高圧研究の新しい地平をめざして：
静水圧実験へのチャレンジ

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- 謝 辞 -　亀卦川卓美（KEK）

藤久裕司 、山脇浩 (AIST)　佐藤恭子　A. Dewaele (CEA, France)
中野智志、小野田みつ子 (NIMS)　A. K. Singh (NAL, India)

熱力学変数としての

圧力（静水圧）の利点

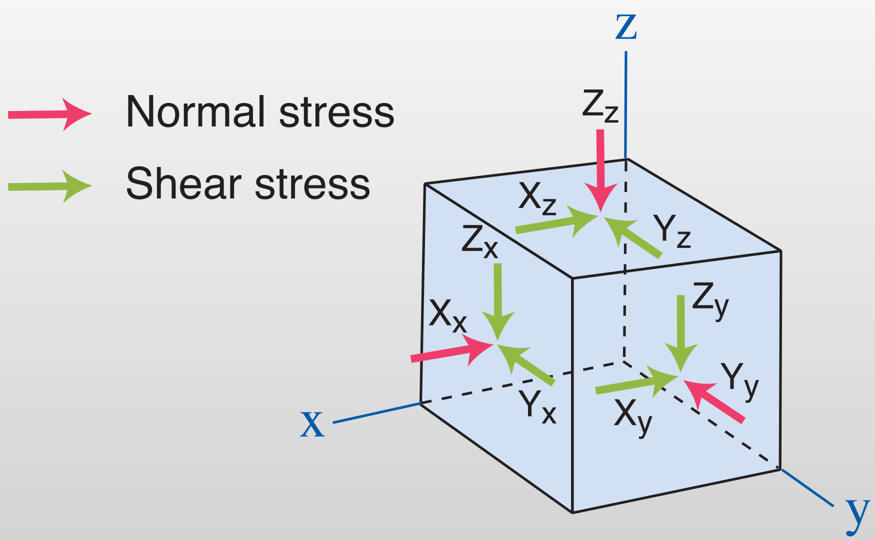
P　　　　　　　　　　　　T

- 均一な圧力場 ―――――――― 温度分布
- 高速変化 ―――――――――― 熱伝導
- 原子間距離を直接変化 ――― 熱膨張

第一原理計算との比較が容易

静水圧

Stress tensor



	Stress Shear	Stress Differential	Spatial Inhomogeneity
Nonhydro.	○	○	○
Uniaxial	—	○	—
Hydro.	—	—	—

Nonhydrostatic

$$\begin{pmatrix} X_x & X_y & X_z \\ Y_x & Y_y & Y_z \\ Z_x & Z_y & Z_z \end{pmatrix}$$

