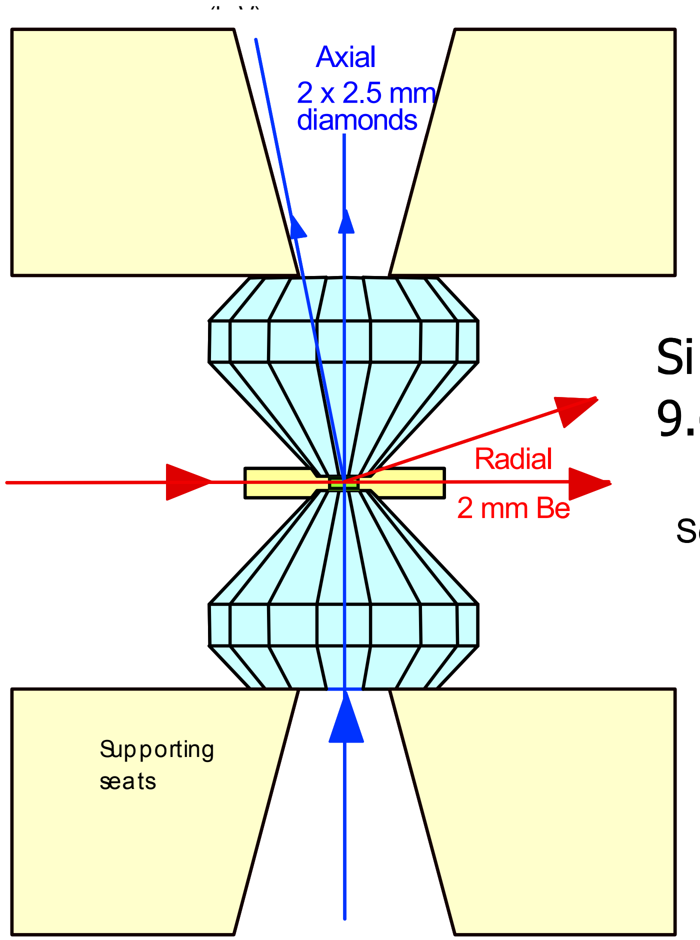
http://eels.kuicr.kyoto-u.ac.jp

Motivation

- How do we probe K-edge of low Z elements at HP?
- Sample environment at HP incompatible with techniques that require vacuum

Element	K 1s	L_1 2s	L_2 $2p_{1/2}$	L_3 $2p_{3/2}$	M_1 3s	M_2 $3p_{1/2}$	M_3 $3p_{3/2}$
1 H	13.6						
2 He	24.6*						
3 Li	54.7*						
4 Be	111.5*						
5 B	188*						
6 C	284.2*						
7 N	409.9*	37.3*					
8 O	543.1*	41.6*					
9 F	696.7*						
10 Ne	870.2*	48.5*	21.7*	21.6*			
11 Na	1070.8†	63.5†	30.65	30.81			
12 Mg	1303.0†	88.7	49.78	49.50			
13 Al	1559.6	117.8	72.95	72.55			
14 Si	1839	149.7*b	99.82	99.42			
15 P	2145.5	189*	136*	135*			
16 S	2472	230.9	163.6*	162.5*			
17 Cl	2822.4	270*	202*	200*			
18 Ar	3205.9*	326.3*	250.6†	248.4*	29.3*	15.9*	15.7*
19 K	3608.4*	378.6*	297.3*	294.6*	34.8*	18.3*	18.3*
20 Ca	4038.5*	438.4†	349.7†	346.2†	44.3 †	25.4†	25.4†
21 Sc	4492	498.0*	403.6*	398.7*	51.1*	28.3*	28.3*
22 Ti	4966	560.9†	460.2†	453.8†	58.7†	32.6†	32.6†

