Beyond SiO$_2$: New tetrahedral and octahedral structures in IV-VI compounds

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Outline

1. Brief overview of SiO_2 and CO_2

2. CS_2 - experiment, our theoretical results

3. SiS_2 - experiment, our theoretical and experimental results

4. Conclusions

IV - VI AB$_2$ compounds

A   B

Group→	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
↓Period																		
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo

*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr
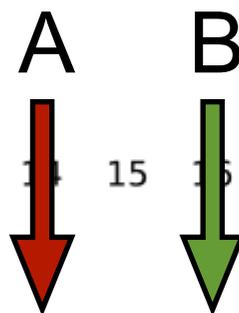
Difference ⟶
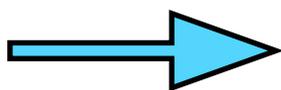
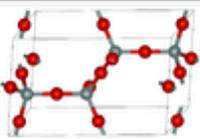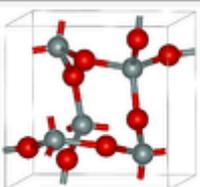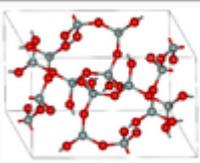- CO_2, CS_2 - molecular
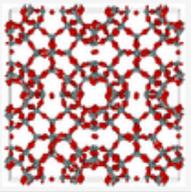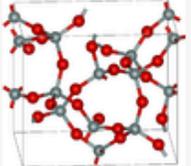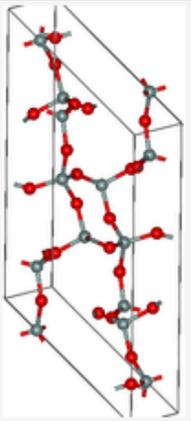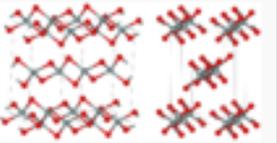- SiO_2, SiS_2 - non molecular

Paradigm: SiO$_2$ (silica)

- important component of Earth's crust (10 %)

- very rich polymorphism

- highly important amorphous phase

- important in many practical applications

- artificially created on Si surface in microelectronics
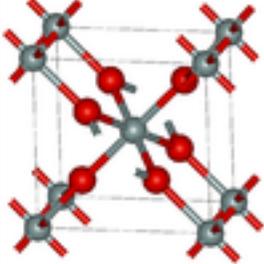
- most common form is α-quartz
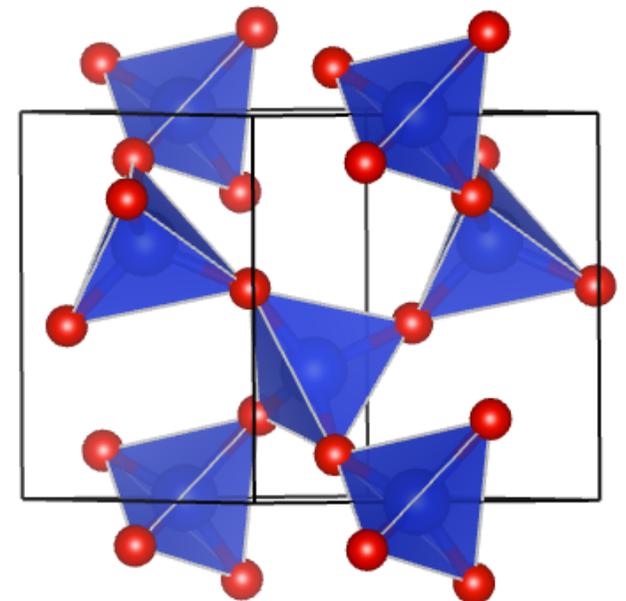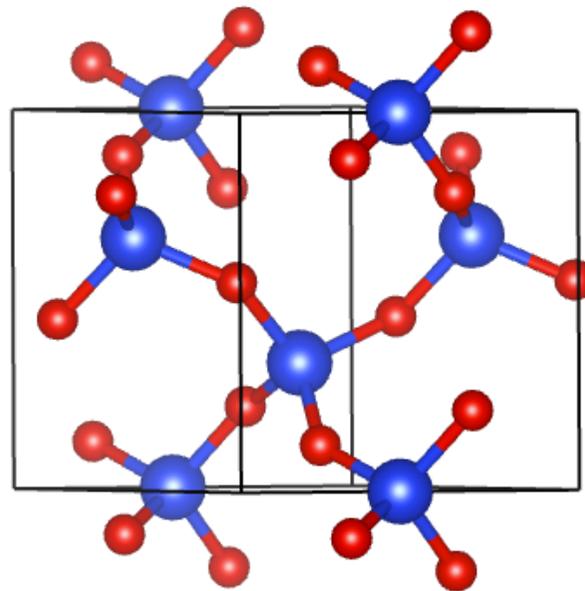
SiO$_2$ polymorphism - tetrahedral 1

Form	Crystal symmetry Pearson symbol, group No.	ρ g/cm^3	Notes	Structure
α-quartz	rhombohedral (trigonal) hP9, P3$_1$21 No.152[33]	2.648	Helical chains making individual single crystals optically active; α-quartz converts to β-quartz at 846 K	
β-quartz	hexagonal hP18, P6$_2$22, No. 180[34]	2.533	closely related to α-quartz (with an Si-O-Si angle of 155°) and optically active; β-quartz converts to β-tridymite at 1140 K	
α-tridymite	orthorhombic oS24, C222$_1$, No.20[35]	2.265	metastable form under normal pressure	
β-tridymite	hexagonal hP12, P6$_3$/mmc, No. 194[35]		closely related to α-tridymite; β-tridymite converts to β-cristobalite at 2010 K	
α-cristobalite	tetragonal tP12, P4$_1$2$_1$2, No. 92[36]	2.334	metastable form under normal pressure	
coesite	monoclinic mS48, C2/c, No.15[43]	2.911	Si$_4$O$_8$ and Si$_8$O$_{16}$ rings; 900 K and 3–3.5 GPa	
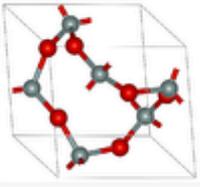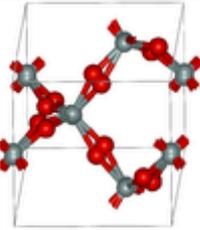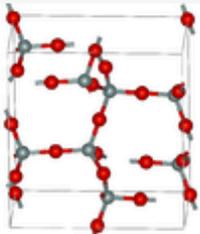
SiO₂ polymorphism - tetrahedral 2

β-cristobalite	cubic cF104, Fd$\bar{3}$m, No.227[37]		closely related to α-cristobalite; melts at 1978 K	
faujasite	cubic cF576, Fd$\bar{3}$m, No.227[38]	1.92	sodalite cages connected by hexagonal prisms; 12-membered ring pore opening; faujasite structure.[14]	
melanophlogite	cubic (cP*, P4₂32, No.208)[10] or tetragonal (P4₂/nbc)[39]	2.04	Si_5O_{10}, Si_6O_{12} rings; mineral always found with hydrocarbons in interstitial spaces-a clathrasil[40]	
keatite	tetragonal tP36, P4₁2₁2, No. 92[41]	3.011	Si_5O_{10}, Si_4O_{14}, Si_8O_{16} rings; synthesised from glassy silica and alkali at 600–900 K and 40–400 MPa	
moganite	monoclinic mS46, C2/c, No.15[42]		Si_4O_8 and Si_6O_{12} rings	
fibrous W-silica[4]	orthorhombic oI12, Ibam, No.72[45]	1.97	like SiS_2 consisting of edge sharing chains, melts at ~1700 K	
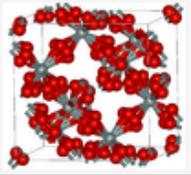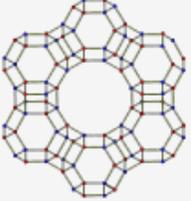
SiO₂ polymorphism - octahedral

stishovite	Tetragonal tP6, P4$_2$/mnm, No.136[44]	4.287	One of the densest (together with seifertite) polymorphs of silica; rutile-like with 6-fold coordinated Si; 7.5–8.5 GPa	
seifertite	orthorhombic oP, Pbcn[46]	4.294	One of the densest (together with stishovite) polymorphs of silica; is produced at pressures above 40 GPa.[47]	
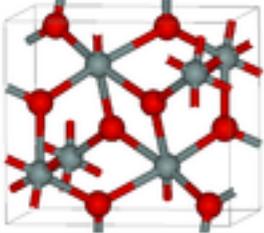
Wikipedia

- further increasing pressure in Mbar range silica acquires pyrite-like structure