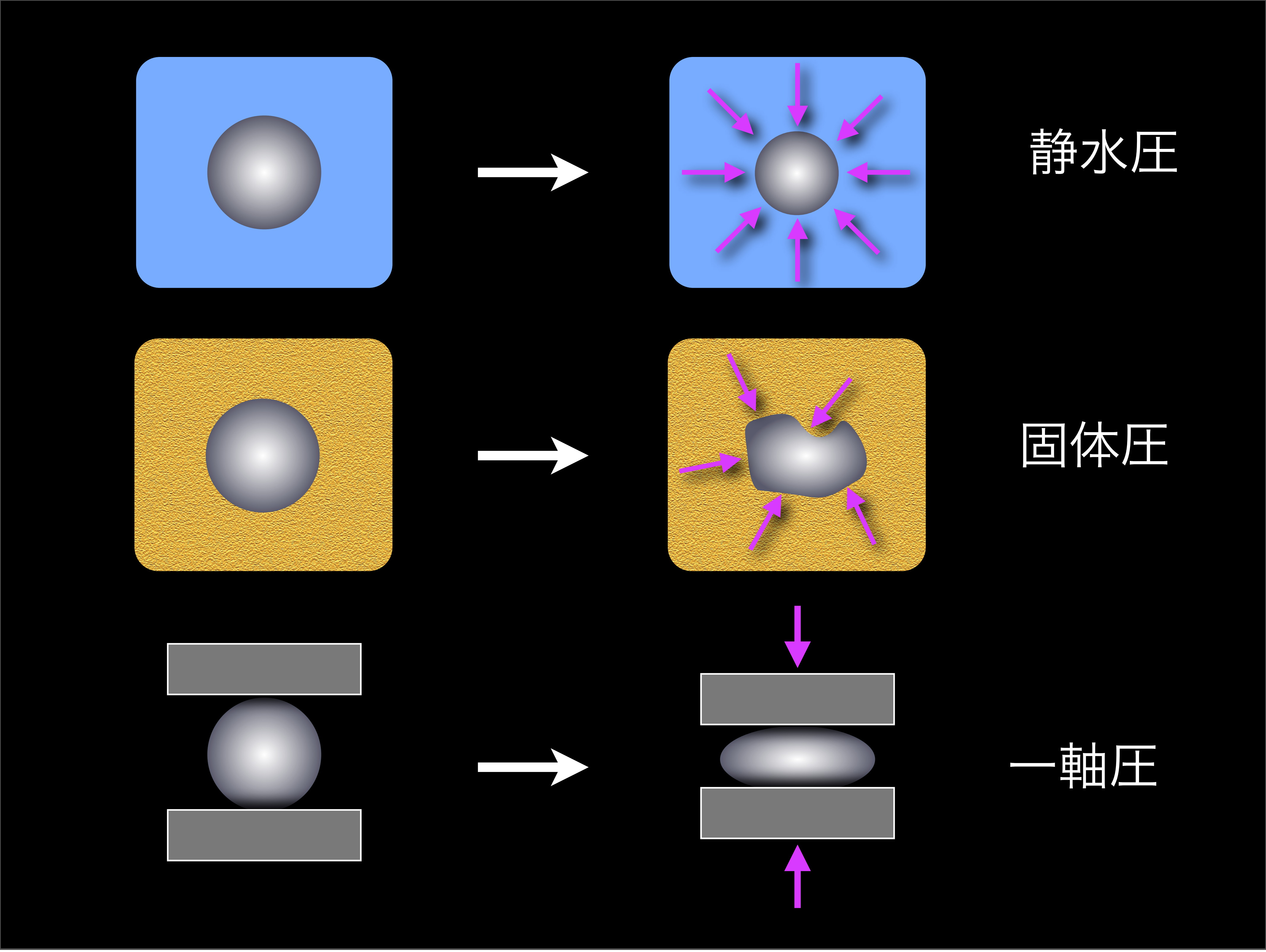
Uniaxial

$$\begin{pmatrix} X_x & 0 & 0 \\ 0 & Y_y & 0 \\ 0 & 0 & Z_z \end{pmatrix}$$

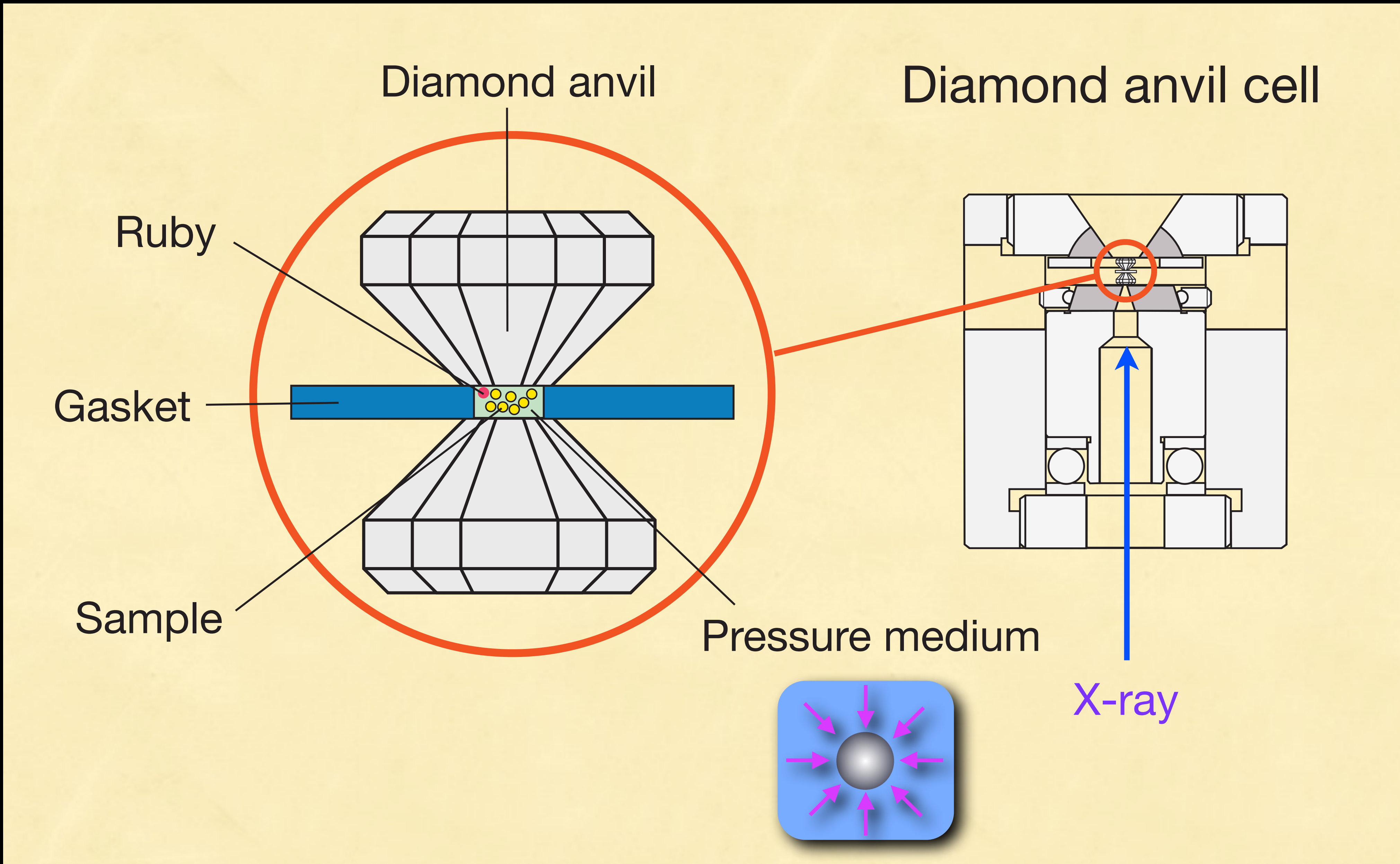
$X_x = Y_y \fallingdotseq Z_z$

Hydrostatic

$$\begin{pmatrix} P & 0 & 0 \\ 0 & P & 0 \\ 0 & 0 & P \end{pmatrix}$$

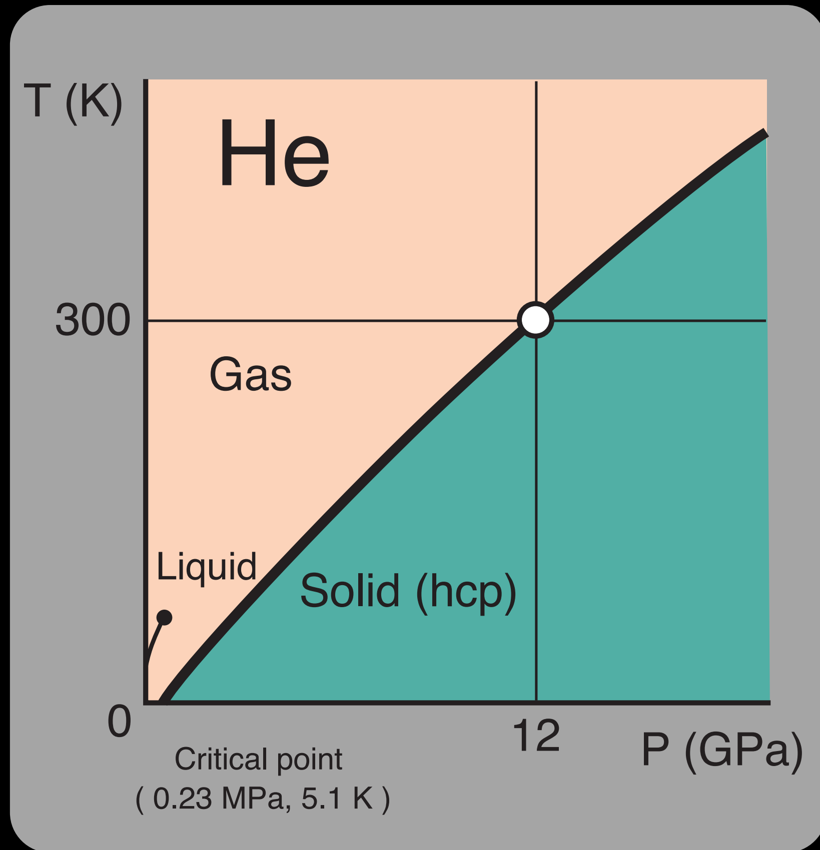

静水圧
固体圧
一軸圧

DAC における　静水圧の実現



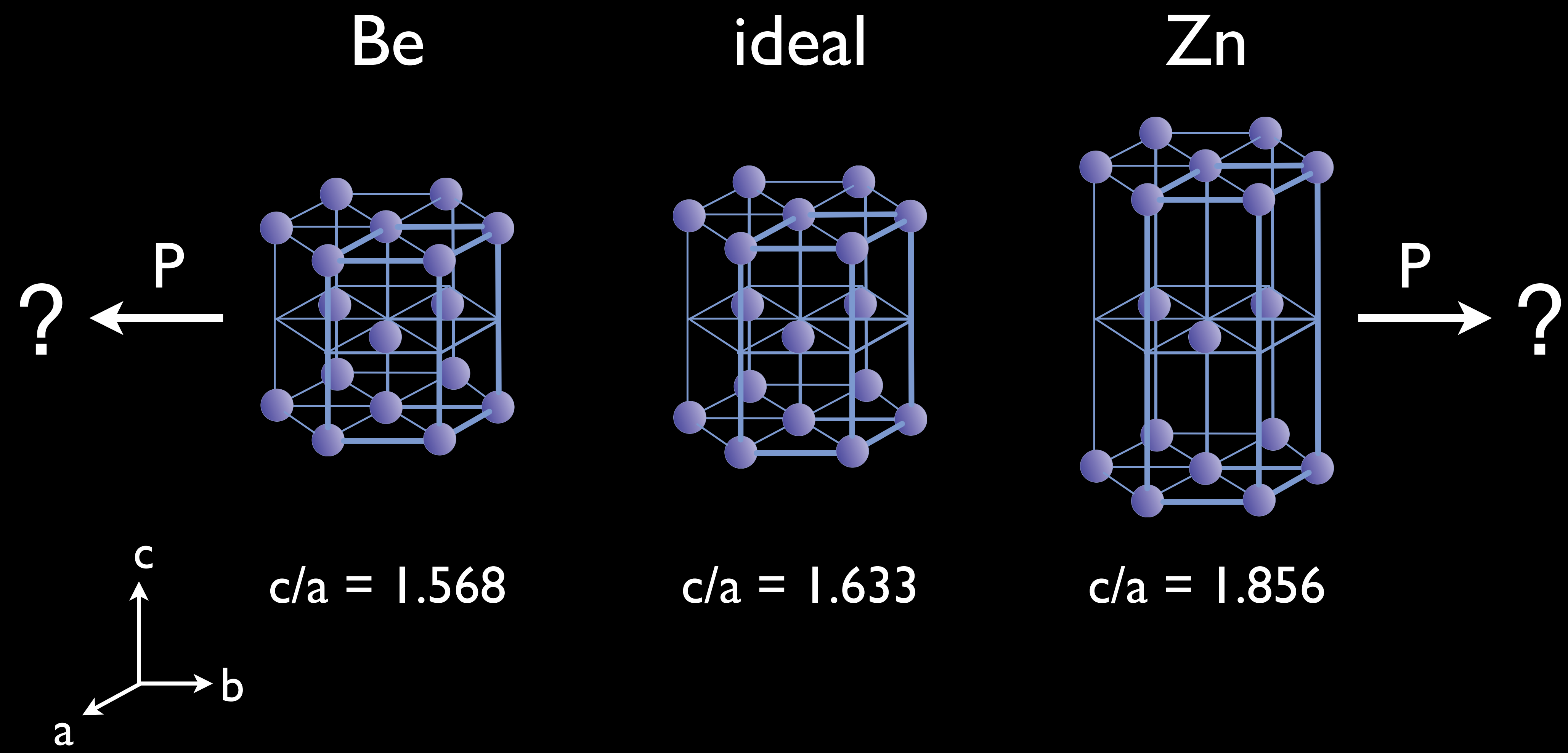
圧力伝達媒体

	P_s (GPa)	P_{HL} (GPa)
He	12	~ 30
Ne	4.8	~ 15
Ar	1.4	~ 9
H_2	5.5	~ 20
N_2	2.4	~ 11
ME	10	
MEW	14	
H_2O	1	
Fluorinert	~2	
Silicone oil	~2	