Inelastic Scattering



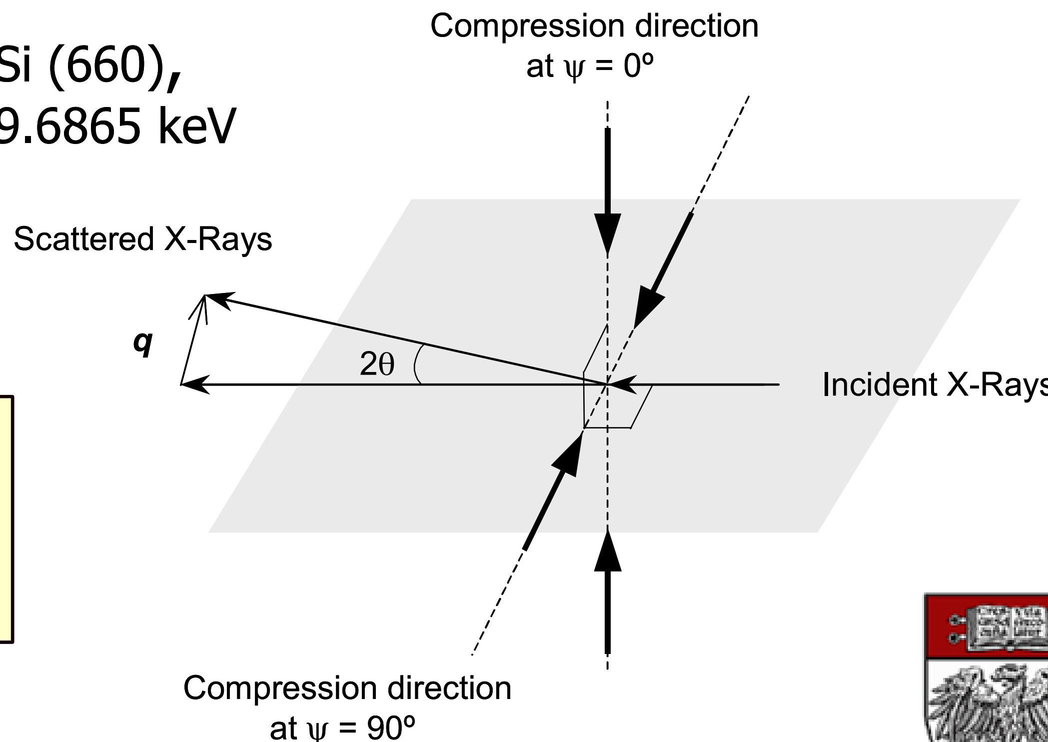
Incident x-rays (monochromator)

Energy loss (k-edge)

Scattered x-rays (analyzer)