- no layered structures

Most important crystalline phases of silica

Figure 1. Crystal structures of principal SiO_2 polymorphs considered in this chapter. Top row, left to right: Quartz, cristobalite, tridymite. Bottom row: Coesite, stishovite.
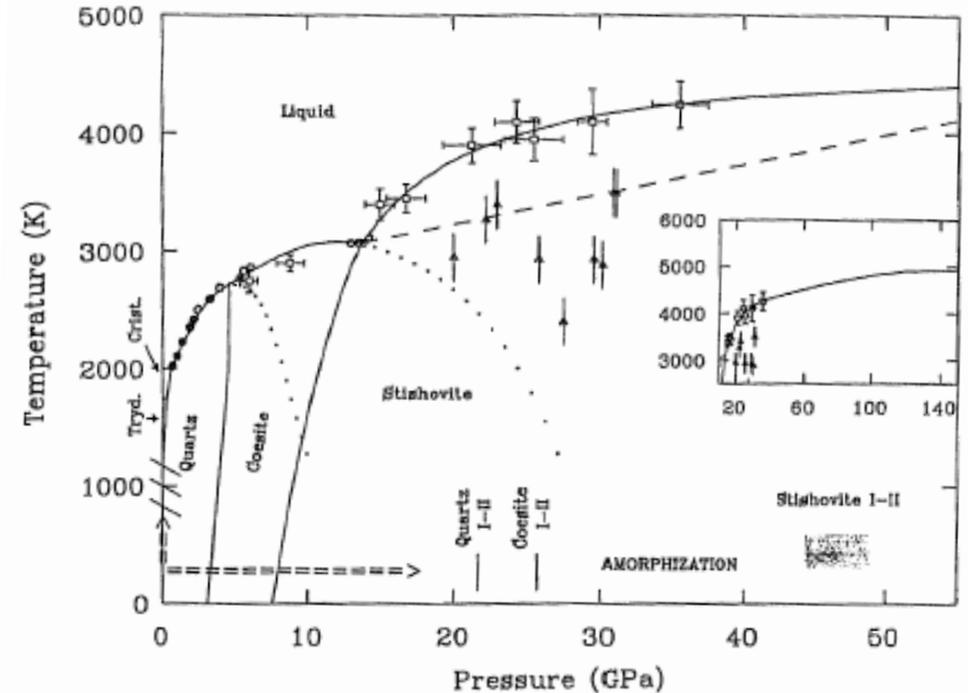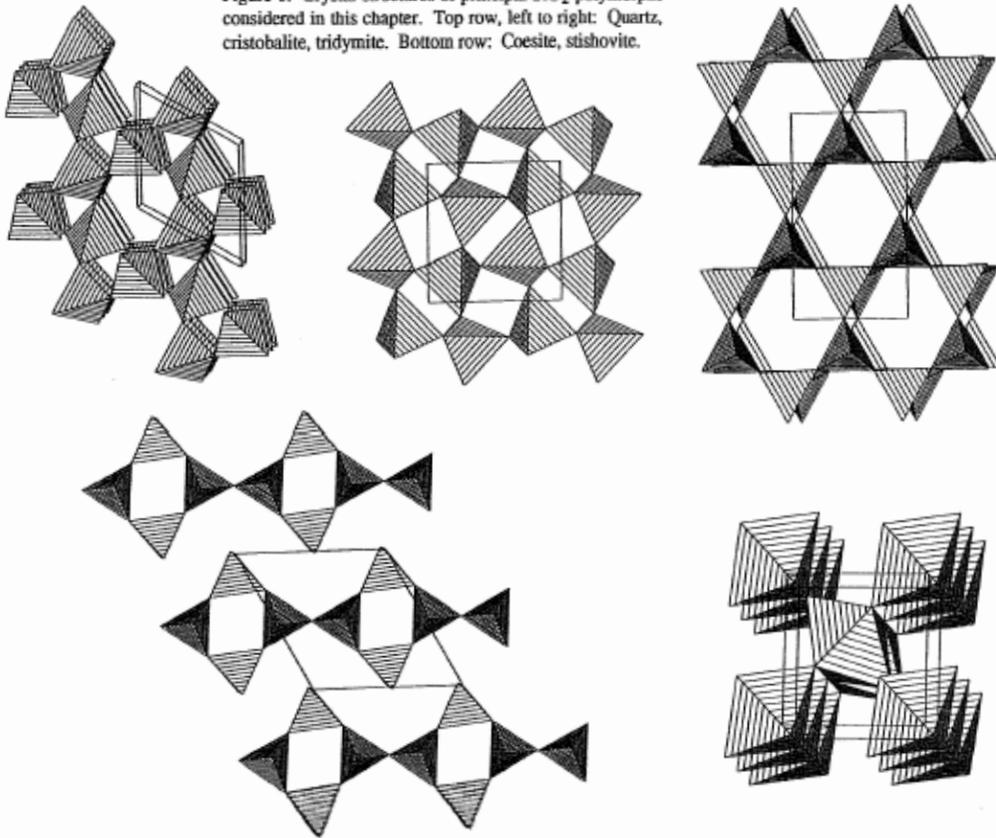

Hemley, Prewitt, Kingma: *High-Pressure Behavior of Silica* 45

Figure 2. High P-T phase diagram of SiO_2 determined from static compression experiments. The solid lines are equilibrium phase boundaries consistent with the available data (see text). Data points for the high-pressure melting curves are shown: closed circles, Jackson (1976); open circles, Kanzaki (1990), Zhang et al. (1993); squares, Shen and Lazor (1994); triangles, shock-compression data from Kondo and Ahrens (1983) and Schmitt and Ahrens (1989). The dashed line is the stishovite melting line suggested by Zhang et al. (1993). The dotted lines are metastable extensions of quartz and coesite melting calculated from thermochemical data (Zhang et al., 1993). The stishovite I-II transition (Cohen, 1992; Kingma, 1994), and the (metastable) quartz I-II (Kingma et al., 1993b) and coesite I-II (Hemley, 1987) transitions, all observed 300 K, are shown. The approximate pressures of extensive room-temperature static pressure amorphization are shown; progressive amorphization associated with microfracture begins at lower pressures (horizontal arrow) (Kingma et al., 1993a). The ambient-pressure amorphization of coesite and stishovite is indicated by the vertical arrow (e.g. Richet, 1989). *Inset*: Higher pressure range determined from shock-wave experiments, adapted from Schmitt and Ahrens (1989) and Lyzenga et al. (1983).

from "High-pressure behaviour of silica", Hemley, Prewitt, Kingma (1994)
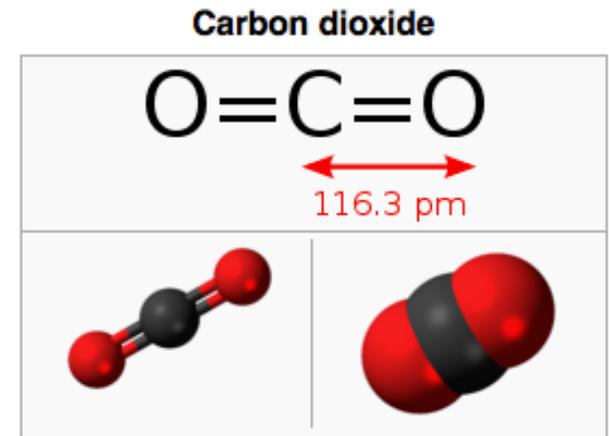
Amorphous silica (glass)

- material used by mankind since many years - Syria, Mesopotamia, Egypt (2500 BC)
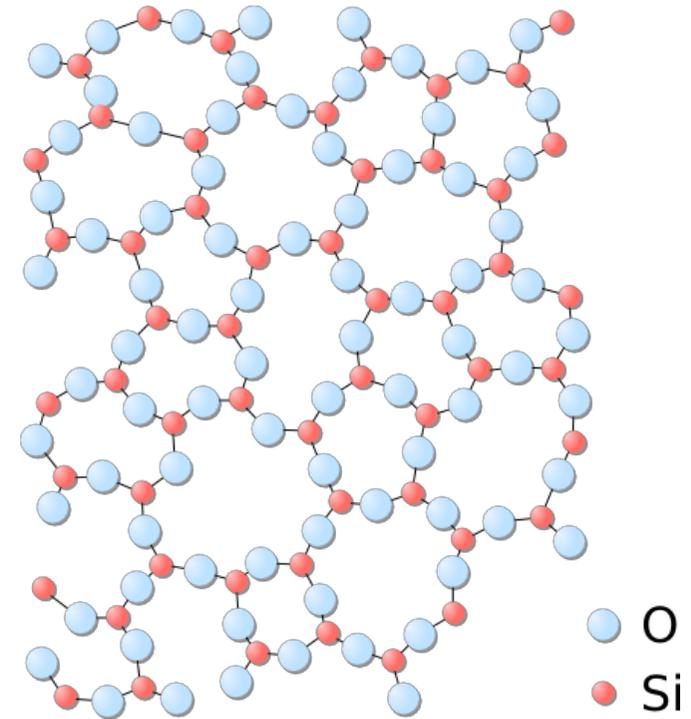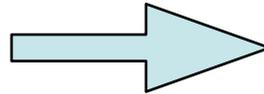

polyamorphism - LDA, HDA silica

Carbon dioxide

O=C=O

116.3 pm

- molecular, at ambient conditions gas

- carbon dioxide counts among most important materials on Earth and in the Solar system

- solid CO_2 has a number of molecular phases - I, II, III, IV

- well-known molecular phase is dry ice (phase I)

- upon compression above 20 GPa dry ice transforms to another molecular phase III (*Cmca*)

- at high pressure double bonds in CO_2 molecules are destabilized and polymeric phases with single bonds are created (similar to those found in SiO_2)

