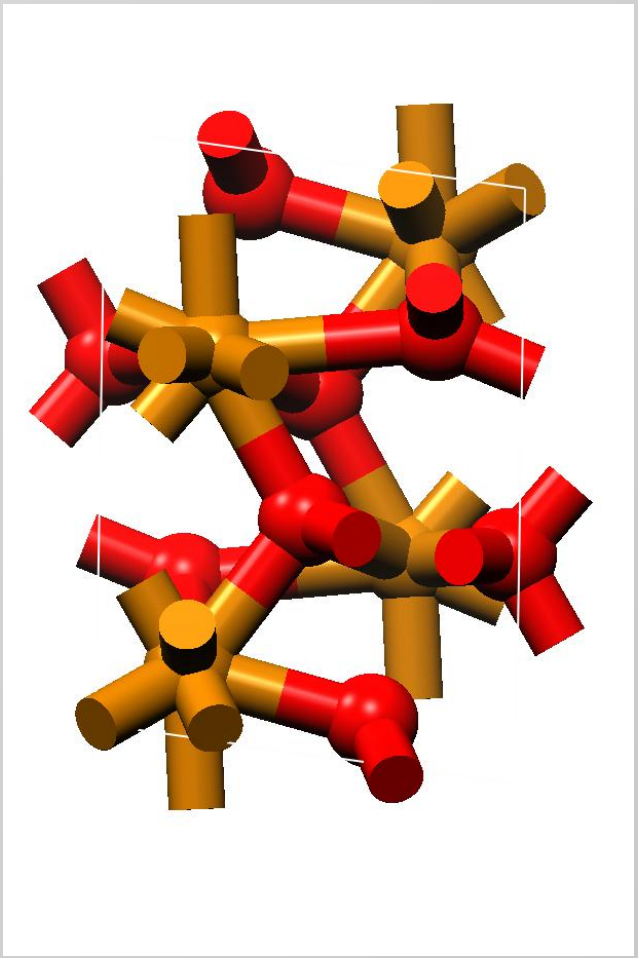
UNIVERSITY OF CAMBRIDGE

Post-Cotunnite Phase of TeO_2

TCM



Phys. Rev. B 72, 092101 (2005)
Post- $PbCl_2$ phase transformation of TeO_2.

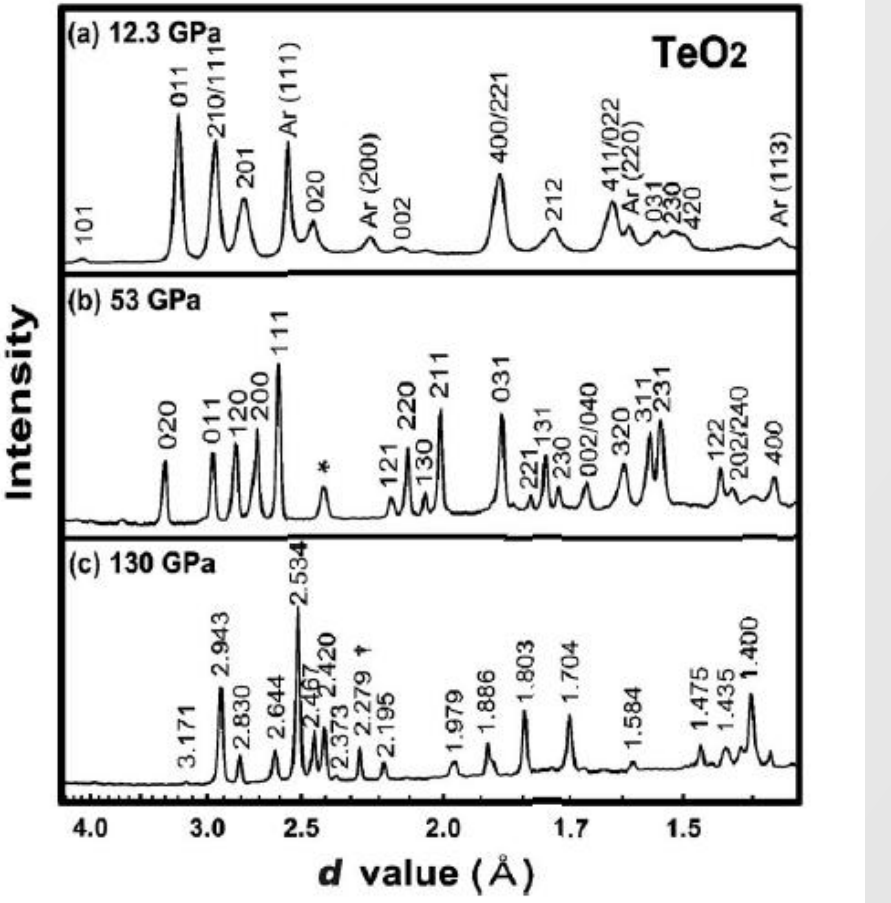
Tomoko Sato, Nobumasa Funamori, Takehiko Yagi, and Nobuyoshi Miyajima