$$\Delta E = E - E_0$$

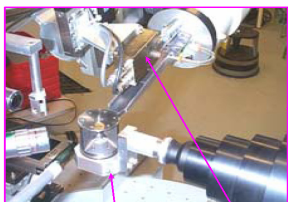
Si (660),
9.6865 keV

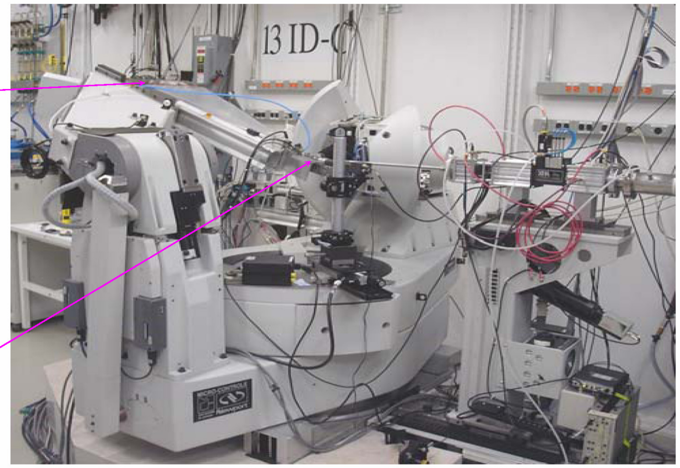


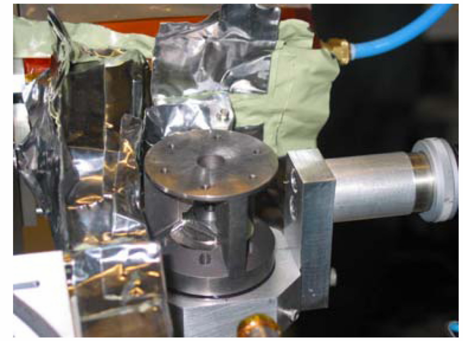
IXS Set-up

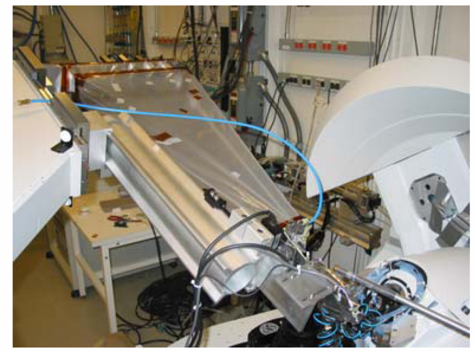
13-IDC, GSECARS, APS, ANL

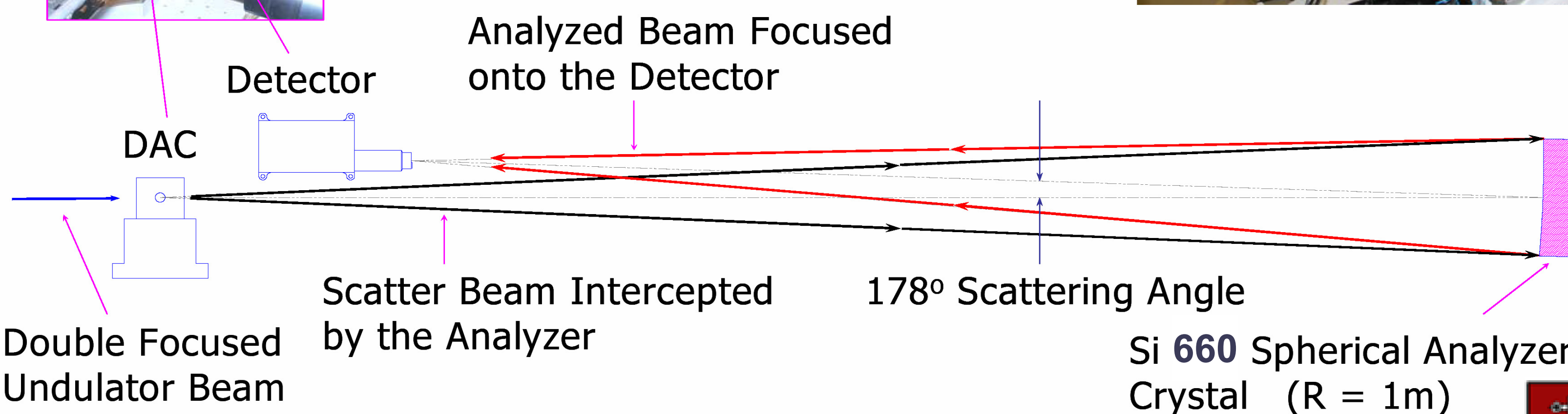
Si Analyzer Crystals