Dry ice
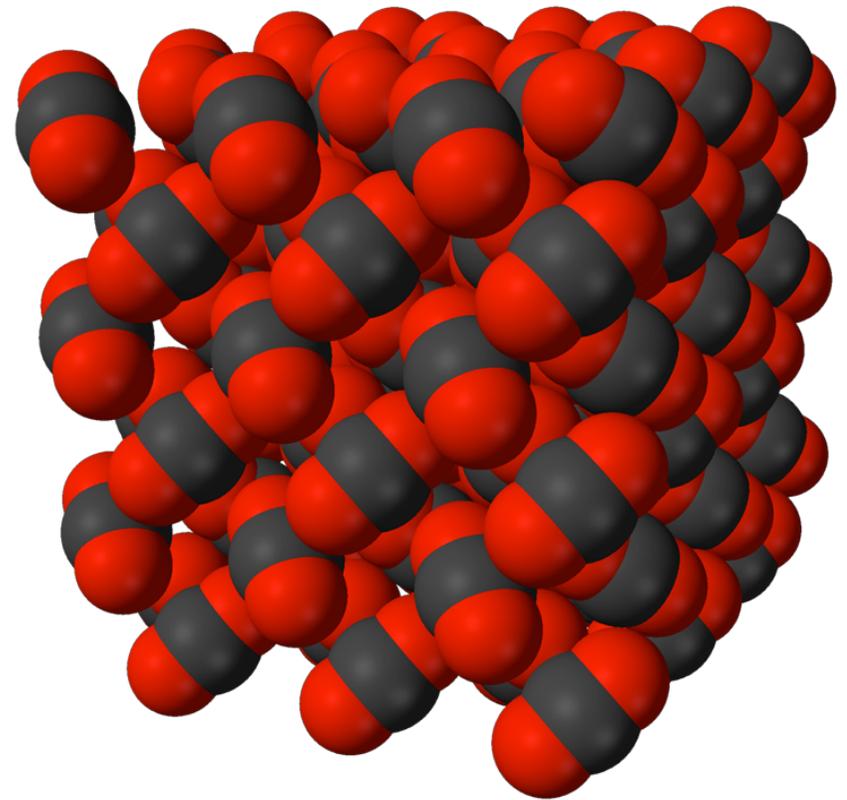
sublimates at −78.5 °C

Wikipedia

Polymerization of CO_2 at high pressure

- SiO_2 at low pressure forms tetrahedral covalent structures
- CO_2 at low pressure forms molecular crystals
- molecular phases of CO_2 under pressure transform to tetrahedral polymeric ones, similar to those of SiO_2
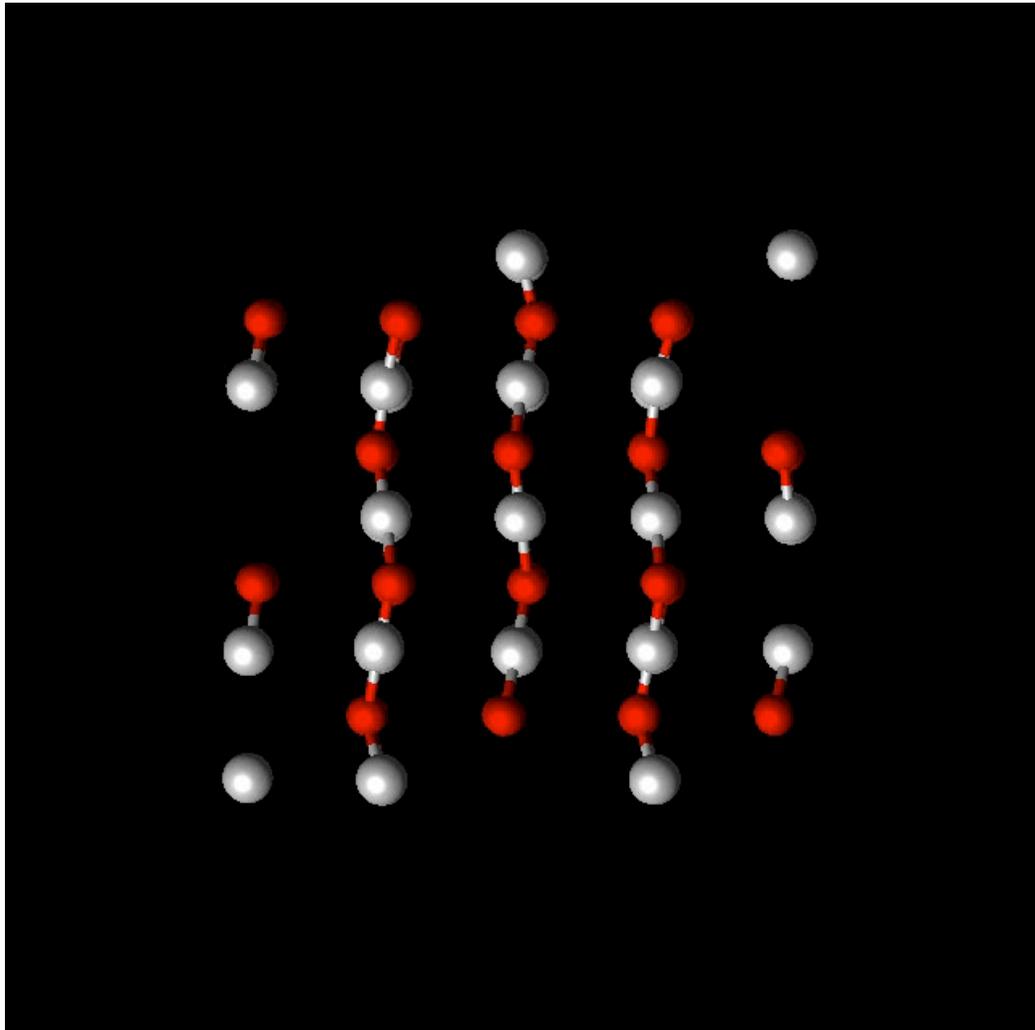- many open questions about structures and transformation paths remain
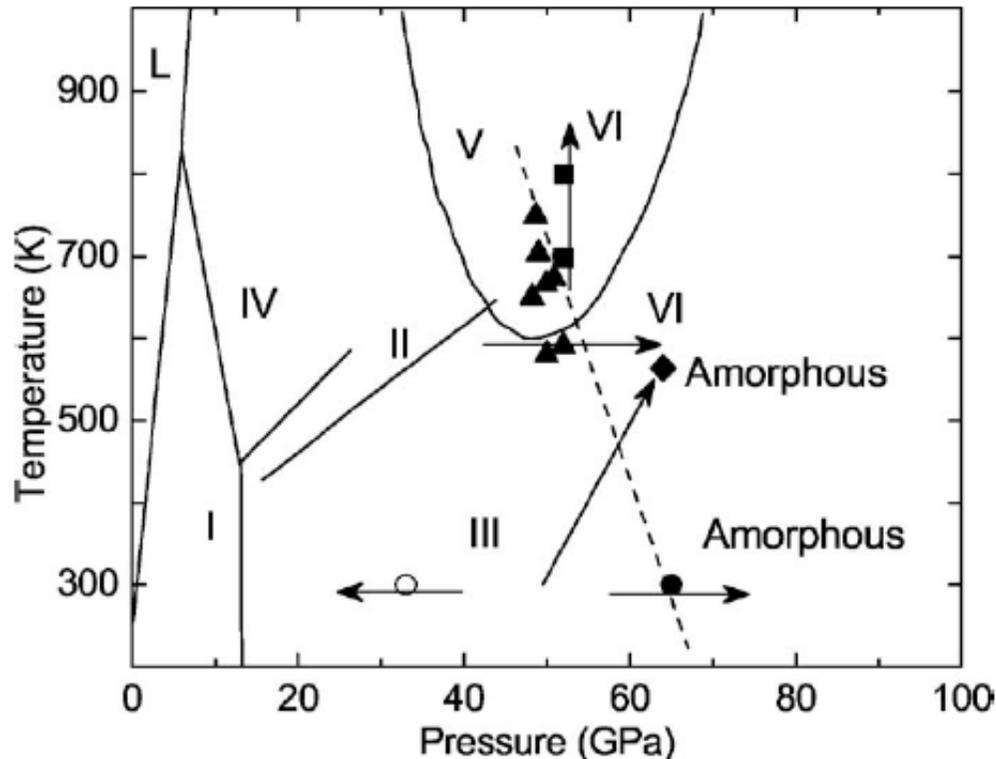
Phase diagram of CO_2, Kume et al. (2007)

Phase III → α-cristobalite-type phase

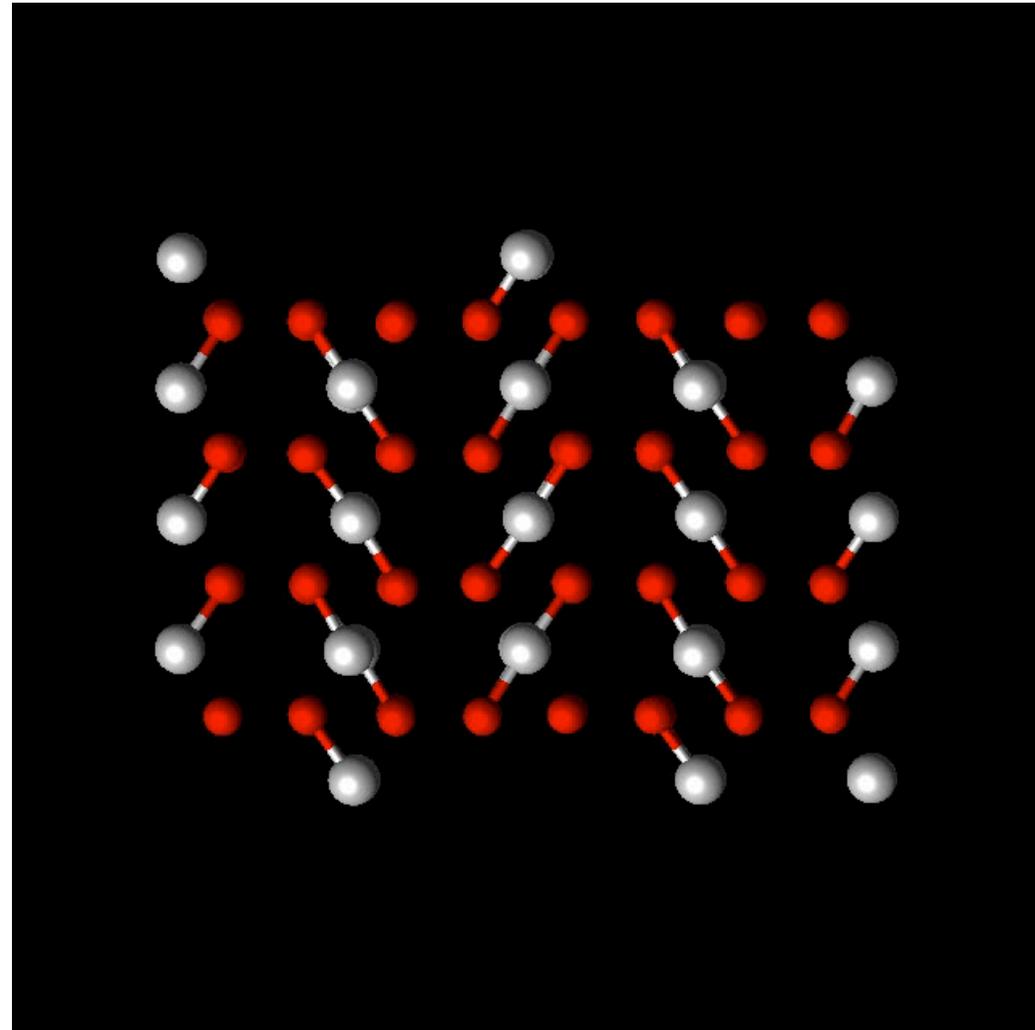## metadynamics, P = 800 kbar, T = 100 K

view along z   view along x

Structure of polymeric CO₂

Structure of Polymeric Carbon Dioxide CO_2-V

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[2]*European Radiation Synchrotron Facility, F-38043 Grenoble Cedex, France*
(Received 2 November 2011; published 19 March 2012)