ME methanol : ethanol = 4:1　MEW methanol : ethanol : water = 16:3:1

Zn hcp structure



VOLUME 75, NUMBER 9 PHYSICAL REVIEW LETTERS 28 AUGUST 1995

Zn under Pressure: A Singularity in the hcp Structure at $c/a = \sqrt{3}$

BL-18C

MEW

Takemura Kenichi*

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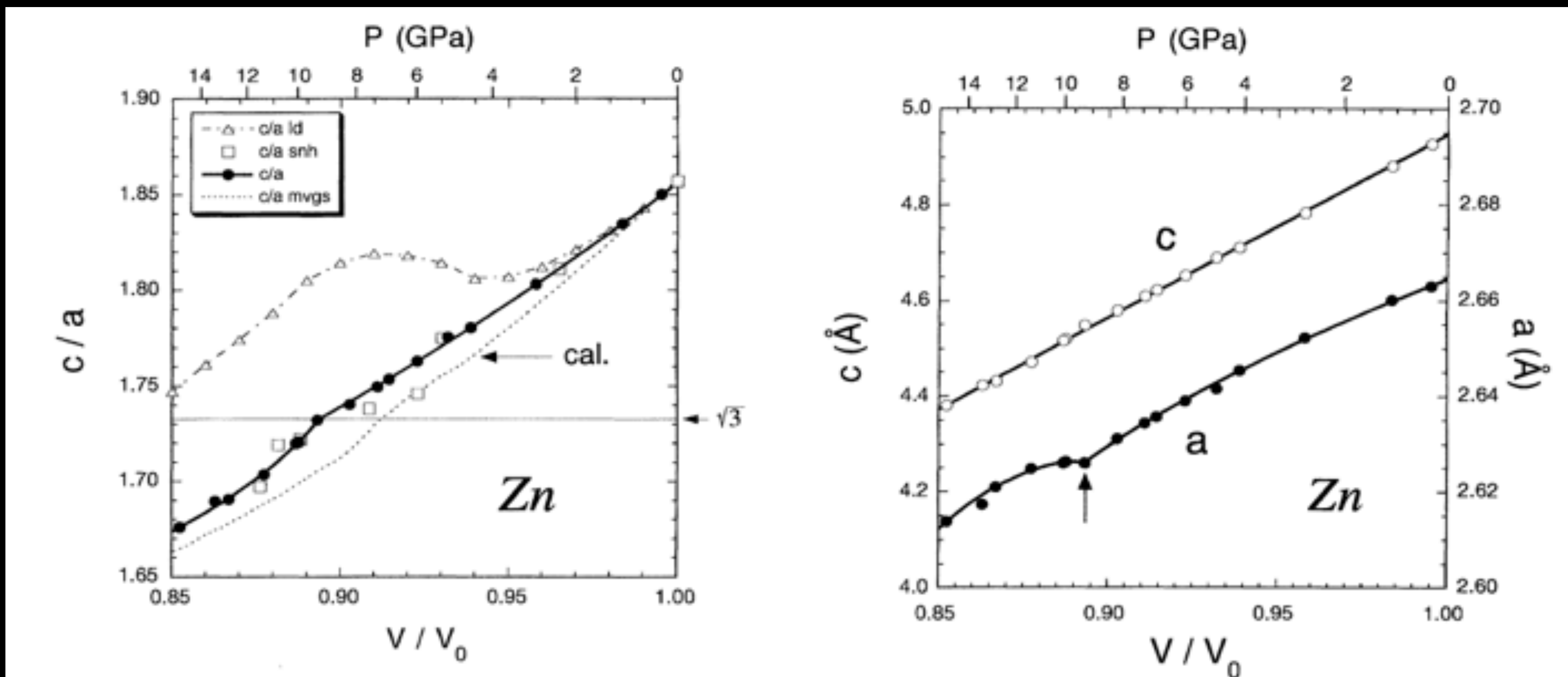
(Received 18 April 1995)

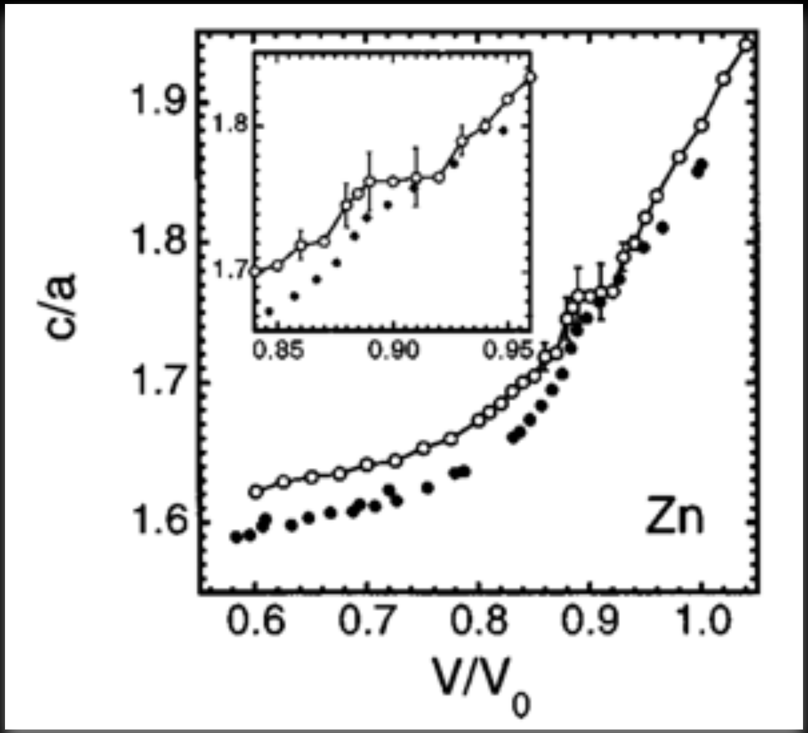
High-pressure powder x-ray diffraction experiments on Zn at room temperature have revealed that the volume dependence of the c/a axial ratio changes the slope at $V/V_0 = 0.893$ ($P = 9.1$ GPa), where the c/a ratio becomes exactly $\sqrt{3}$. The anomaly is most likely related to the electronic topological transition recently found with Mössbauer spectroscopy. The special value ($\sqrt{3}$) of the axial ratio at the anomaly is, however, difficult to explain simply by the electronic topological transition.



K. Takemura, *PRL* **75**, 1807 (1995).

Theories

- Anomaly in c/a ratio of Zn under pressure L. Fast *et al.*, PRL (1997)
- LDA simulations of pressure-induced anomalies in c/a and electric-field gradients for Zn and Cd D.L. Novikov *et al.*, PRB (1997)



Electronic topological transition?

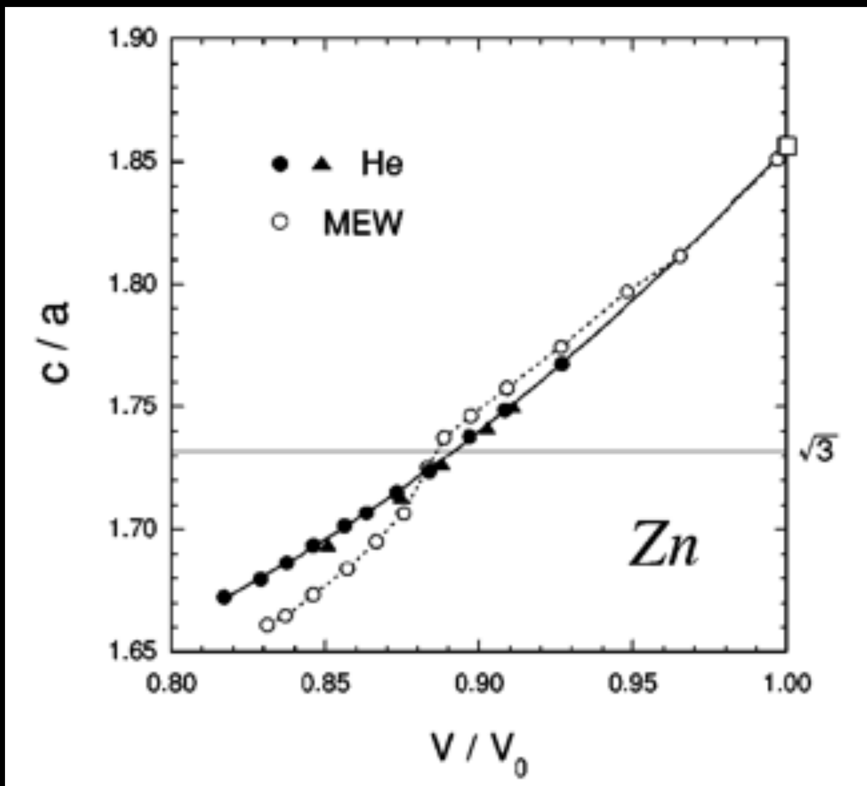
Theories

- Anomaly in c/a ratio of Zn under pressure L. Fast *et al.*, PRL (1997)
- LDA simulations of pressure-induced anomalies in c/a and electric-field gradients for Zn and Cd D.L. Novikov *et al.*, PRB (1997)
- Phonon anomaly in high-pressure Zn Z. Li & J.S. Tse, PRL (2000)
- Electronic topological transitions in Zn under compression V.V. Kechin, PRB (2001)
- Does an electronic topological transition cause lattice strain anomalies in zinc at high pressure? G. Steinle-Neumann *et al.*, PRB (2001)
- First-principles derivation of structural anomalies in hcp Zn and hcp Fe under pressure S.L. Qui & P. M. Marcus, J. Phys.: Condens. Matter (2003)
- Multiple minima on the energy landscape of elemental zinc: A wave function based ab initio study N. Gaston *et al.*, PRL (2008)

Absence of the c/a anomaly in Zn under high pressure with a helium-pressure medium

Takemura Kenichi*
National Institute for Research in Inorganic Materials (NIRIM), Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan
(Received 8 April 1999)