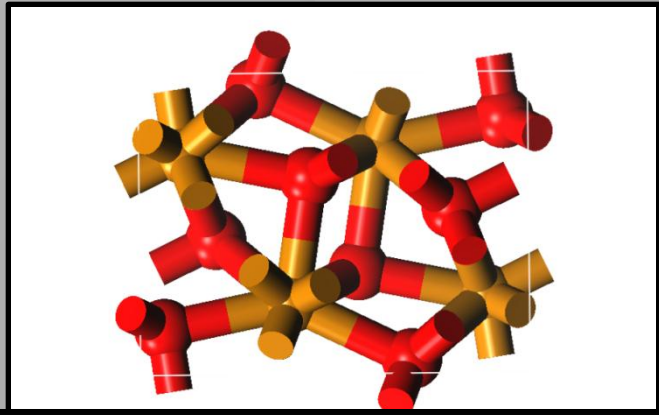
Phys. Rev. B 80, 184115 (2009)

Post-cotunnite phase of TeO_2 obtained from first-principles density-functional theory methods with random-structure searching.

Gareth I. G. Griffiths, Chris J. Pickard, and R. J. Needs

The Problem / motivation





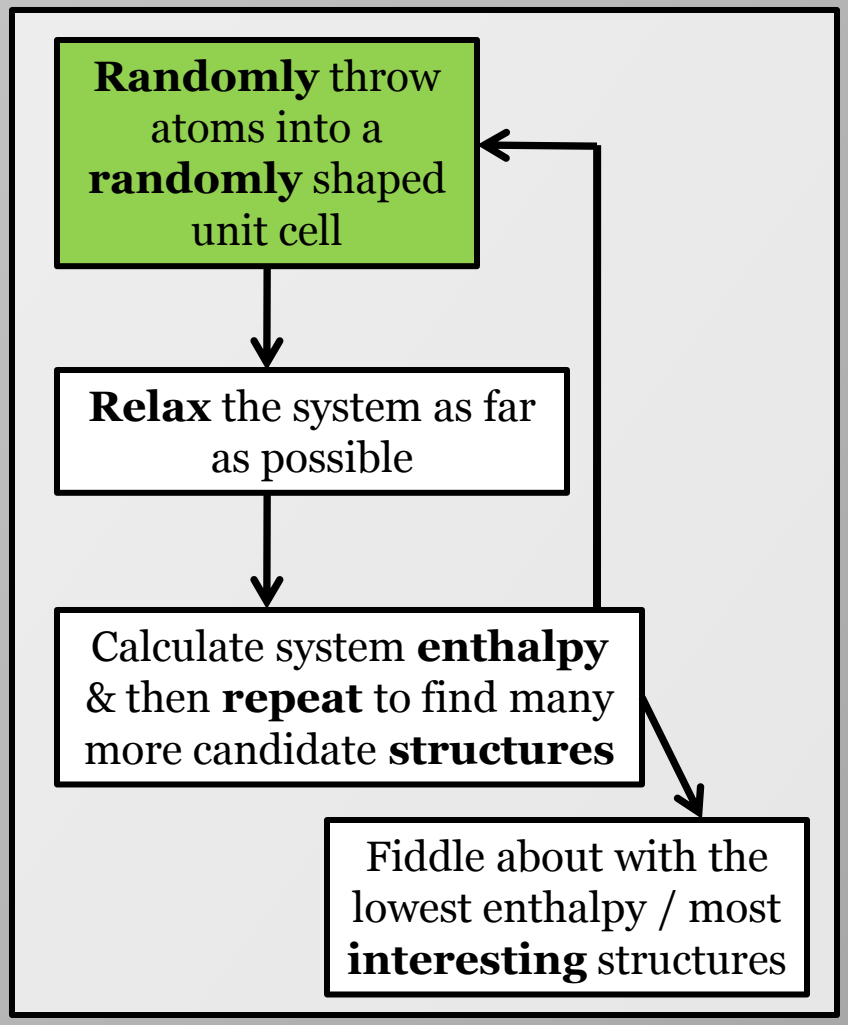
Cotunnite ($PbCl_2$) structure

TiO_2 ZrO_2 HfO_2 CeO_2 PbO_2
PuO_2 UO_2 **TeO_2** ThO_2
Predicted SiO_2 @ 690 Gpa

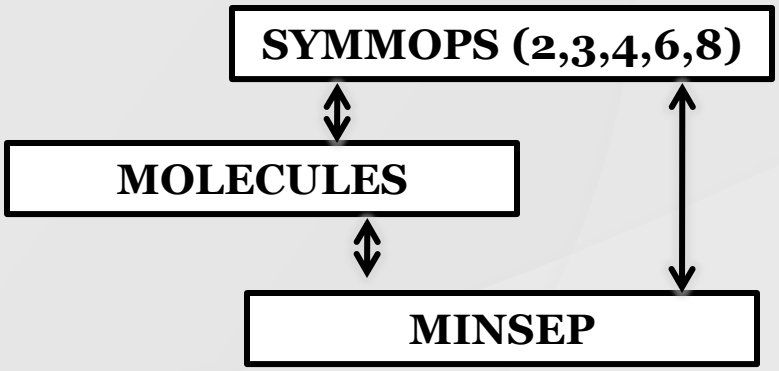
CN=9 → CN=10 as reported for dihalides, with increased pressure?

TeO_2 used for nonlinear optical devices, potentially from nano-crystals.