The structure of polymeric carbon dioxide (CO_2-V) has been solved using synchrotron x-ray powder diffraction, and its evolution followed from 8 to 65 GPa. We compare the experimental results obtained for a 100% CO_2 sample and a 1 mol % CO_2/He sample. The latter allows us to produce the polymer in a pure form and study its compressibility under hydrostatic conditions. The high quality of the x-ray data enables us to solve the structure directly from experiments. The latter is isomorphic to the β-cristobalite phase of SiO_2 with the space group $I\bar{4}2d$. Carbon and oxygen atoms are arranged in CO_4 tetrahedral units linked by oxygen atoms at the corners. The bulk modulus determined under hydrostatic conditions, $B_0 = 136(10)$ GPa, is much smaller than previously reported. The comparison of our experimental findings with theoretical calculations performed in the present and previous studies shows that density functional theory very well describes polymeric CO_2.
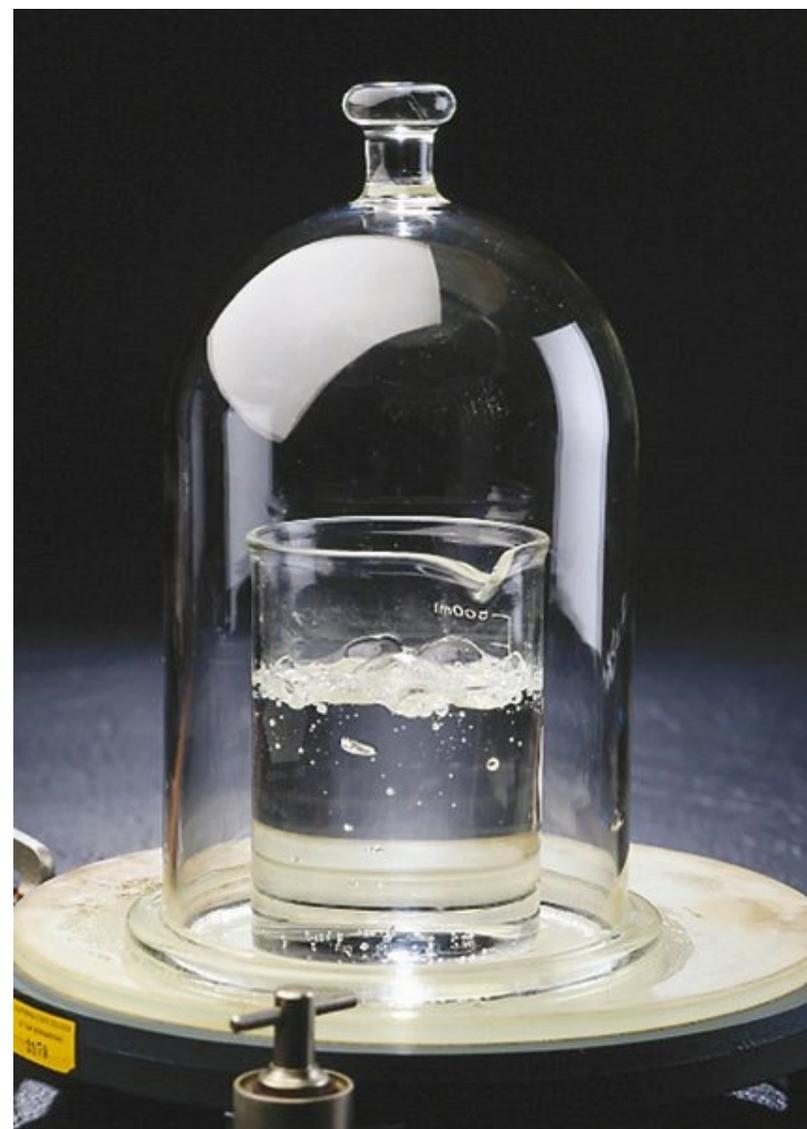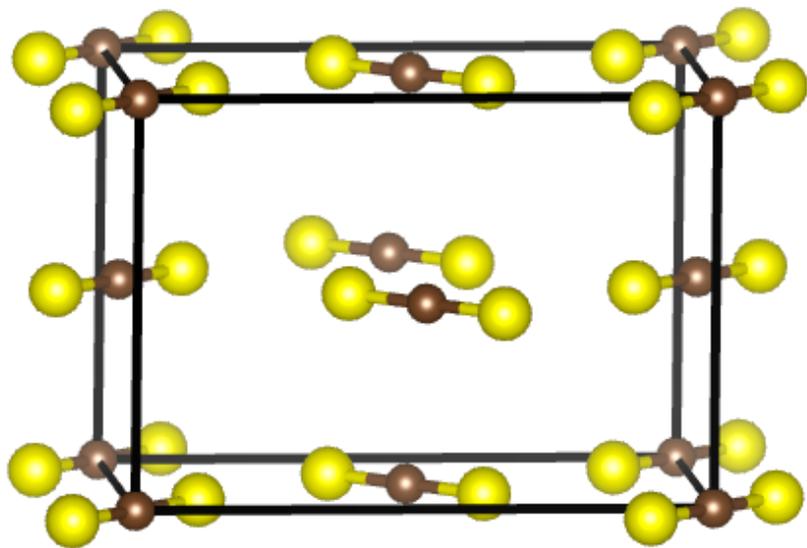
β-cristobalite-like *I-42d*

# CS₂

Carbon disulfide
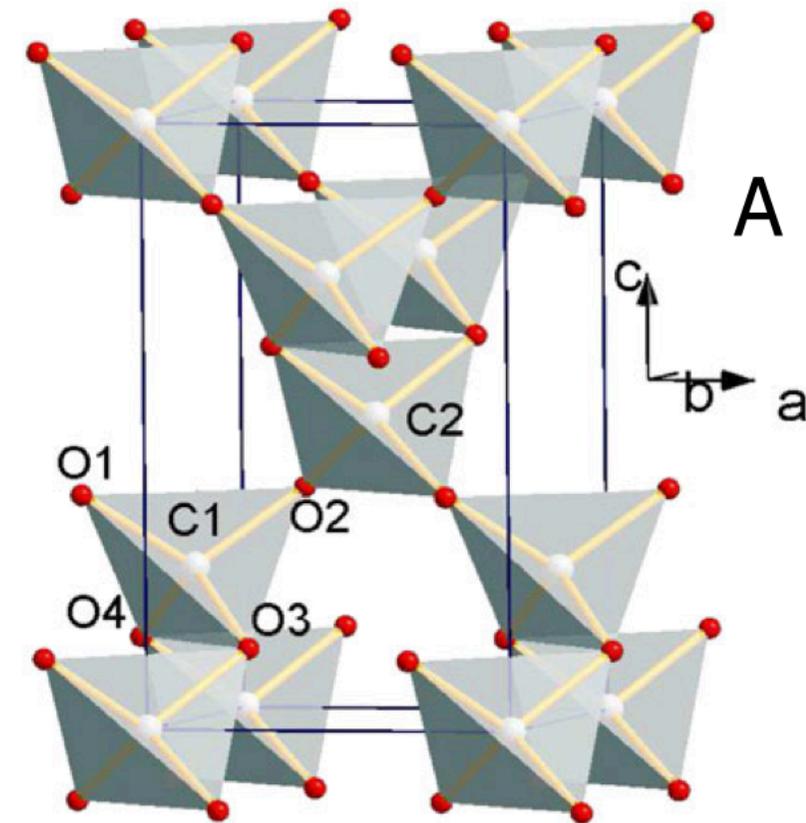
Wikipedia
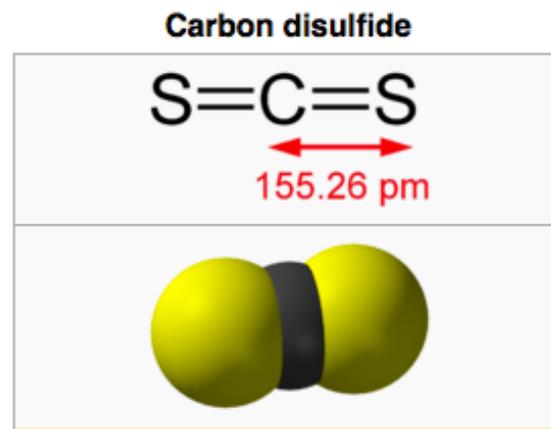
- **metastable compound** - enthalpy of formation 88.7 kJ/mol
- at ambient conditions molecular liquid
- below 161 K freezes to *Cmca* molecular crystal