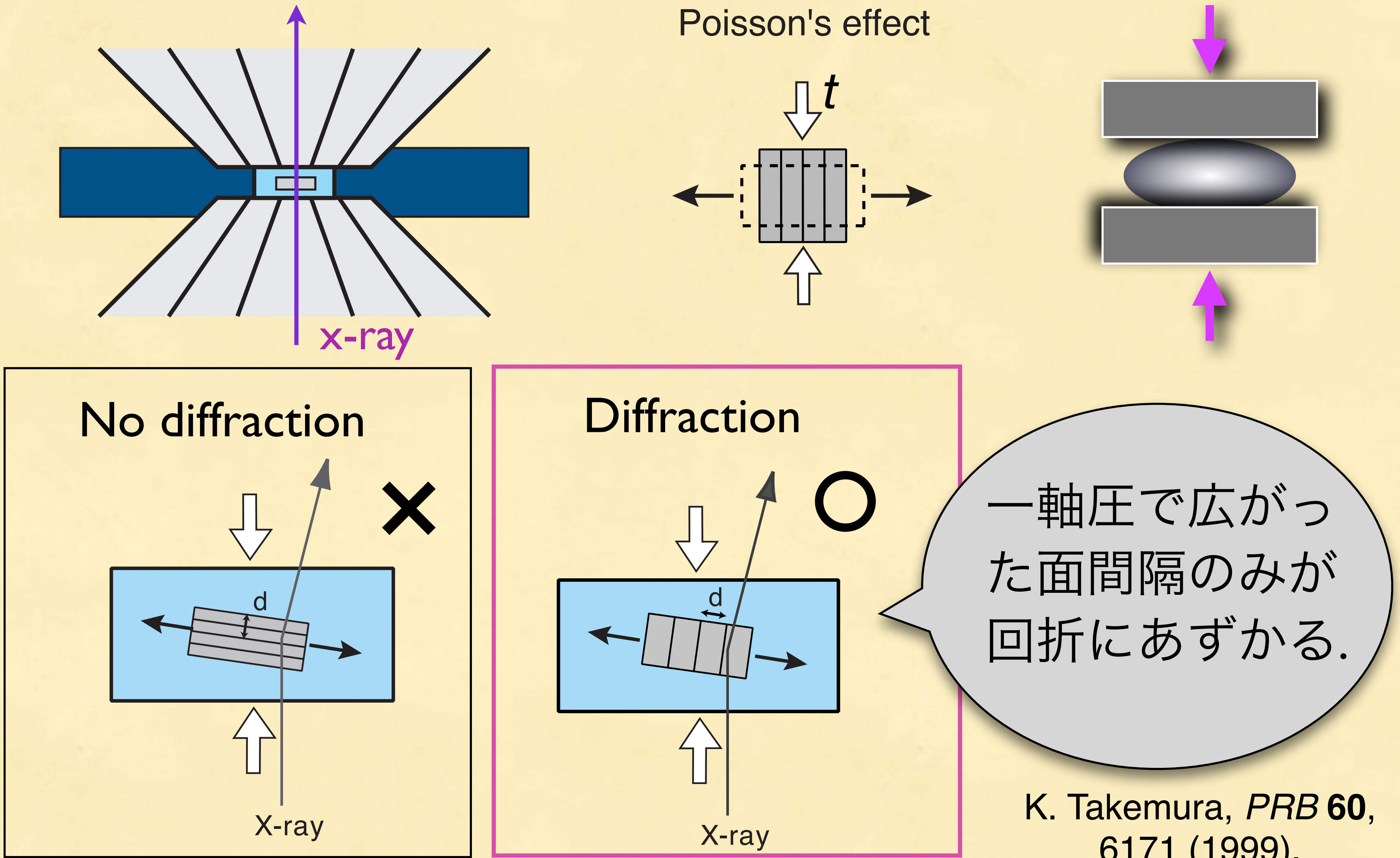
A high-pressure powder x-ray diffraction experiment on Zn has been carried out at room temperature with He pressure-transmitting medium in order to achieve the best hydrostatic conditions. The anomaly in the volume-dependence of the c/a axial ratio, which has been observed previously, can no longer be observed. Hence the anomaly is most probably induced by the nonhydrostaticity associated with the solidification of the methanol-ethanol-water pressure-transmitting medium used in the previous studies. The present results suggest reconsideration of the calculated c/a anomaly based on the electronic topological transition.



K. Takemura, *PRB* **60**, 6171 (1999).

The c/a anomaly in Zn disappeared with He.

圧力伝達媒体（MEW）の固化による一軸圧の発生



K. Takemura, *PRB* **60**, 6171 (1999).

Os

W 19.3 g/cm^3

Pt 21.4 g/cm^3

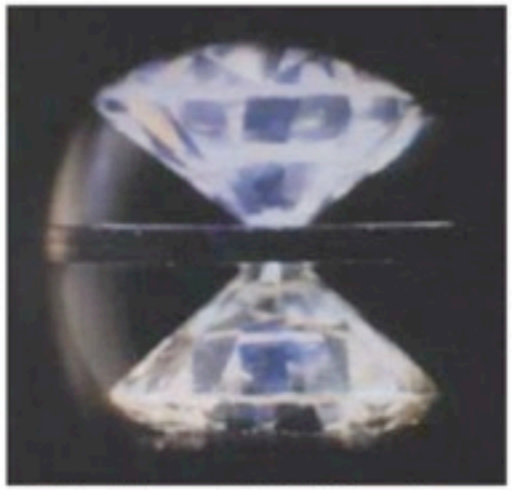
Os 22.5 g/cm^3

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra																
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Phys. Rev. Lett. **88**, 135701
(print issue of 1 April 2002)
Title and Authors
27 March 2002

Osmium is Stiffer than Diamond

Move over diamond: the element osmium can withstand compression better than any known material, according to the 1 April print issue of PRL . A research team squeezed a tiny sample of the metal to extremely high pressure and found that it shrunk even less than diamond, the former record holder. The finding may allow researchers to develop new superhard materials.



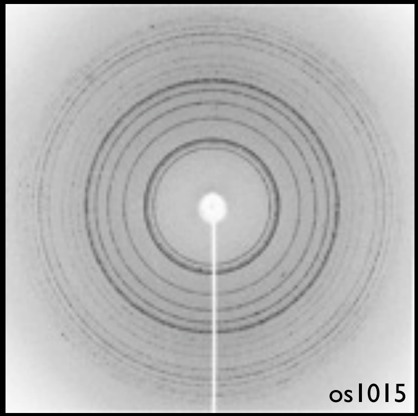
D. Mao/Carnegie Institution of Washington

Test under pressure. *Osmium holds up better than any other known material when squeezed at extremely high pressures in a diamond anvil (above).*