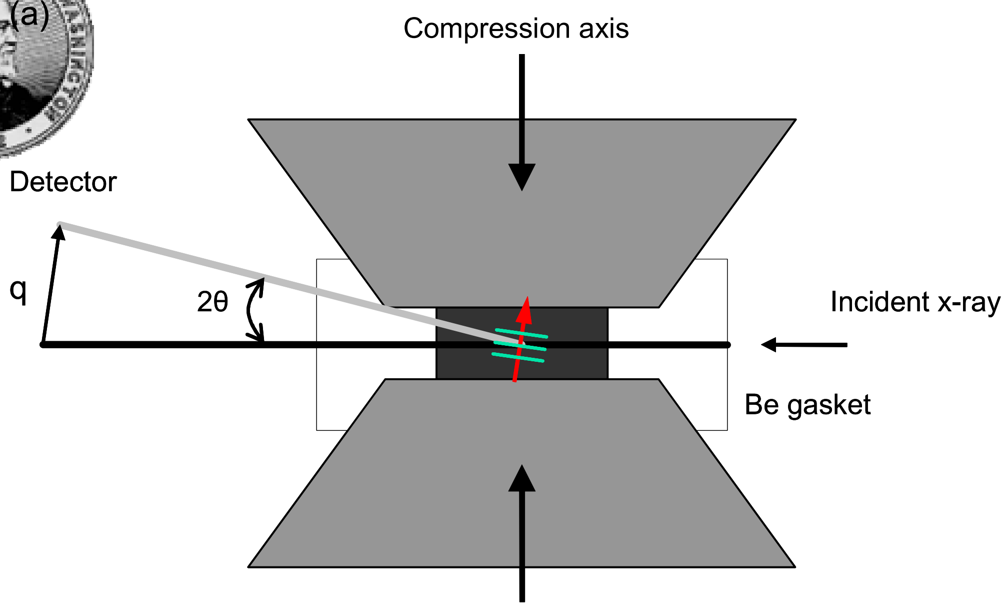




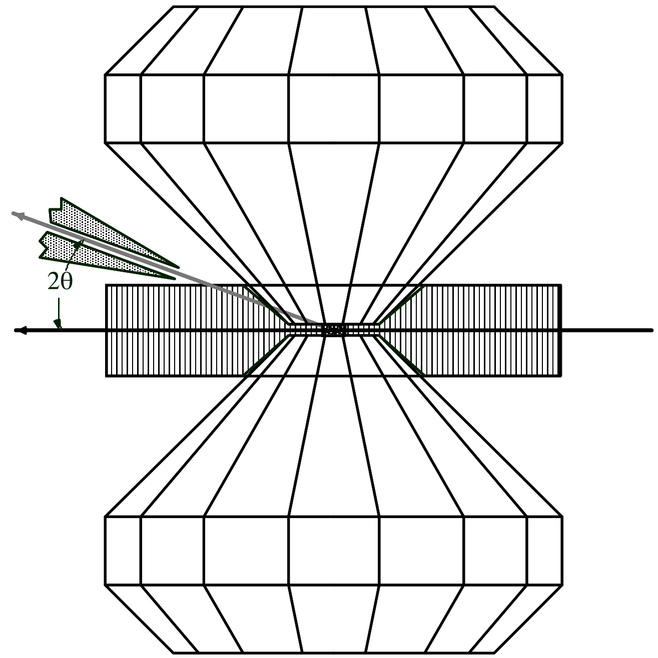


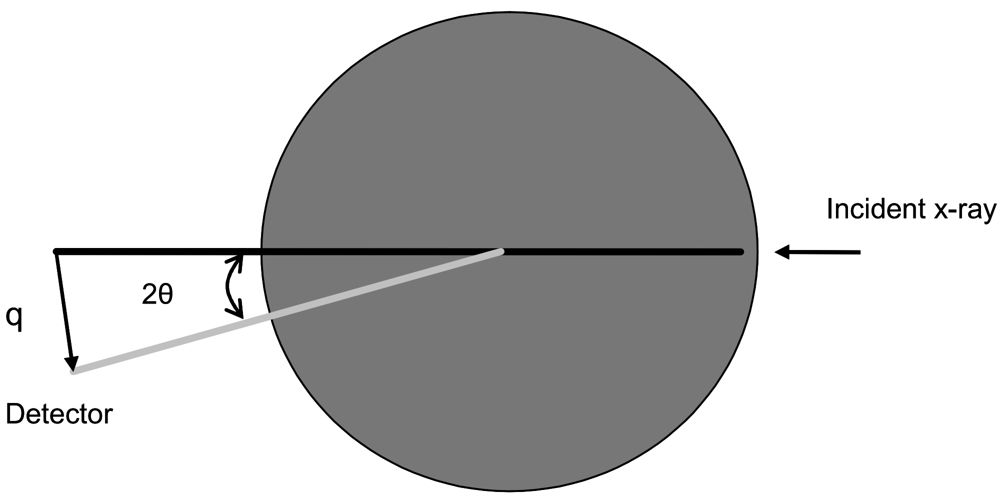




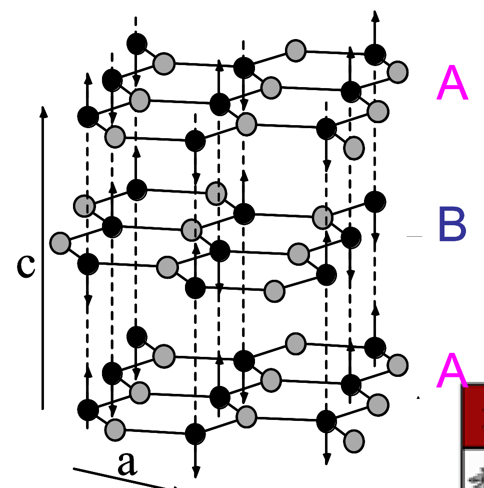


Vertical geometry - measures c-axis

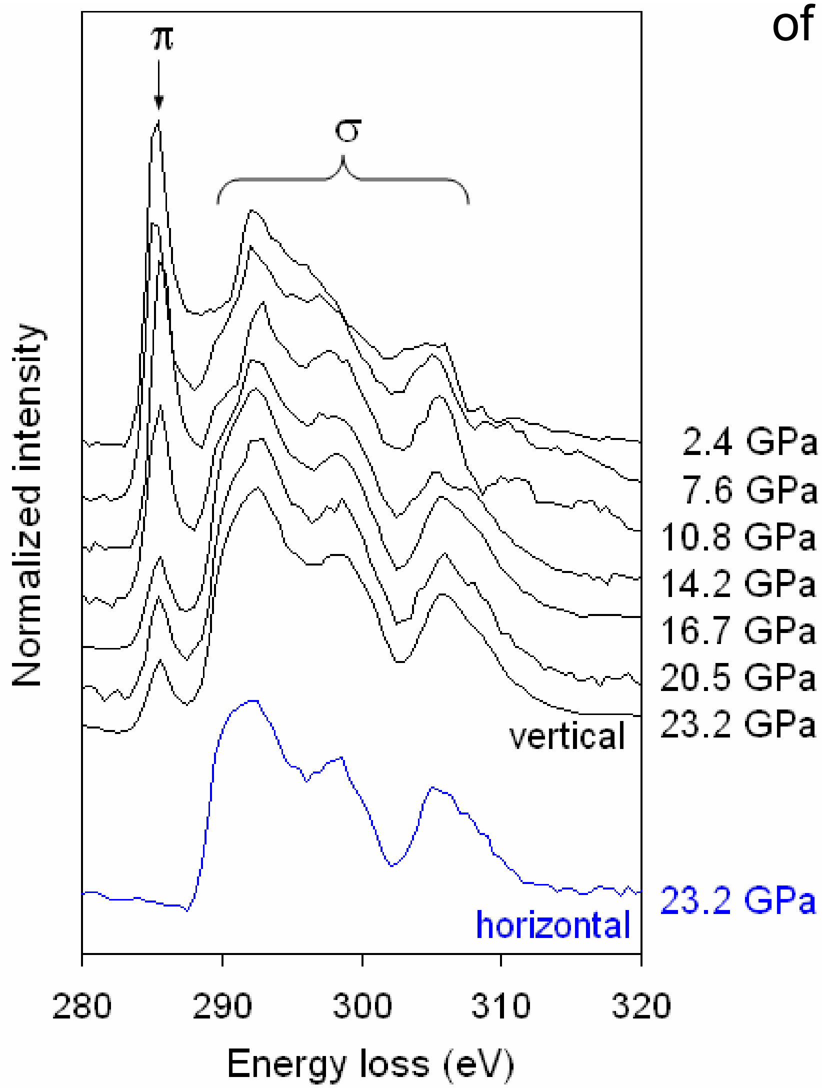




Horizontal geometry - measures a-axis