CS$_2$ at high pressure

Nobel prize 1946 - Percy Williams Bridgman

- Bridgman (1941) compressed Cmca CS$_2$ to 4.5 GPa at 175 C
- transformation to black polymer observed
- Whalley (1960) proposed a polymeric structure based on a group
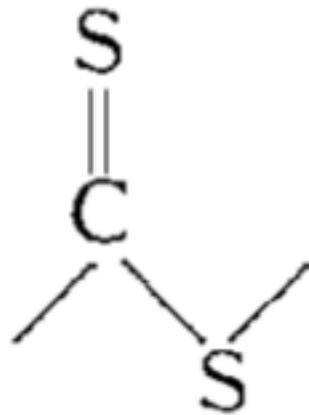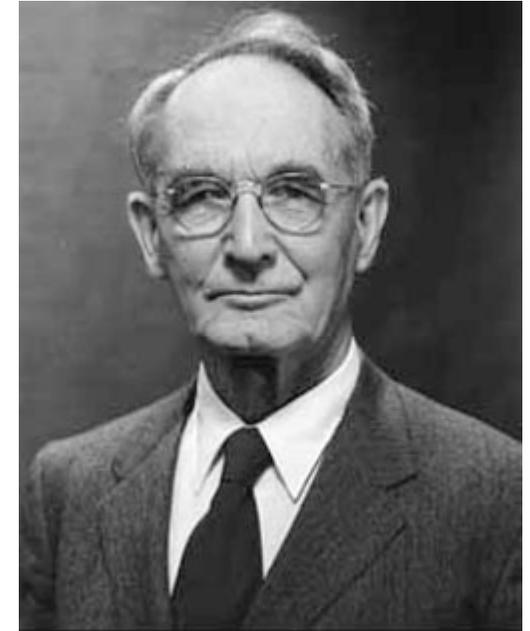
- exact crystal structure is not known

CS$_2$ at high pressure

Insulator-metal transition of highly compressed carbon disulfide

Ranga P. Dias,[1] Choong-Shik Yoo,[1,*] Minseob Kim,[1] and John S. Tse[2]

[1]*Institute for Shock Physics, Department of Chemistry and Department of Physics, Washington State University, Pullman, Washington 99164, USA*

[2]*Department of Physics and Engineering Physics, University of Saskatchewan, Saskatchewan, Canada, S7N 5E2*

We present integrated spectral, structural, resistance, and theoretical evidences for simple molecular CS$_2$ transformations to an insulating black polymer with threefold carbon atoms at 9 GPa, then to a semiconducting polymer above 30 GPa, and finally to a metallic solid above 50 GPa. The metallic phase is a highly disordered three-dimensional network structure with fourfold carbon atoms at the carbon-sulfur distance of ∼1.70 Å. Based on first-principles calculations, we present two plausible structures for the metallic phase: α-chalcopyrite and tridymite, both of which exhibit metallic ground states and disordered diffraction features similar to that measured. We also present the phase and chemical transformation diagram for carbon disulfide, showing a large stability field of the metallic phase to 100 GPa and 800 K.
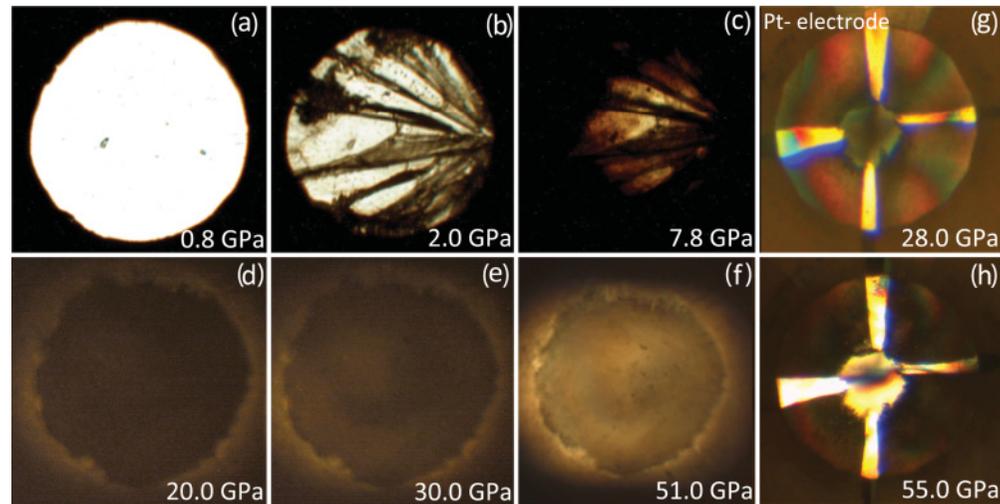

FIG. 1. (Color online) Microphotographs of carbon disulfide under high pressure showing its transformation from (a) transparent fluid to (b) and (c) molecular solid (*Cmca*) at ∼1 GPa, to (d), (e), and (g) black polymer above 10 GPa ((-S-(C=S)-)$_p$ or *CS3*) and eventually to (f) and (h) a highly reflecting extended solid above 48 GPa (*CS4*) at ambient temperature. The rightmost image (h) illustrates the metallic reflectivity of CS$_2$ samples above 55 GPa similar to those of Platinum (Pt) metal probes in a four-probe configuration for resistance measurements.

CS₂ at high pressure
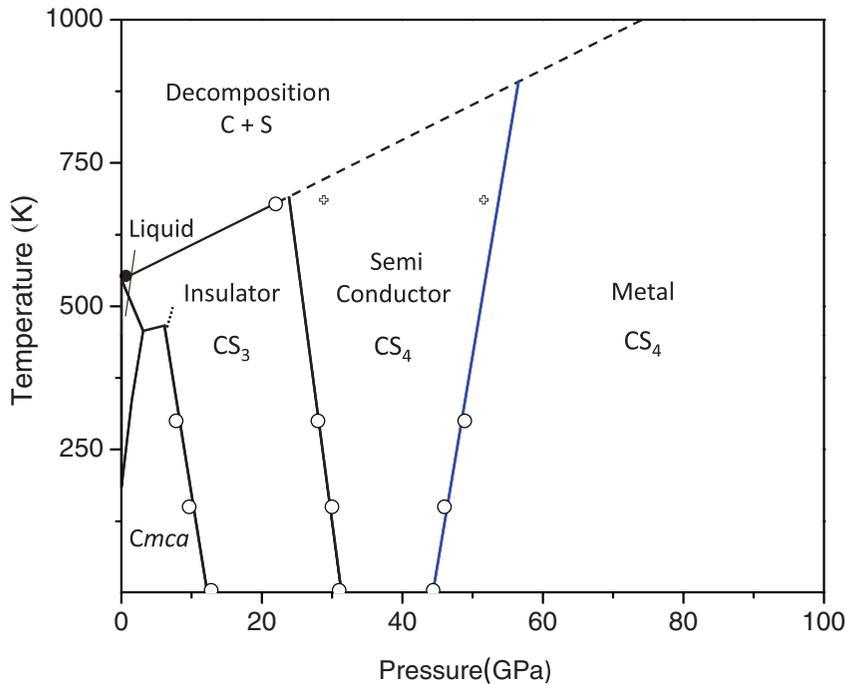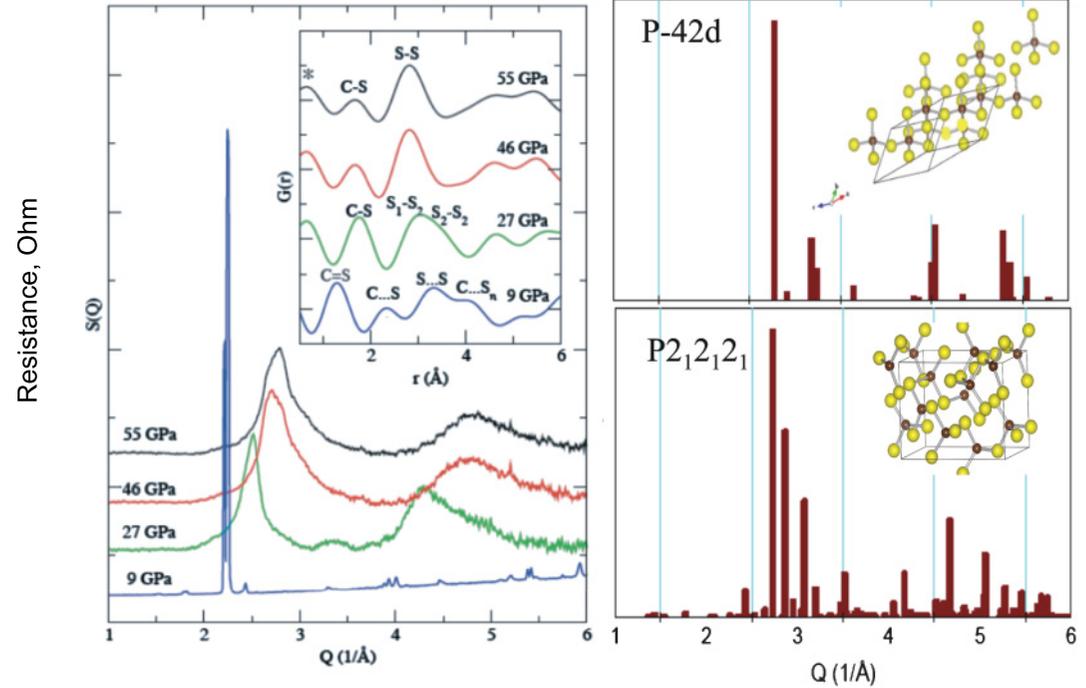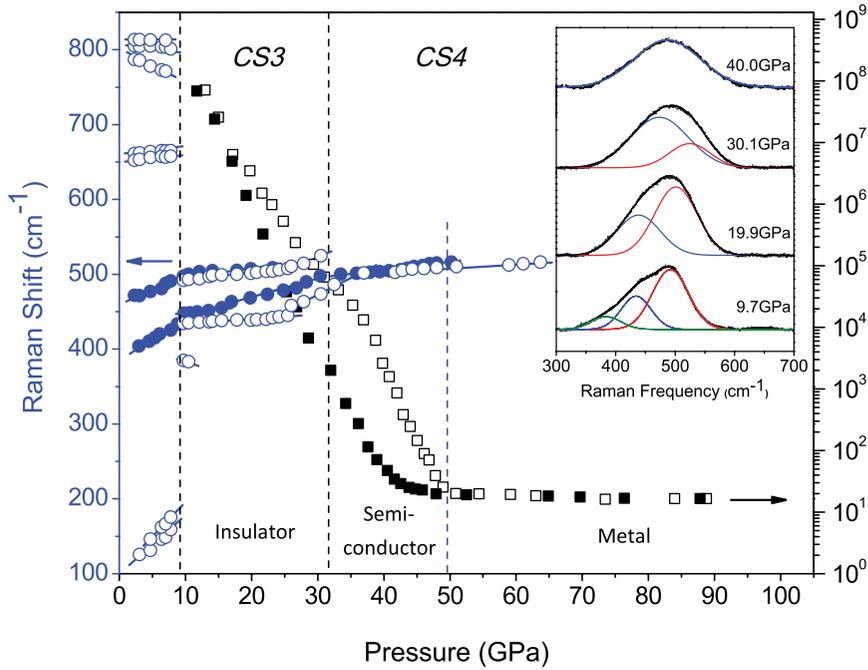
here the notation CS₃, CS₄ refers to carbon coordination, not to stoichiometry