Random Structure Searching



"One of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition."
J. Maddox *Nature* **335**, 201(1988)



Searching & the Structures

The searches:

~1800 relaxed structures in total

Unconstrained 2 units
Unconstrained 4 units

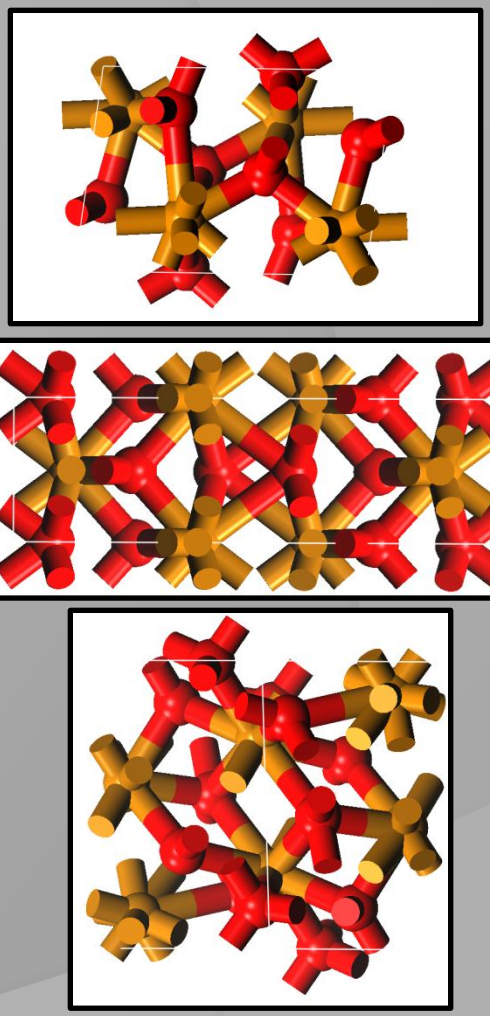
1 unit * 3 symmetry ops.
1 unit * 4 symmetry ops.
1 unit * 6 symmetry ops.
1 unit * 8 symmetry ops.

1 * 120° molecule * 4 symmetry ops.
2 * 120° molecules * 4 symmetry ops.
3 * 120° molecules * 4 symmetry ops.

150 GPa

1 * 120° molecule * 4 symmetry ops.
3* 120° molecules * 2 symmetry ops.
4* 120° molecules * 2 symmetry ops.

280 GPa



Convergence / Pseudopotentials

Pseudopotentials

All results use the standard CASTEP On The Fly Oxygen and Te pseudopotentials.

Standard Te_OTF.usp treats the 5*s* and 5*p* orbitals explicitly.

Tested (both further relaxation and searching) with an OTF Te pseudopotential that treated the 4*d*, 5*s* and 5*p* orbitals explicitly, for which results were essentially unchanged.

Convergence

<u>Searching:</u>

490 eV plane wave cutoff

2π 0.07 $Å^{-1}$ MP grid spacing.