Diamond is the hardest material, resisting scratches, dents, and

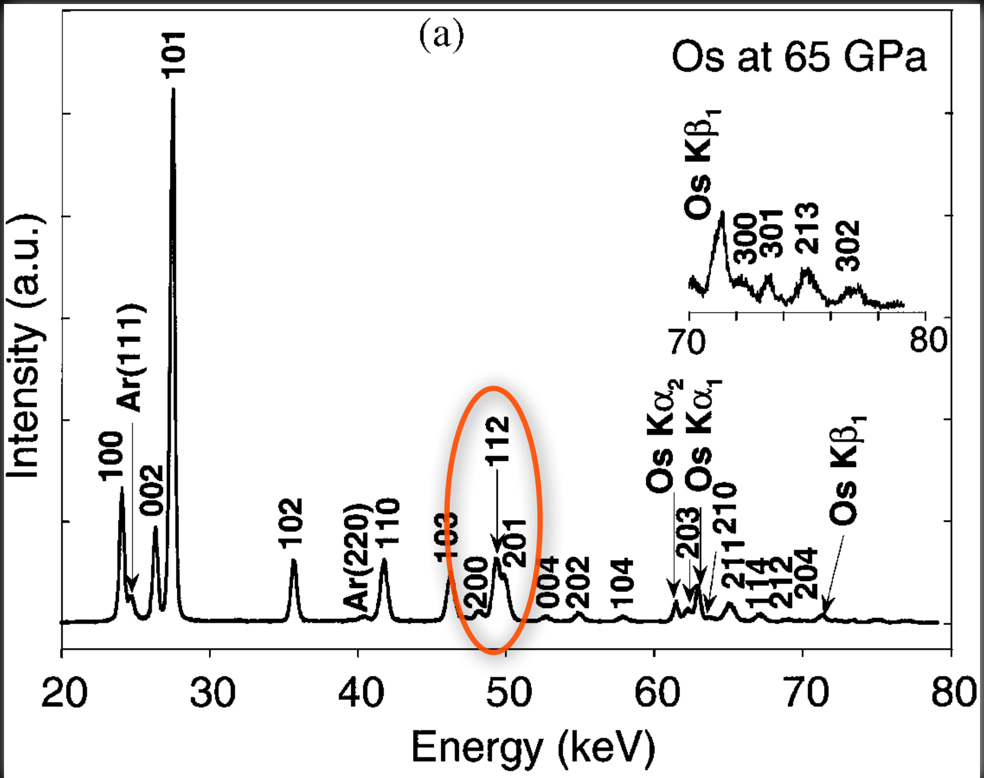
X-ray diffraction patterns

PF BL-13A

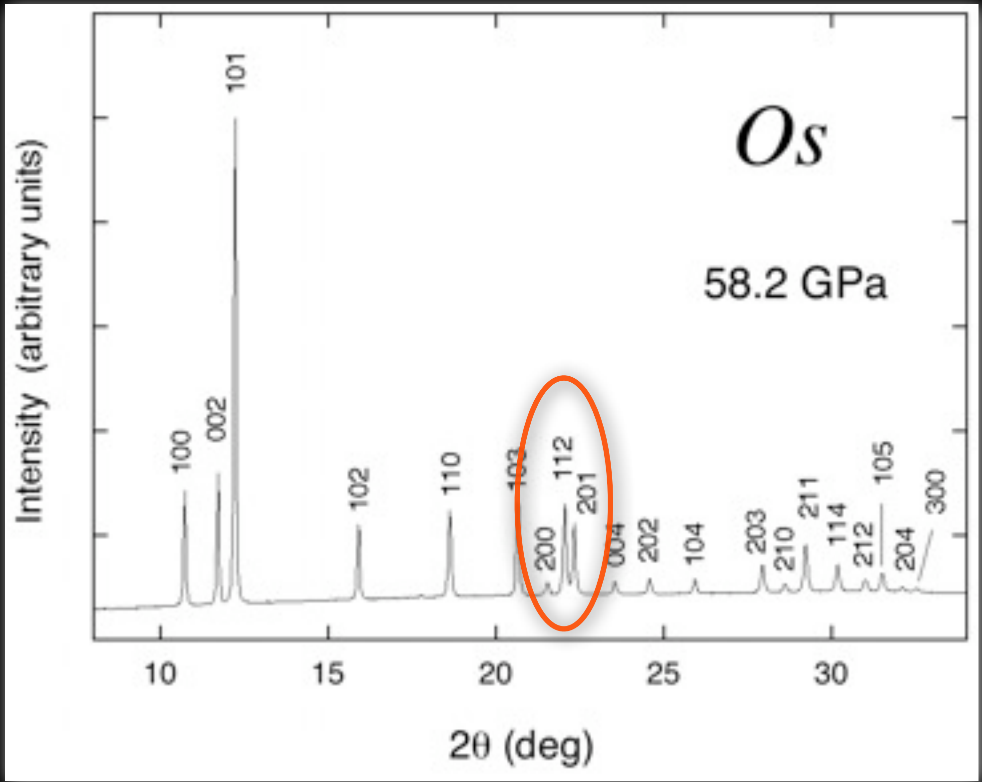


Pressure medium: Ar | He

Diffraction mode: Energy-dispersive | Angle-dispersive

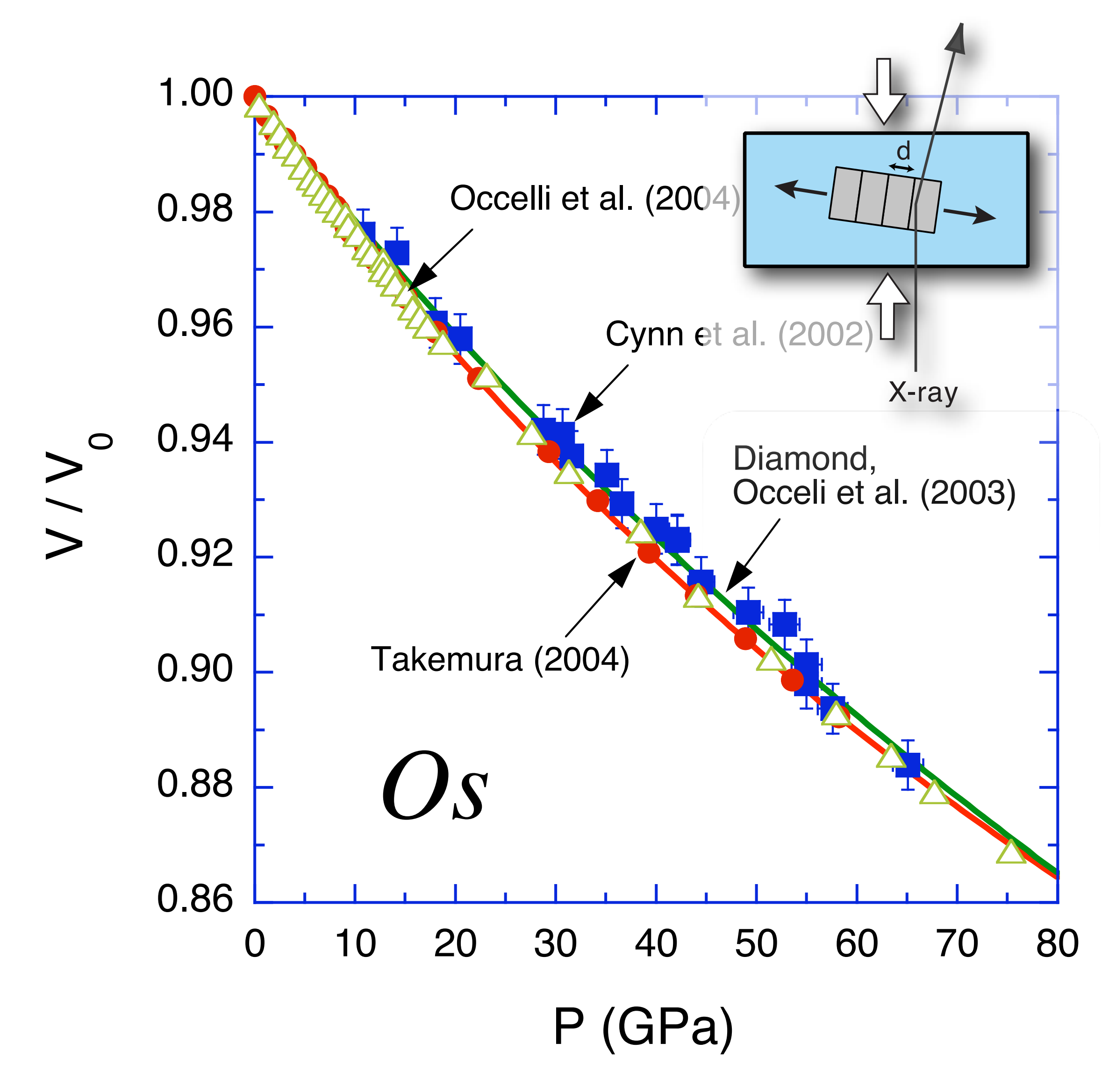


Cynn et al. PRL (2002)



Takemura, PRB (2004)

Equation of state for Os

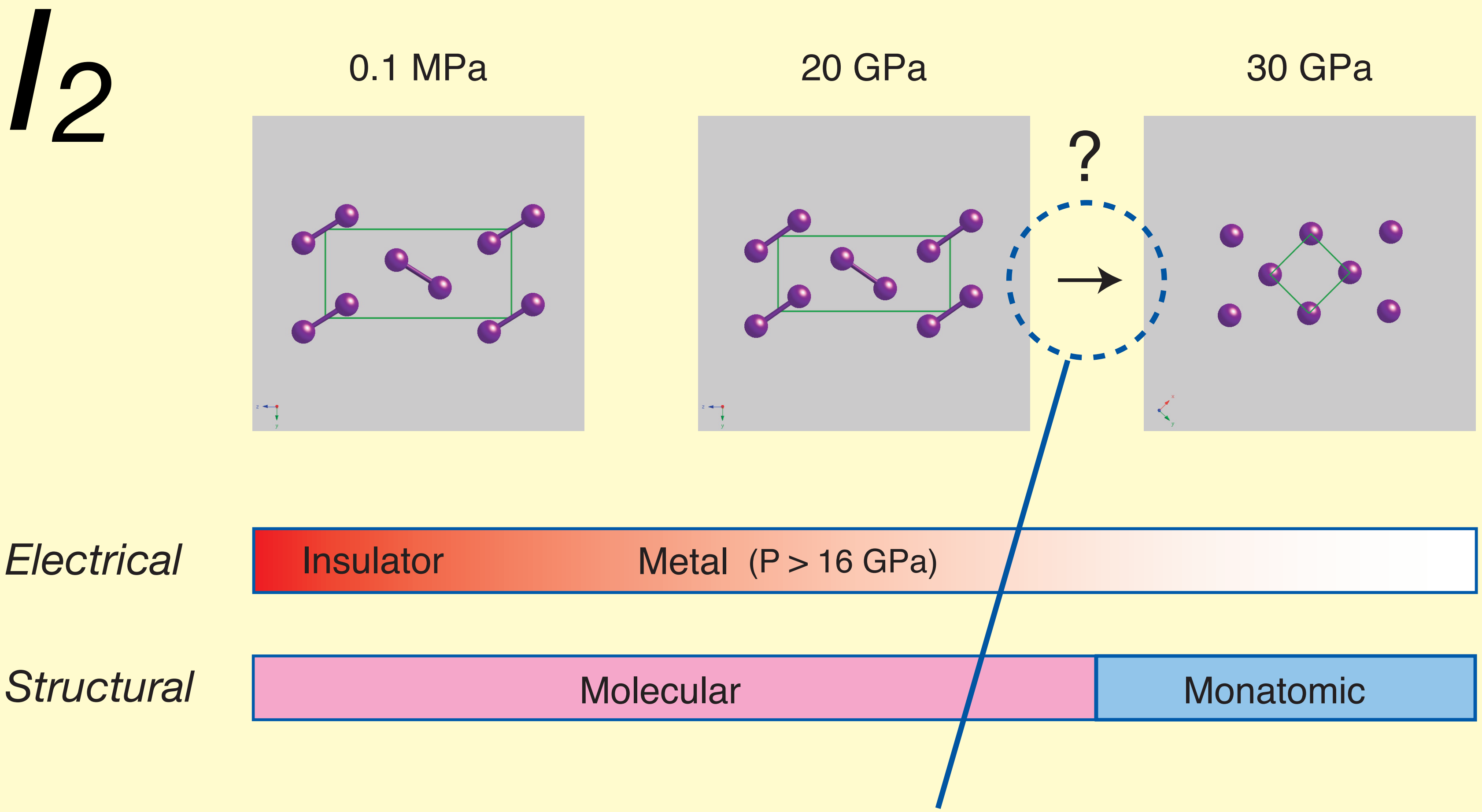


Os is not stiffer than diamond.