Proposed interpretation

- based on analogy with CO_2, tridymite and β-cristobalite were proposed as candidates for tetrahedral CS_2
- comparison to experiment elusive because of disorder
- does the analogy with CO_2 really work well for CS_2?
- why not considering also analogy with e.g. SiS_2?

Our goal

- address the problem with state-of-the-art ab initio crystal structure search techniques

Crystal structure prediction -
ab initio genetic algorithms

- we work at T=0 and optimize enthalpy H = E + PV

- we used the USPEX software (Oganov, Glass 2006)

- ab initio calculations and structural relaxations performed by VASP

- plain PBE functional used for structural search

- enthalpies calculated by the optB86b-vdW scheme of Klimeš et al. (2010, 2011) based on the vdW functional of Dion et al. (2004)

- phonon, Raman and IR calculations performed by Quantum Espresso using LDA functional

Problem with decomposition in CS_2

intrinsic metastability towards decomposition
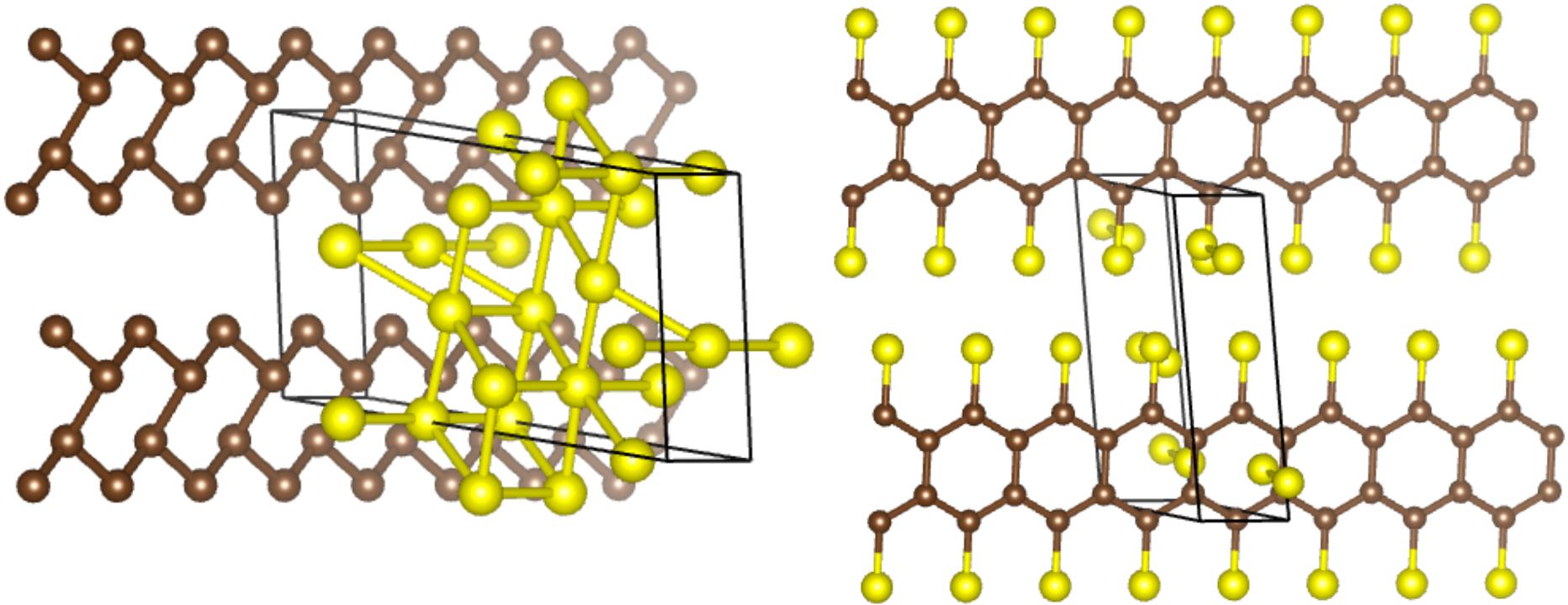
Solution - constraint on C-C and S-S bond lengths