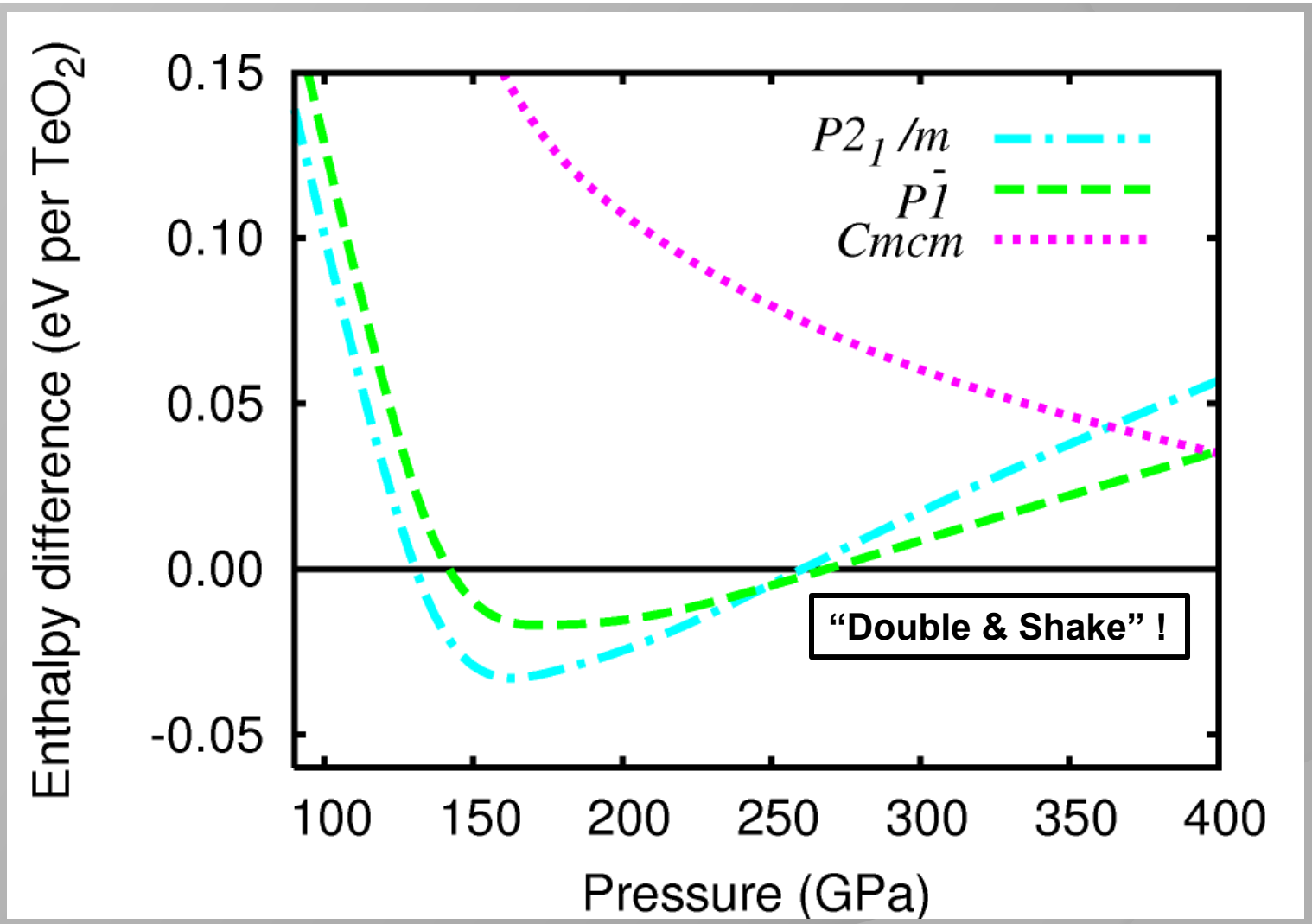
<u>Polishing / refinement:</u>

800 eV plane wave cutoff

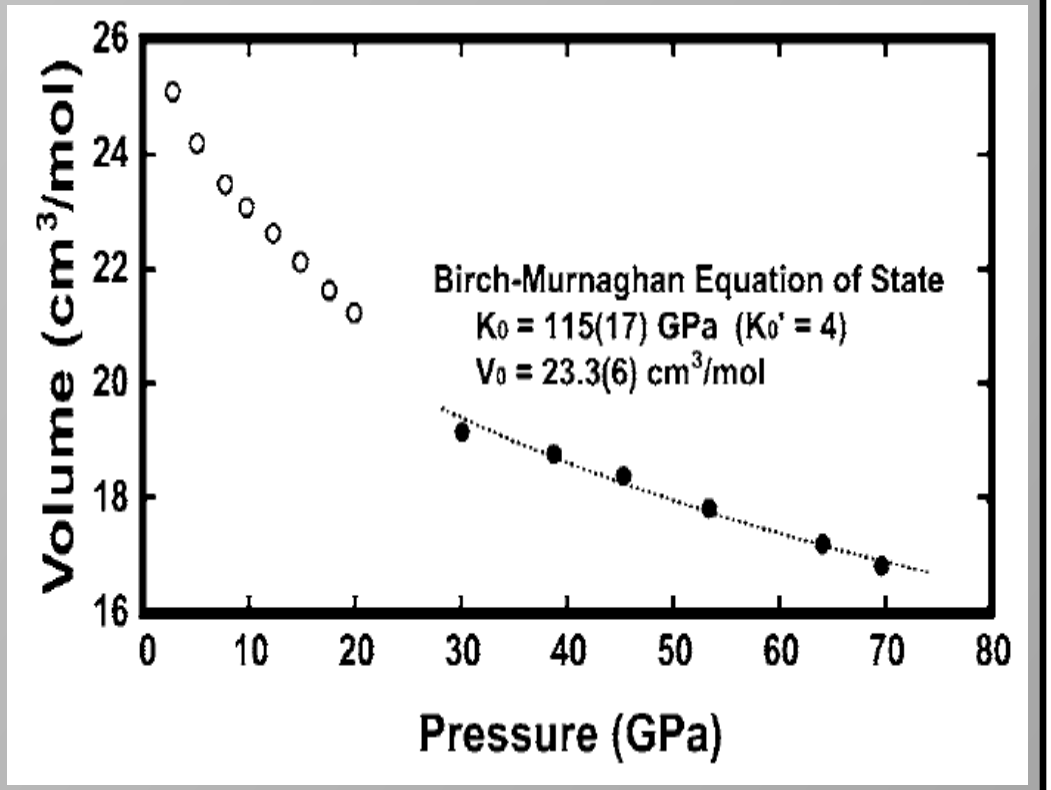
2π 0.03 $Å^{-1}$ MP grid spacing.

Enthalpy difference between Cotunnite and Post-cotunnite structures at 130 Gpa changed by less than 0.0001 eV per TeO2 unit upon doubling the plane wave cutoff & no# of kpoints.