	B_0 (GPa)	B_0'
Os (Takemura)	**395** (15)	4.5 (5)
Os (Cynn)	462 (12)	2.4 (5)
Os (Occelli)	411 (6)	4.0 (2)
Diamond (Occelli)	**446** (1)	3.0 (1)

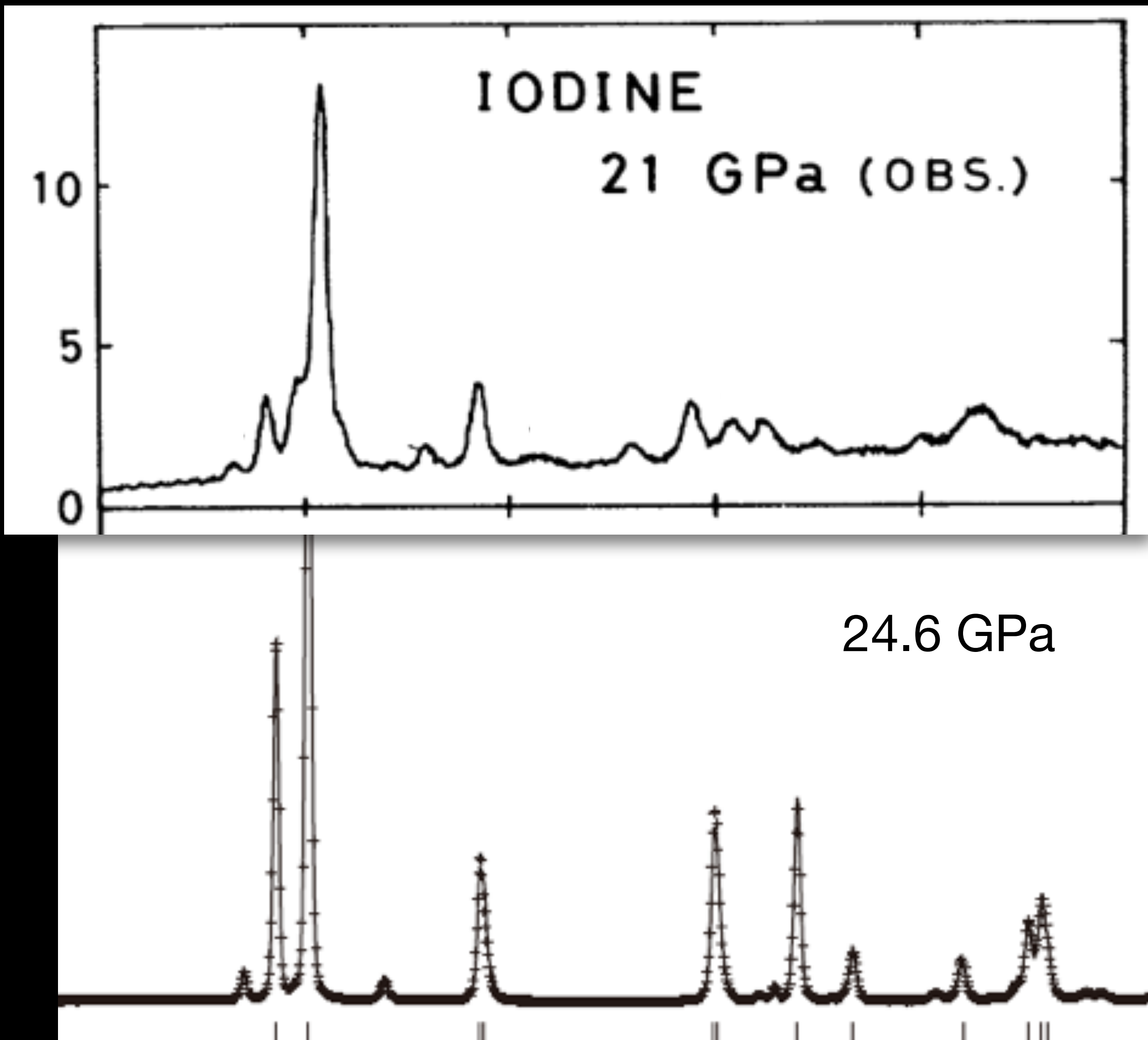
K. Takemura, *PRB* **70**, 012101 (2004).

Pressure-induced molecular dissociation



Is the molecular dissociation single process ?

分子解離近傍のヨウ素のX線回折パターン



圧力媒体なし

X 線管球 Mo-Kα

位置敏感型検出器

Takemura *et al*., PRL (1980)

He 圧力媒体

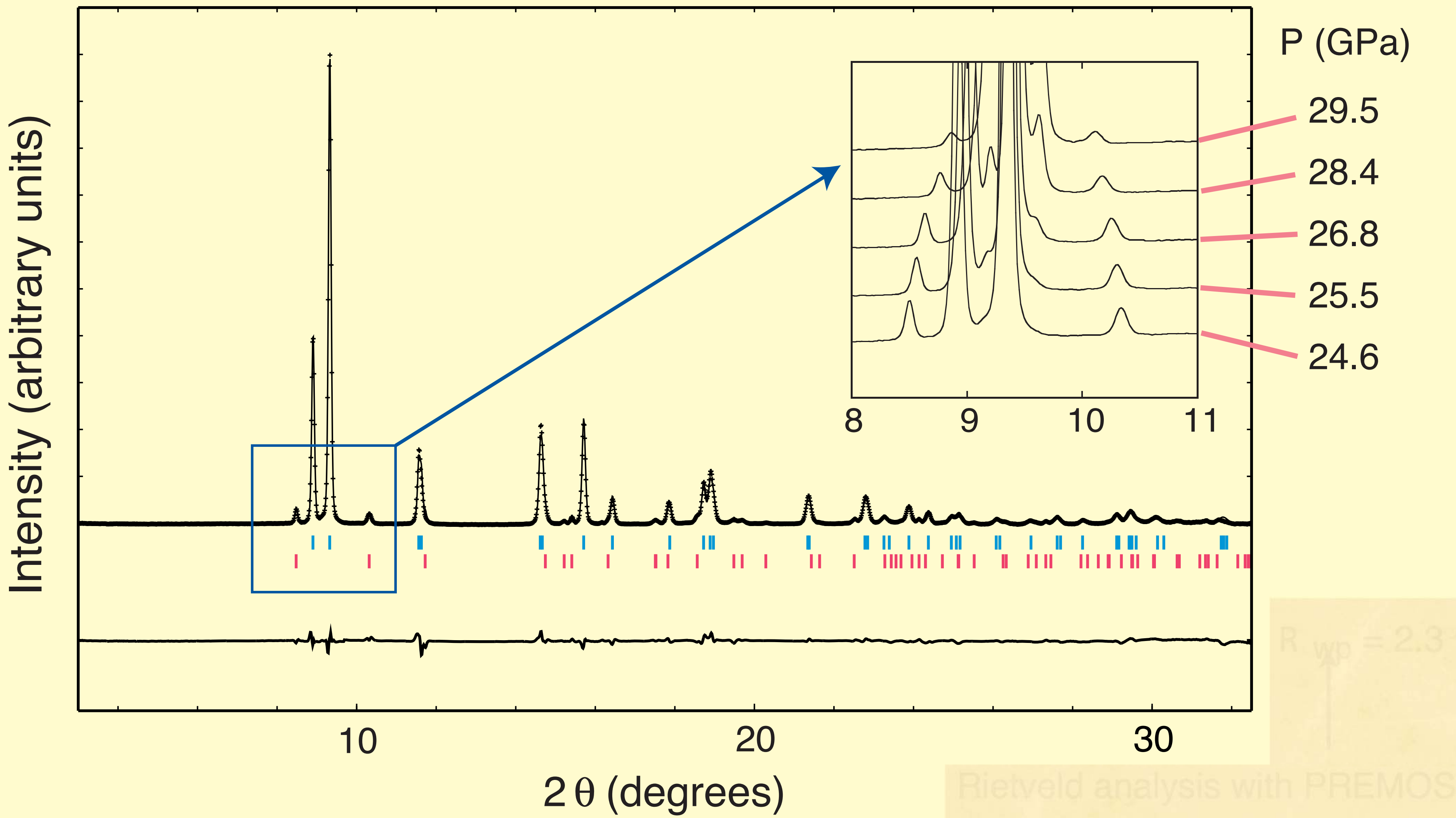
PF BL-13A, 30 keV

Imaging plate

Takemura *et al*., Nature (2003)

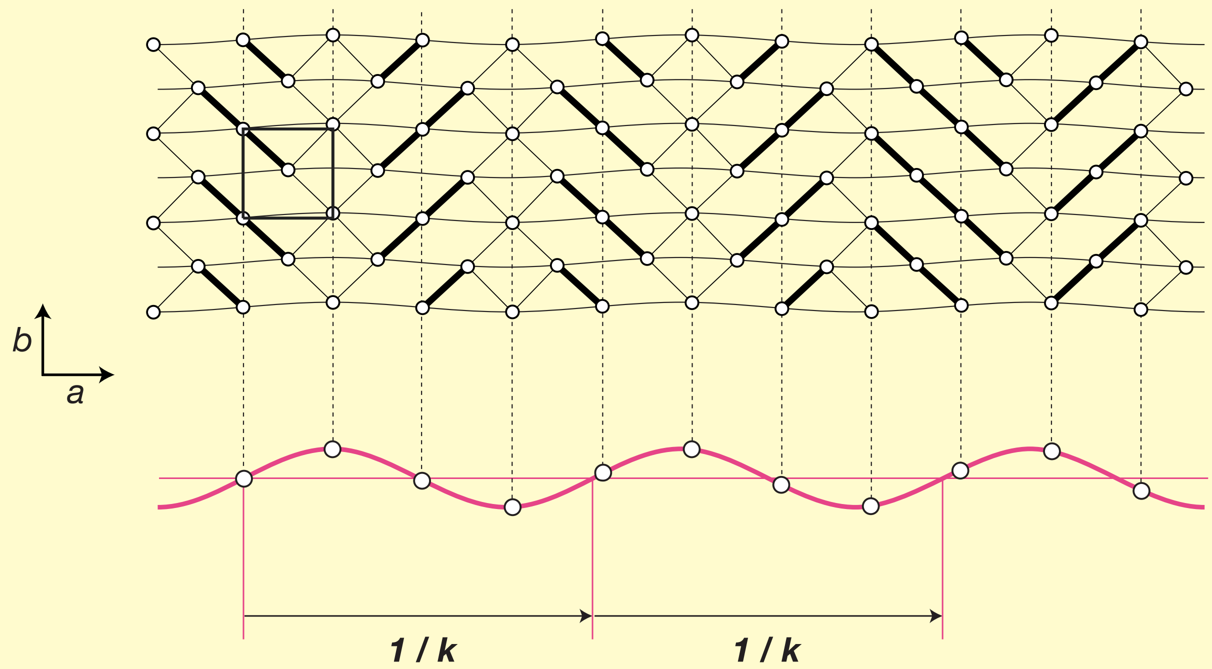
Powder x-ray diffraction pattern of iodine at 24.6 GPa