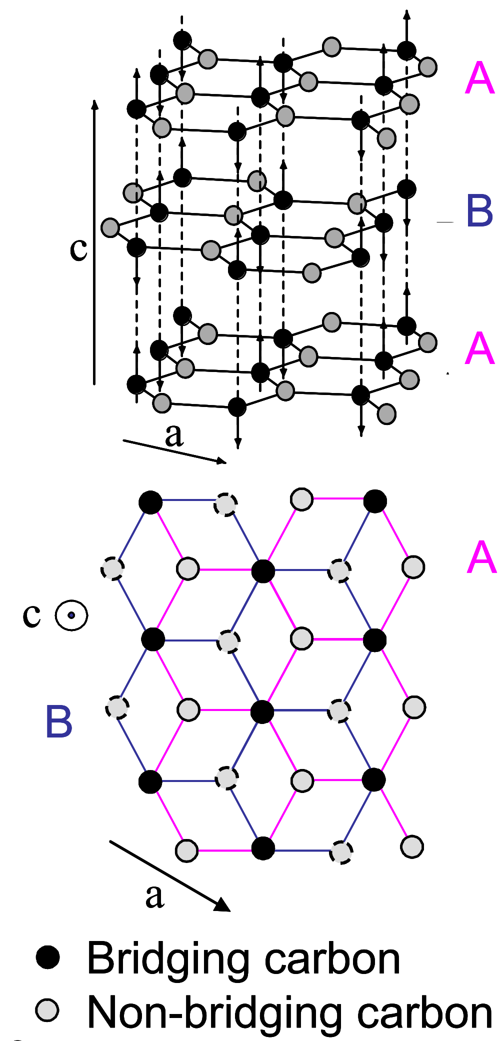


IXS Spectra

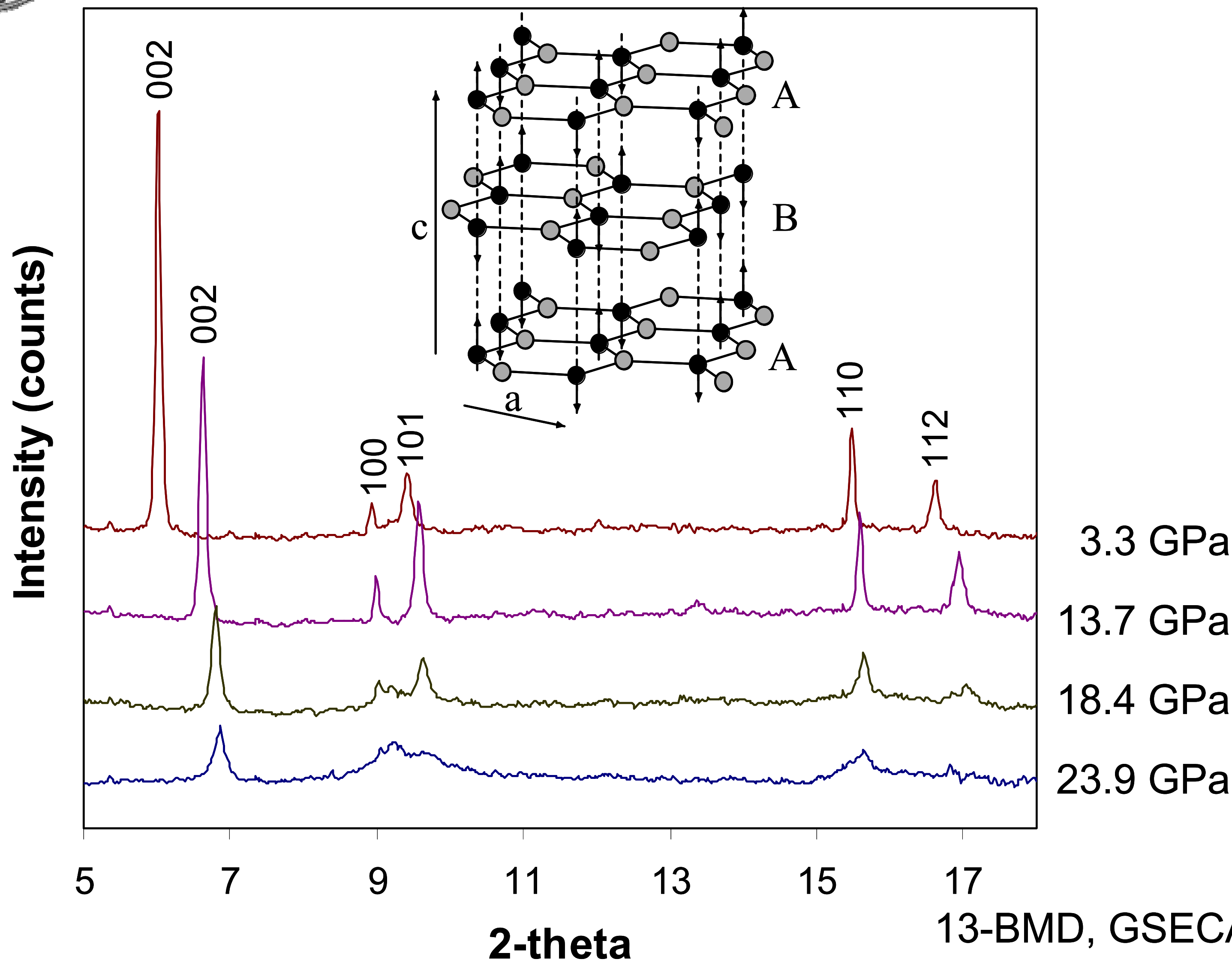


W. Mao *et al*, Science 2003

•Conversion of approximately half of π-bonds ~17 GPa

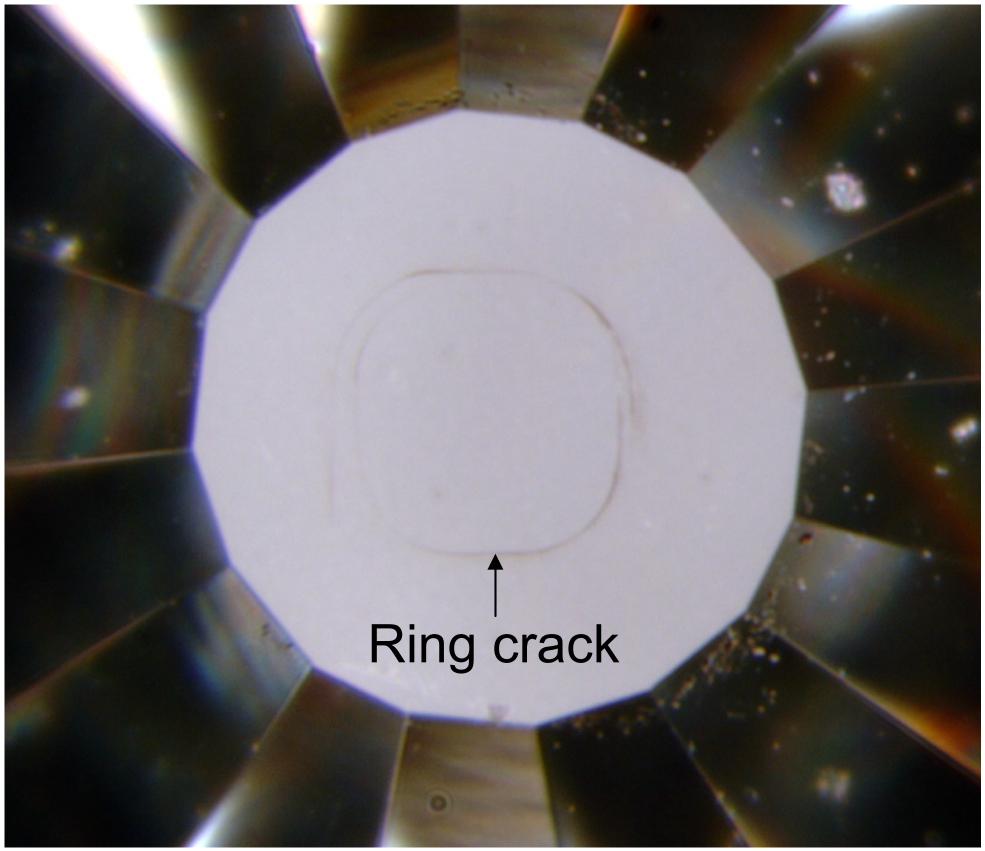


X-ray diffraction (He medium)



13-BMD, GSECARS
16-IDB, HPCAT

Superhard material



Conclusions

- Under compression, graphite exhibits reversible, orders-of-magnitude change in strength from very soft graphite to superhard material.
- This cold-compressed graphite is a new, distinct phase of carbon.
- IXS can be used to probe bonding changes in 2nd row elements *in-situ* at high pressure.

Acknowledgments

GSECARS

- Peter Eng
- Tom Trainor (now University of Alaska)
- Matt Newville
- Vitali Prakapenka

HPCAT

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CIW

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- Jinfu Shu
- Rus Hemley

U CHICAGO

- Dion Heinz

NSLS

- Chi-chang Kao