Enthalpy vs Pressure



Bulk Modulus



Experiment (Sato) Cotunnite over 30-70 Gpa with $K'_0 = 4$

$K_0 = 115 \pm 17$ Gpa

$V_0 = 152.8 Å^3$

Calculated Cotunnite 30-70 Gpa

$K_0 = 119$ Gpa

$V_0 = 155.3 Å^3$

$K'_0 = 4.43$

Calculated Cotunnite 0-16 Gpa

$K_0 = 46.5$ Gpa

$V_0 = 170.9 Å^3$

$K'_0 = 5.35$

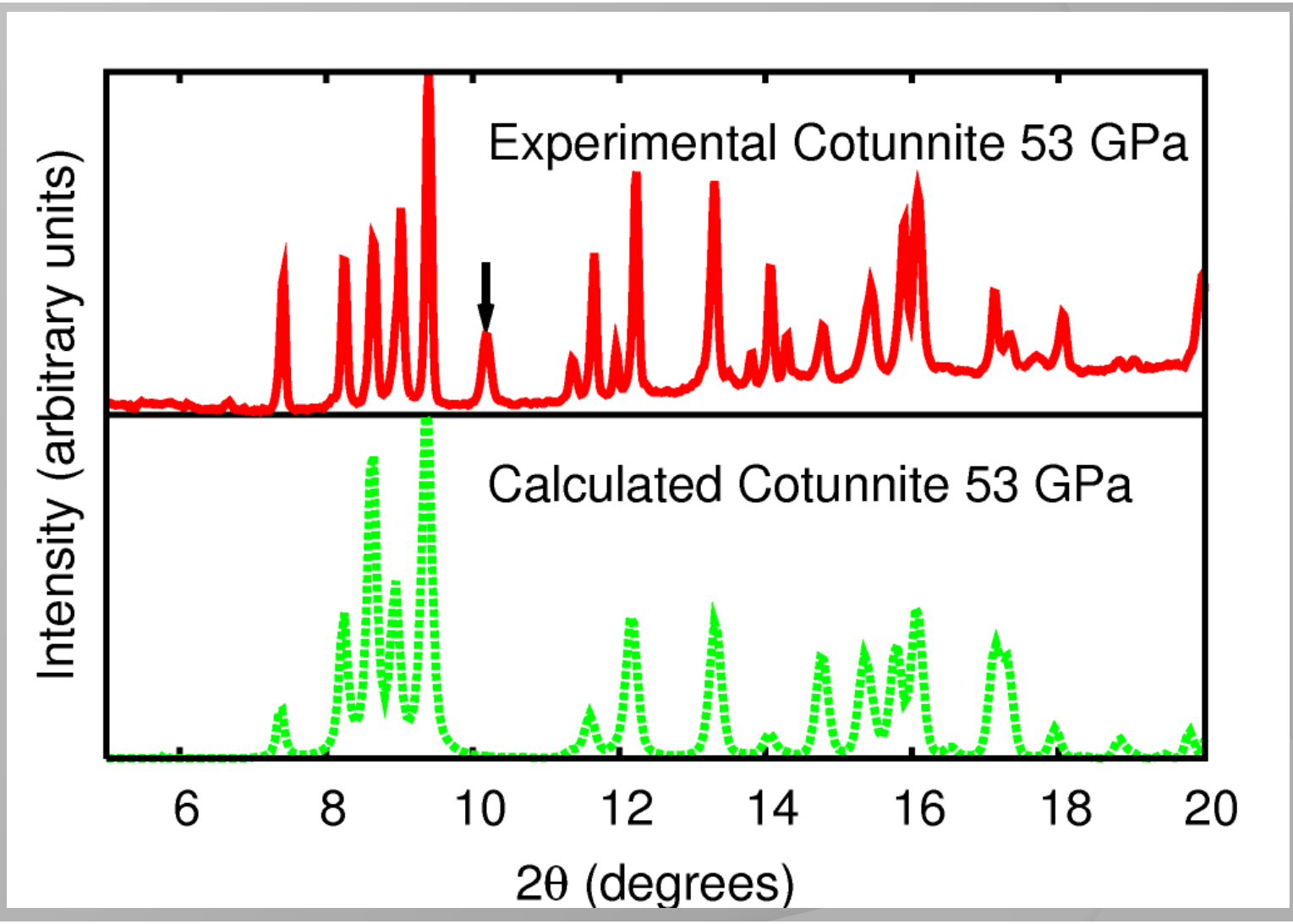
Calculated *P2₁/m* 125-200 Gpa

$K_0 = 114$ Gpa