PF-BL13A



Incommensurately modulated structure of iodine

Takemura, Sato, Fujihisa, Onoda, *Nature* **423**, 971 (2003).

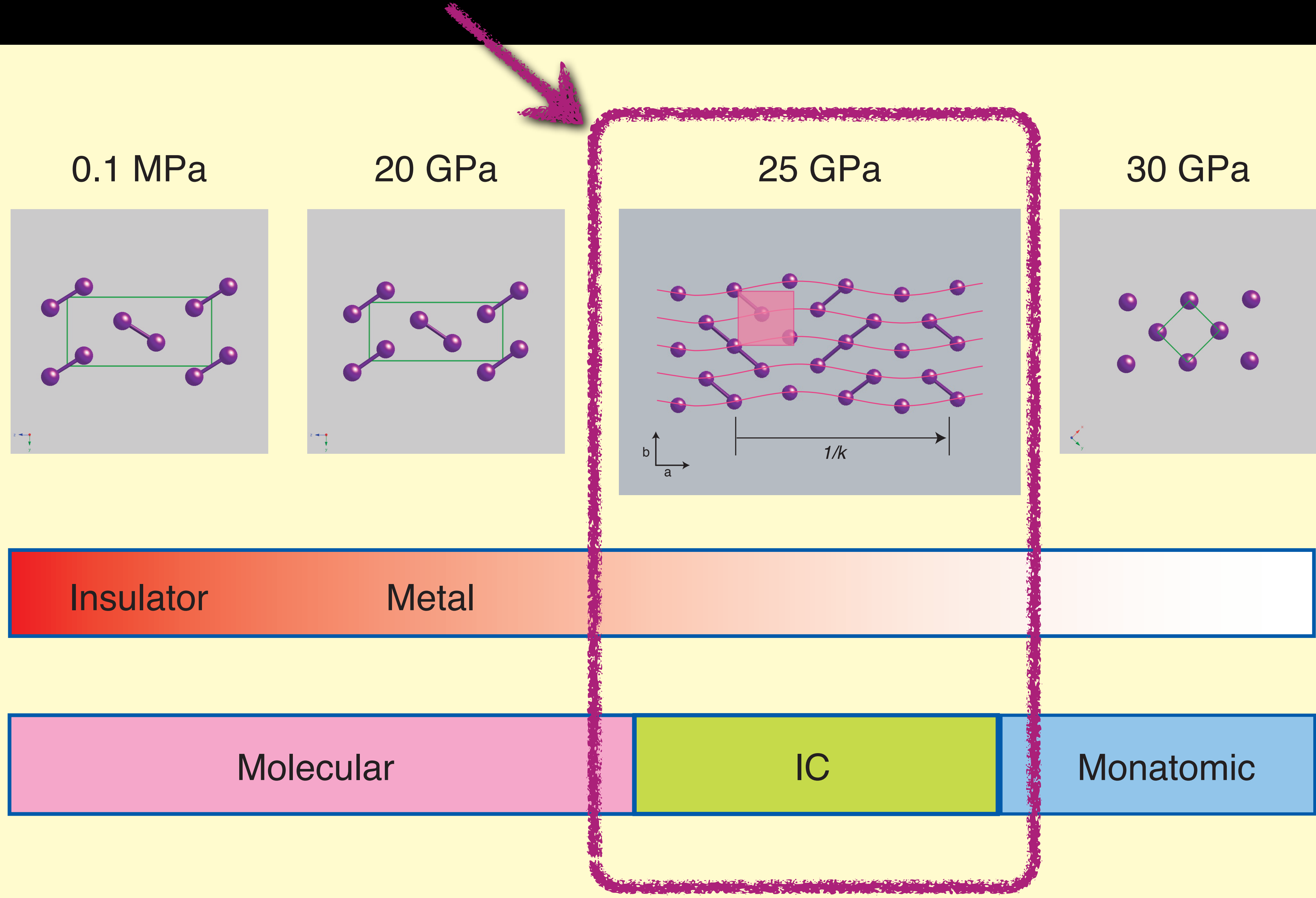


Superspace group: *Fmm2* (α00)0*s*0 4*a* (0, 0, z) z = 0

Lattice parameters of the basic cell: a = 4.2280, b = 4.2039, c = 5.4868 Å

Modulation wave: ***k*** = (0.257, 0, 0) B_1(y) = 0.053 *(phase V @ 24.6 GPa)*

Hidden phase discovered under hydrostatic pressure

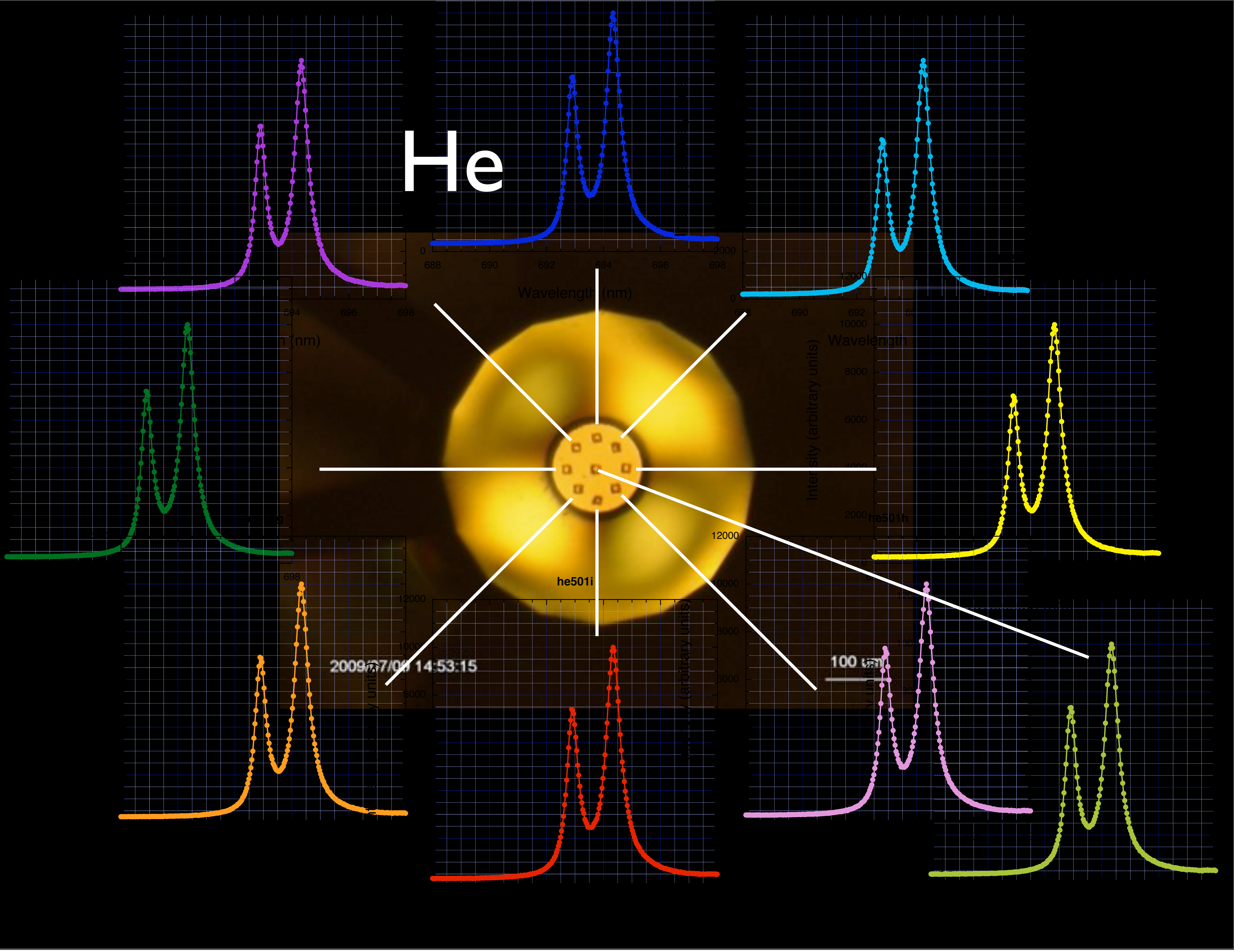


課 題

1. 固体 He の「静水圧性」のチェック
2. 等方的固体圧縮の実現

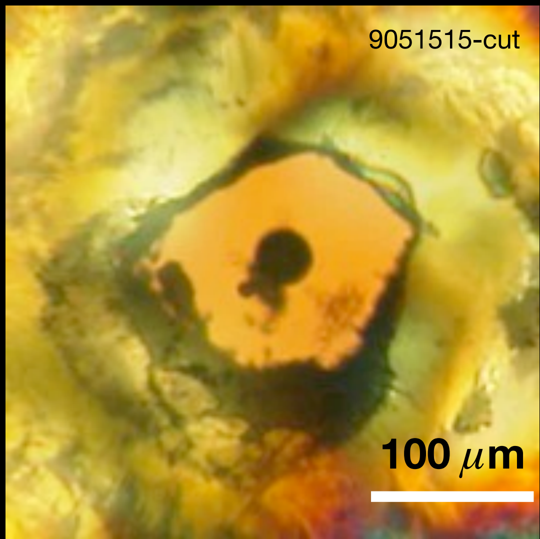
   最小限の試料変形が重要

3. アニーリング
4. 一軸圧・ずれ応力の積極利用

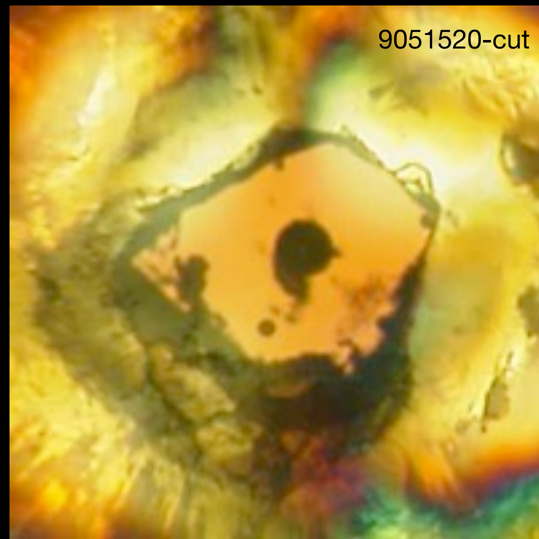