Results of EA search
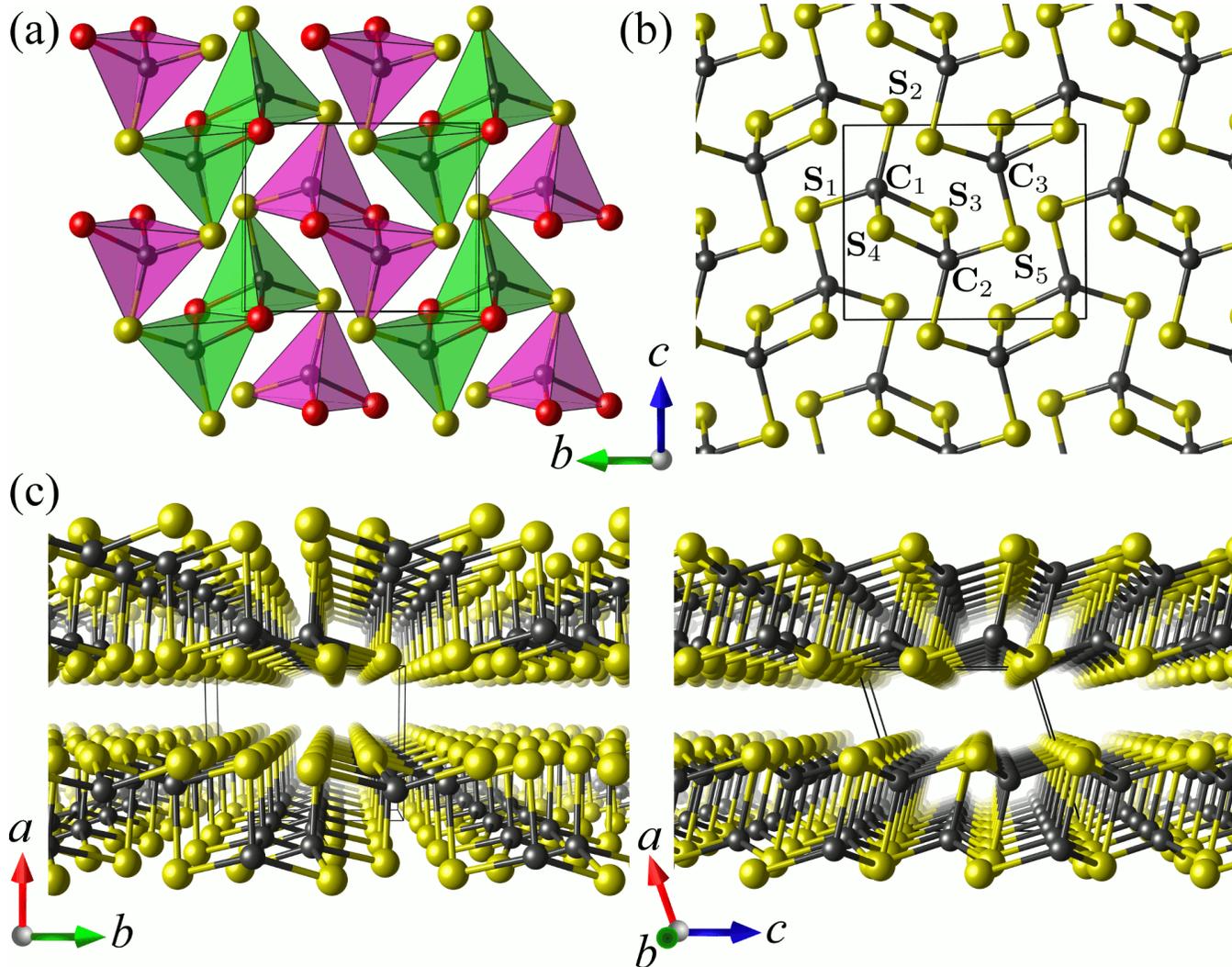
- search performed at p= 0, 26, 38, 75, 120, and 170 GPa
- at p=0 we reproduced the molecular *Cmca* phase
- at higher p we found various tetrahedral structures, α- and β-cristobalite
- new tetrahedral layered structure with space group *P2$_1$/c*
- also various octahedral structures with high enthalpy
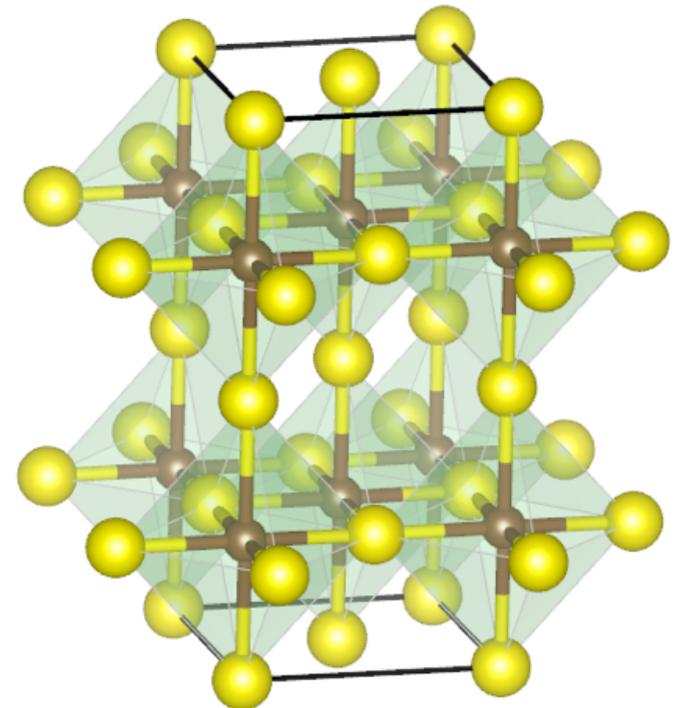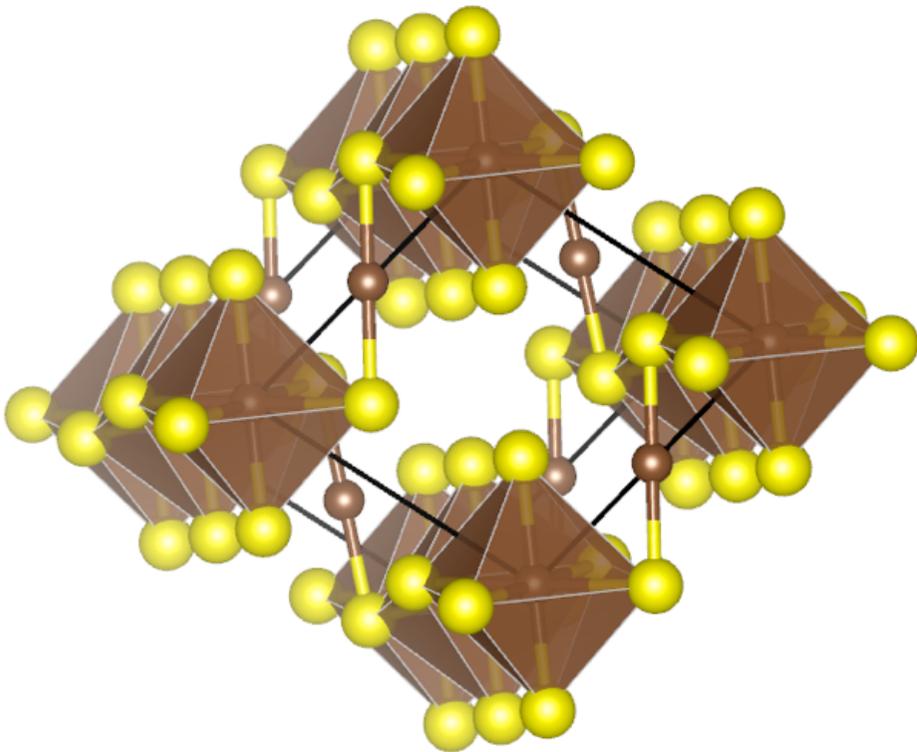
Results of EA search
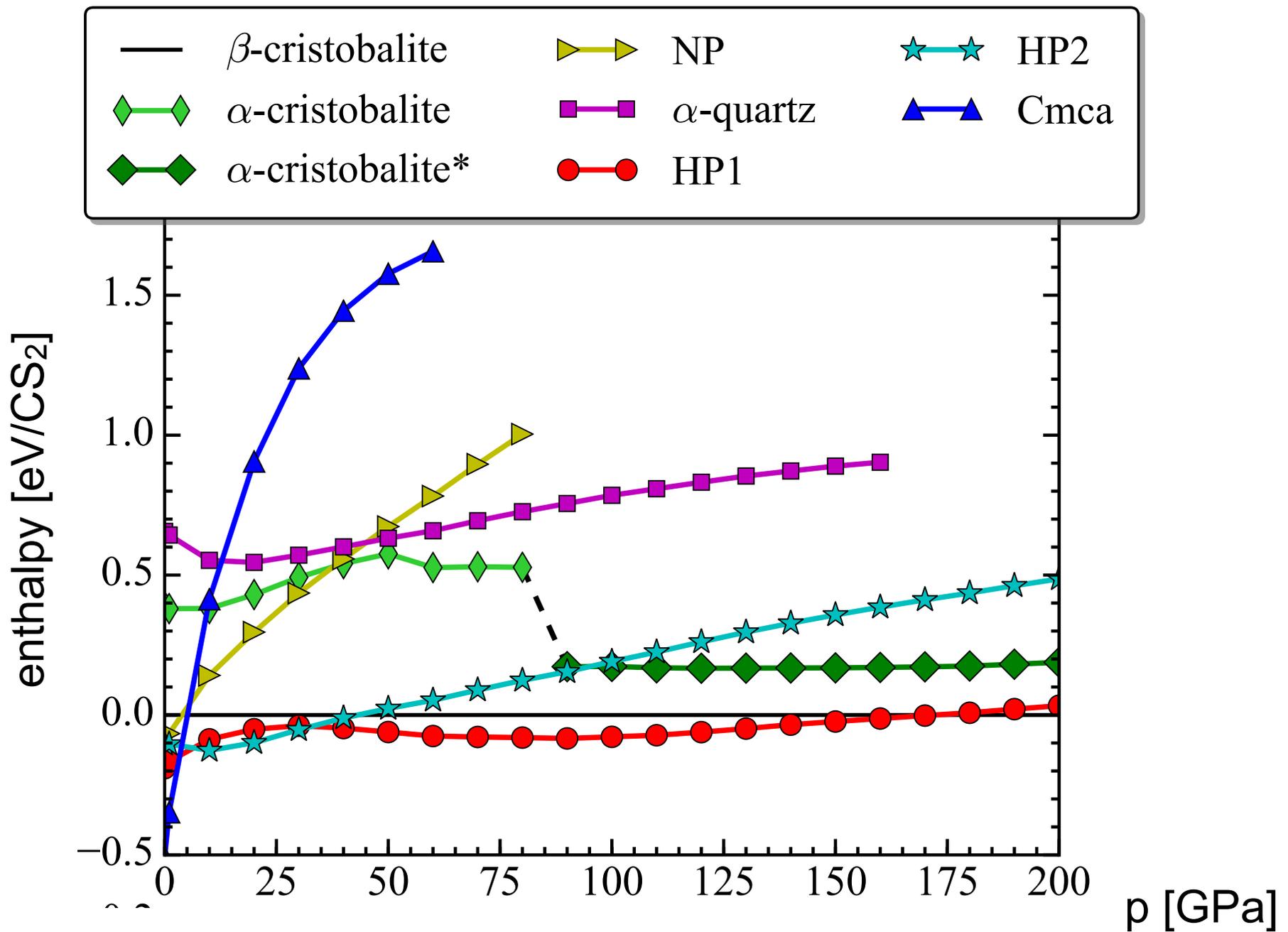
Best tetrahedral structure *P2₁/c* (HP1)

"shahabite" - layered with edge-sharing octahedra

3rd Pauling's rule (1929)

The sharing of edges and particularly faces by two anion polyhedra decreases the stability of an ionic structure.

- comparison: in CO_2 the *P21/c* structure is higher in enthalpy with respect to β-cristobalite by 0.4 eV/molecule

- Bader charge analysis
- partial charges on atoms C (+2), O (-1)
- in CS_2 it is quite different C (-0.55), S (+0.27)
- not only smaller charge, but opposite polarity
- electronegativities: C 2.55, S 2.58
- edge-sharing more plausible in less ionic CS_2