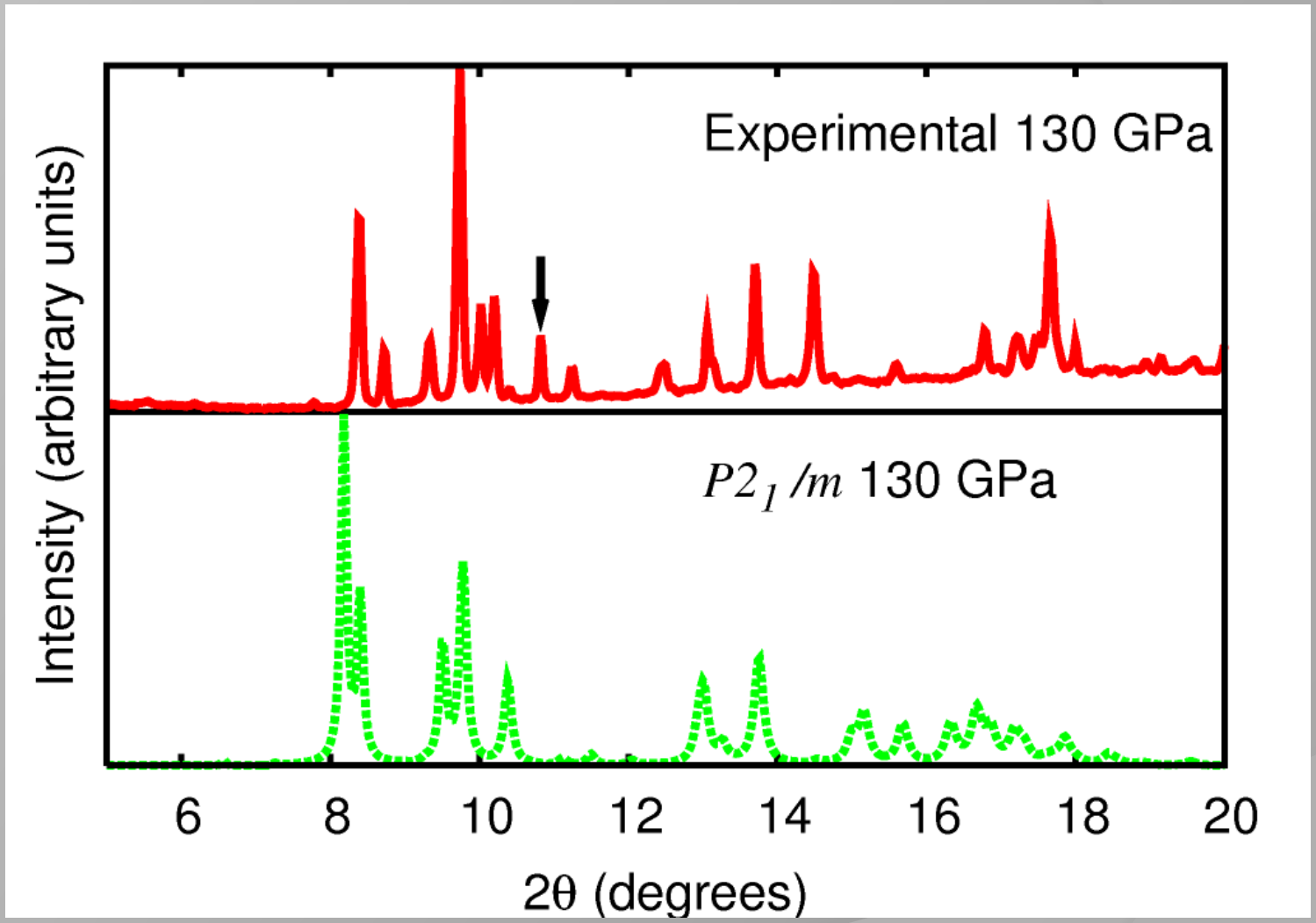
$V_0 = 152.4 Å^3$

$K'_0 = 4.6$

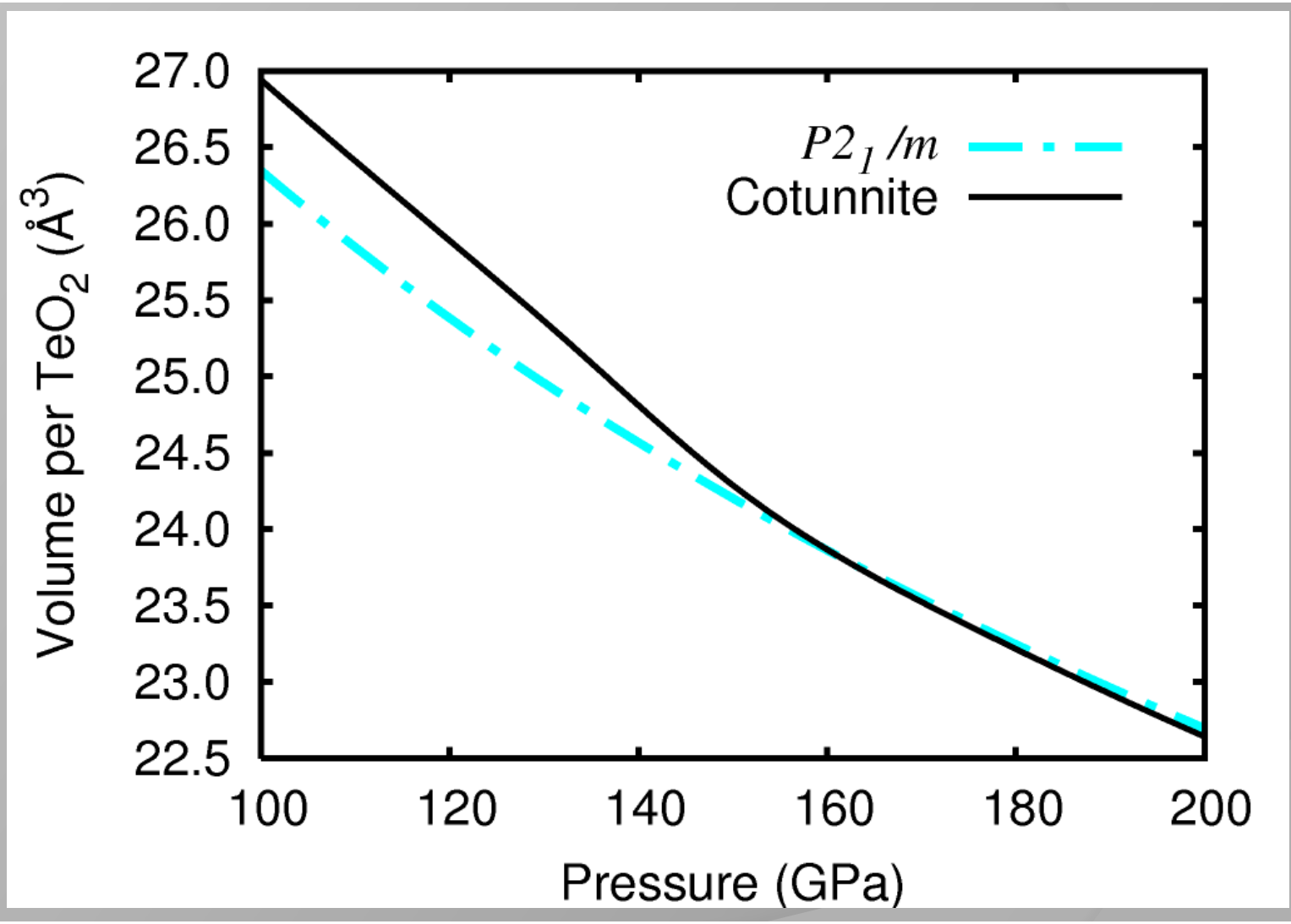
X-ray diffraction



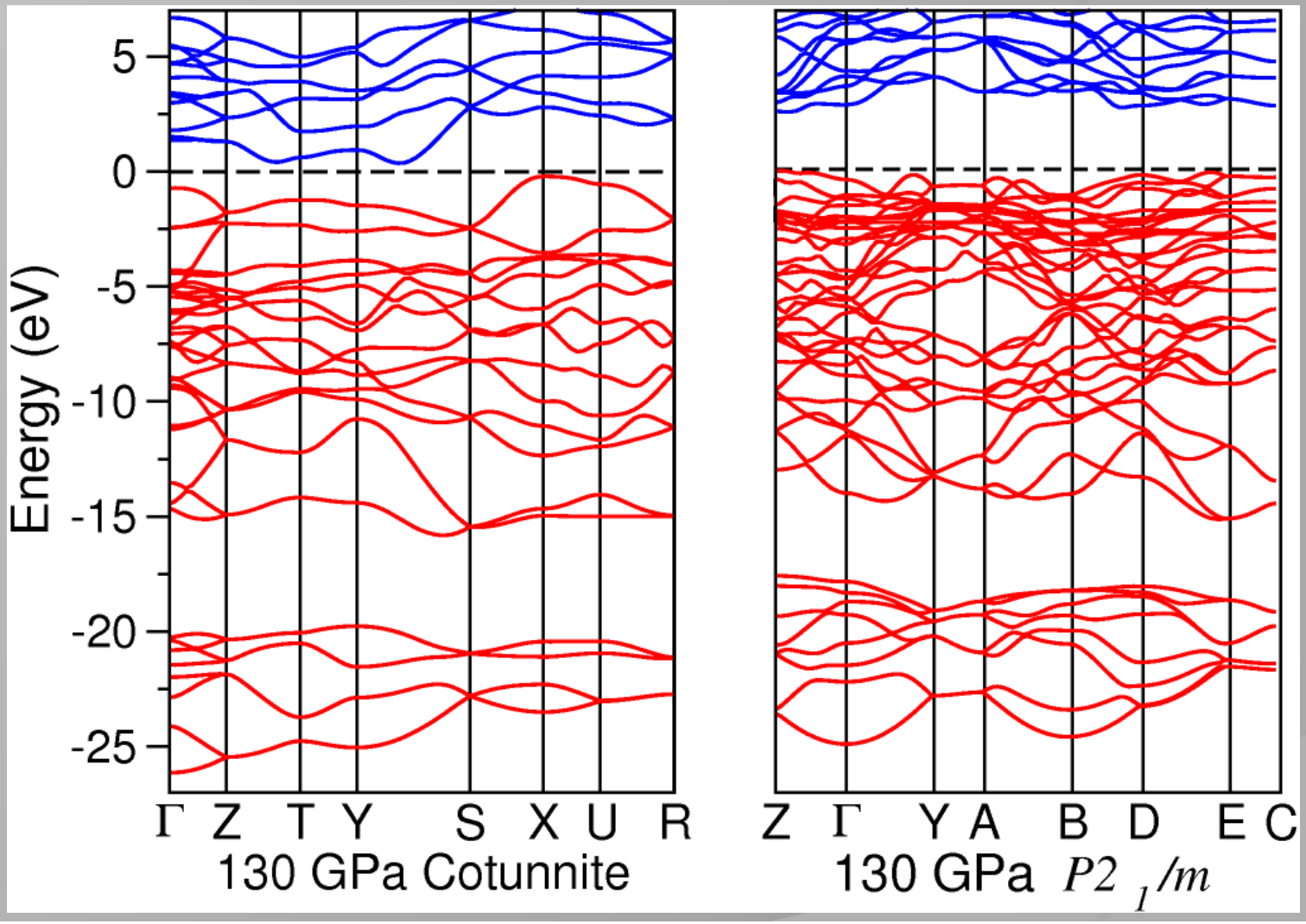
X-ray diffraction



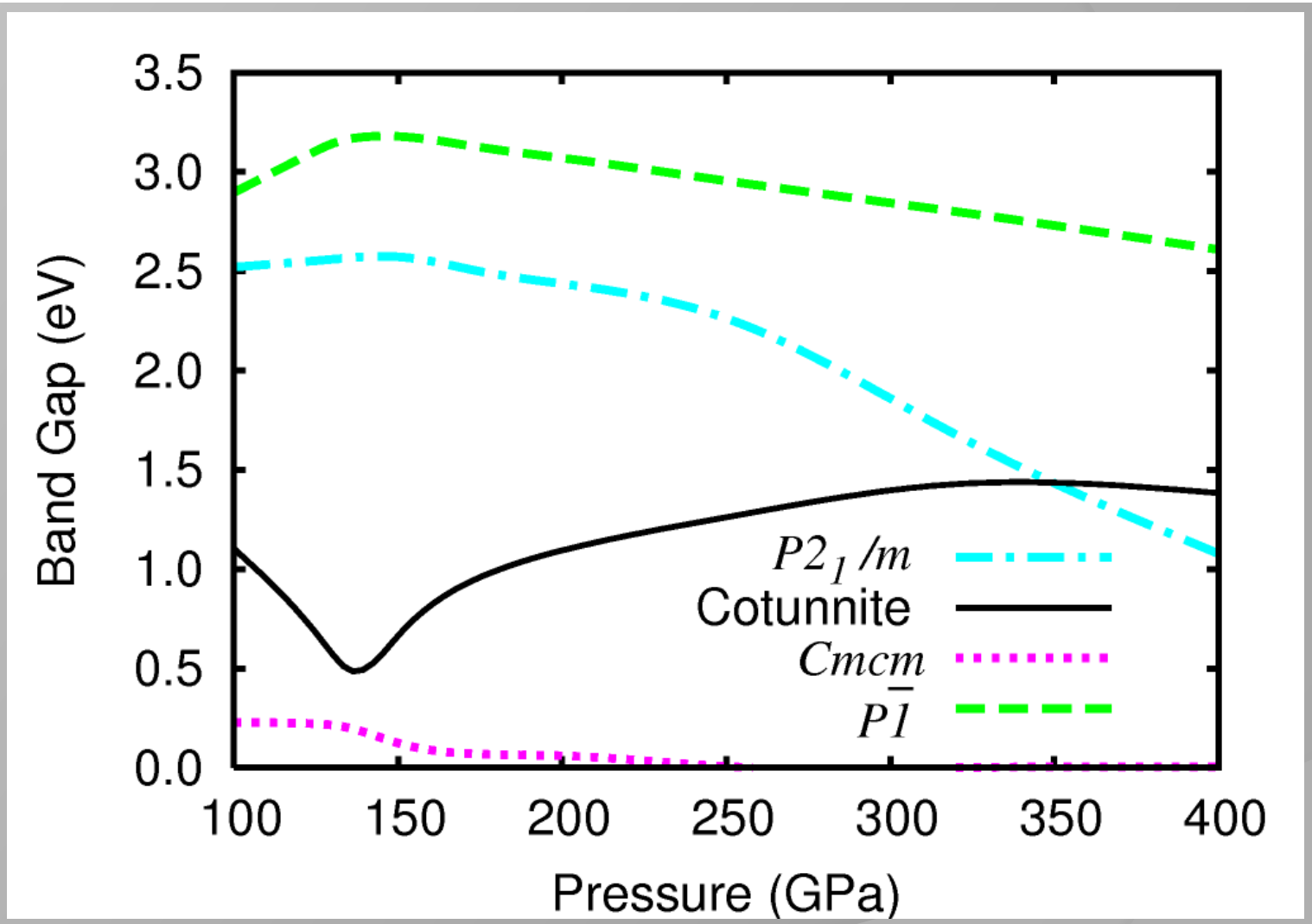
Cotunnite volume 'kink'



Band Structure



Band Gaps


Band Gap (eV)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
100
150
200
250
300
350
400
Pressure (GPa)
$P2_1/m$
Cotunnite
$Cmcm$
$P\bar{1}$

Summary / Conclusions

- Study supports experimental observation of post-cotunnite phase at pressures accessible to a diamond anvil cell.
- Predict transition to $P2_1/m$ phase at 130 Gpa.
- New $P2_1/m$ phase does not appear to be a general post-cotunnite phase (shame...TiO_2 !)
- Cotunnite re-enters at 260 Gpa
- Higher quality x-ray diffraction data required to confirm.

UNIVERSITY OF CAMBRIDGE

Acknowledgments

TCM

EPSRC

Engineering and Physical Sciences Research Council

This work was performed using the Darwin Supercomputer of the University of Cambridge High Performance Computing Service (http://www.hpc.cam.ac.uk/), provided by Dell Inc. using Strategic Research Infrastructure Funding from the Higher Education Funding Council for England.