He
he501i
2009/07/09 14:53:15
100 um
Wavelength (nm)
Intensity (arbitrary units)

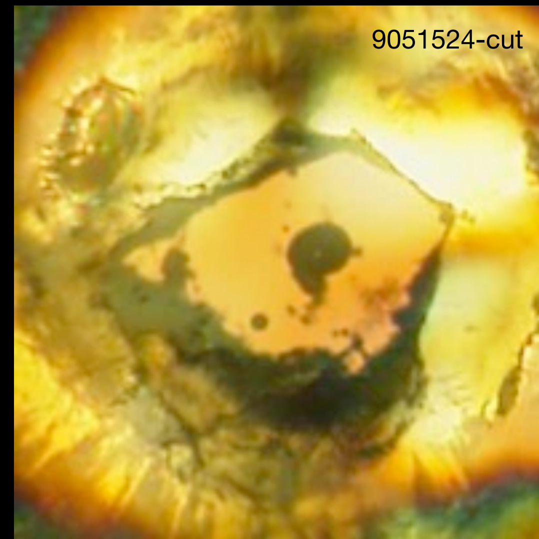
Solid Hg in a solid He medium



11.3 GPa
(fluid He)



15.2 GPa



17.5 GPa

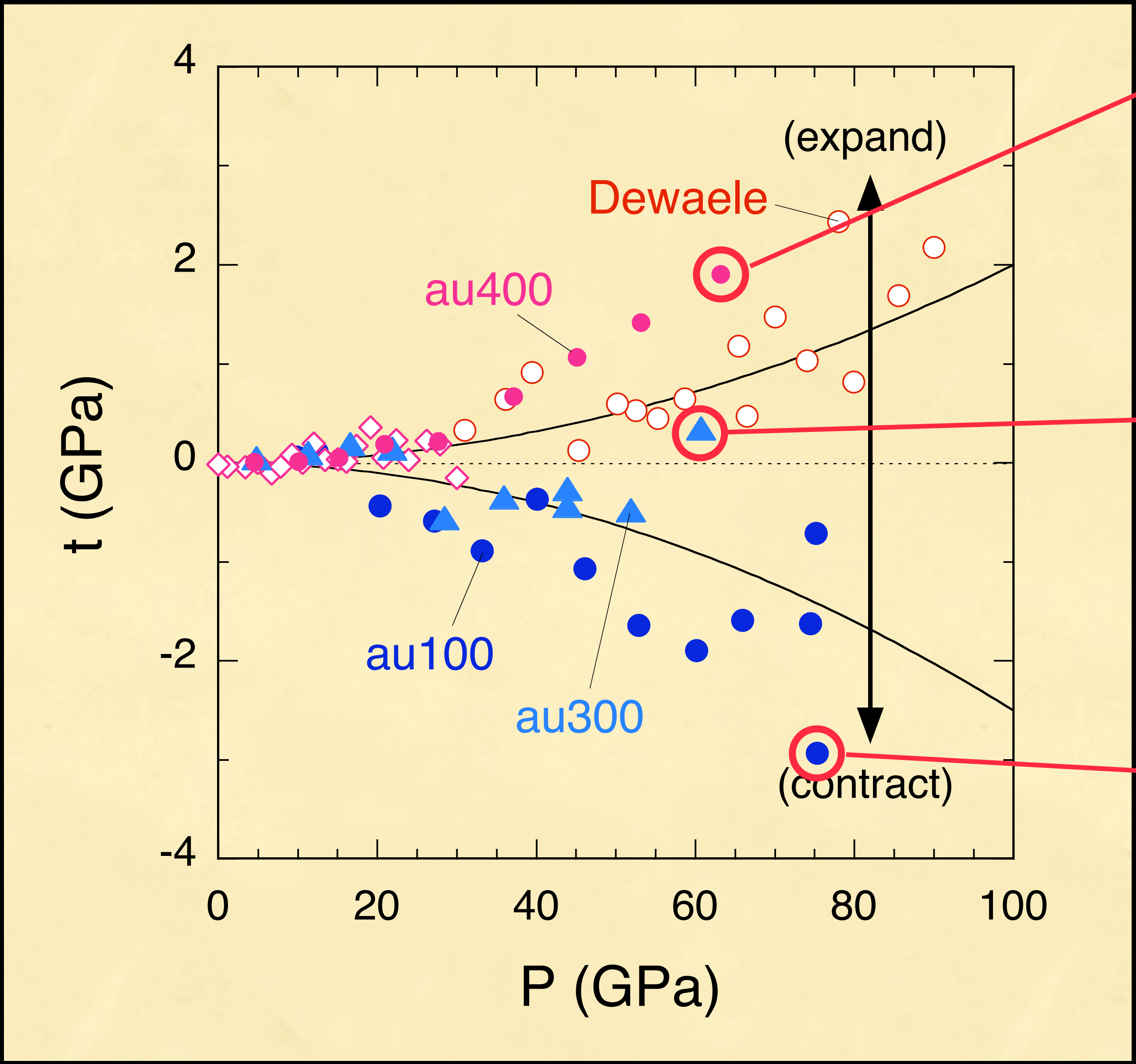
~14 GPa

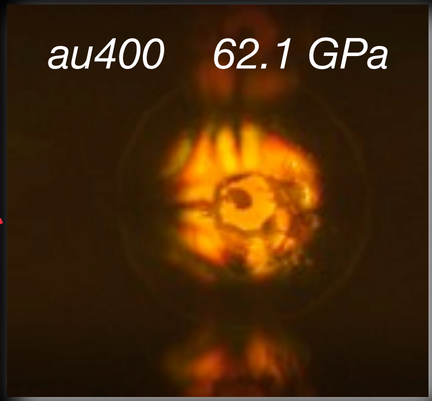
Solid Hg becomes elongated in the direction exactly the same as the gasket hole flows!

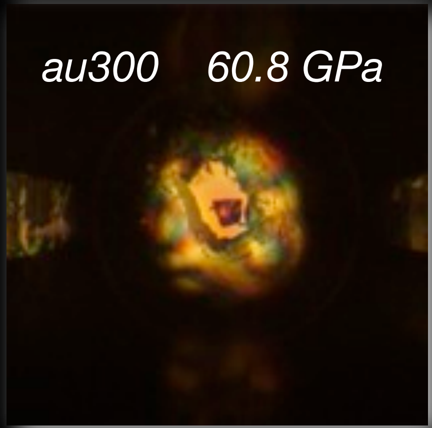
↓

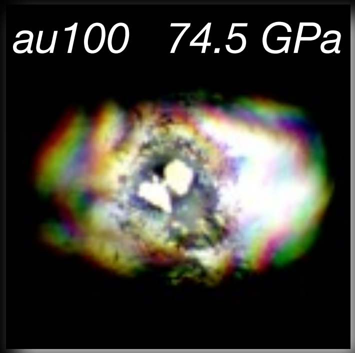
Evidence for the solidity of He.

試料室の変形により一軸圧は変化









Takemura & Dewaele,
PRB **78**, 104119 (2008).

放射光を最大限に生かすための

静水圧実験の重要性

- Zn　　幻の「構造異常」
- Os　　正確な状態方程式
- I_2　　隠れていた中間相