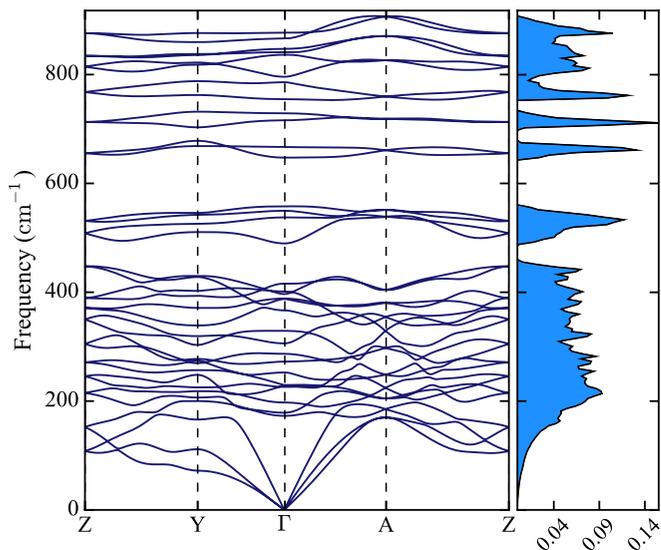# Diffraction patterns
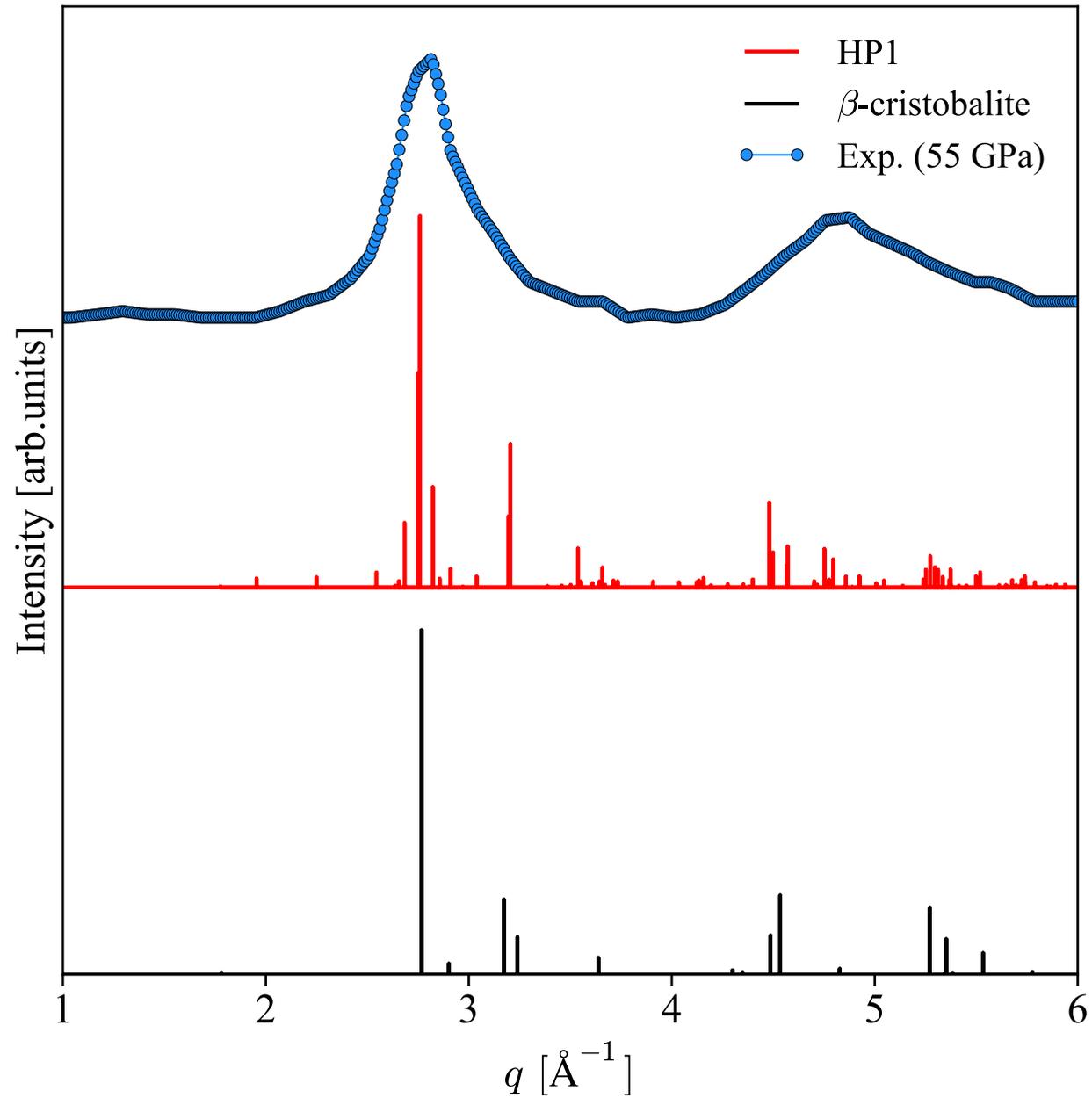
Phonons and spectroscopy

FIG. 5. (Color online) Calculated phonon spectrum of the $P2_1/c$ layered structure of CS_2 at 50 GPa.
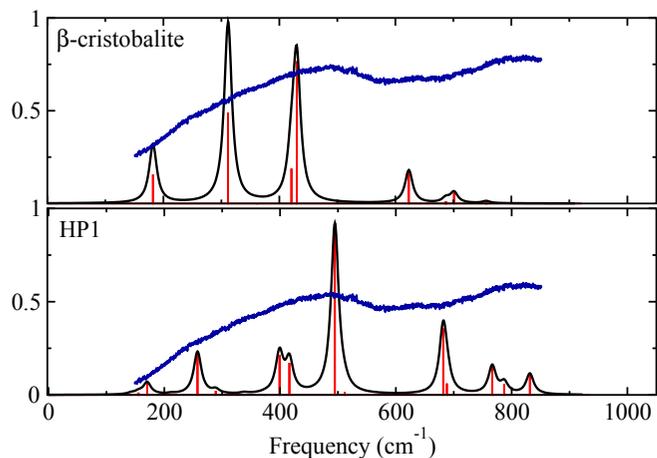

FIG. 6. (Color online) Predicted Raman spectra of two competing CS_2 structures at 50 GPa, compared with measurements at 50 GPa, 297 K.[7] The high frequency secondary peak near 800 cm^{-1} is only present in layered $P2_1/c$ and absent in β-cristobalite. Also the low frequency spectrum is better reproduced by HP1 than by β-cristobalite.
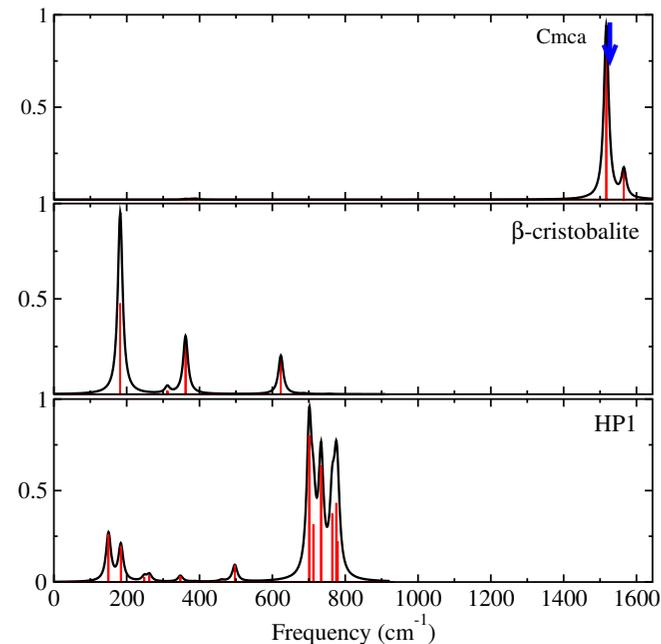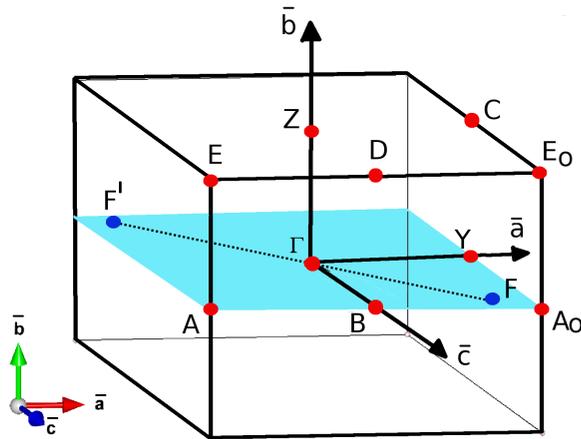

FIG. 7. (Color online) Calculated IR spectra of different CS_2 structures. Note the stiffer frequencies of layered HP1 compared with β-cristobalite. Blue arrows indicate the experimental IR peak positions of molecular CS_2.[28,29]

Metallization

- in PBE metallization at 30 GPa
- in B3LYP at 50 GPa
- closes indirect gap
- unlike tetrahedral CO_2, CS_2 metalizes very easily with pressure
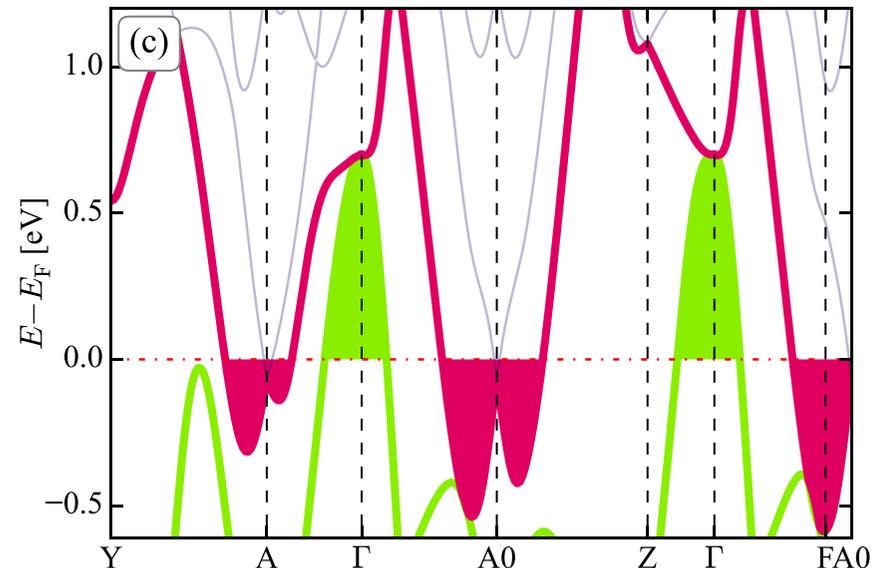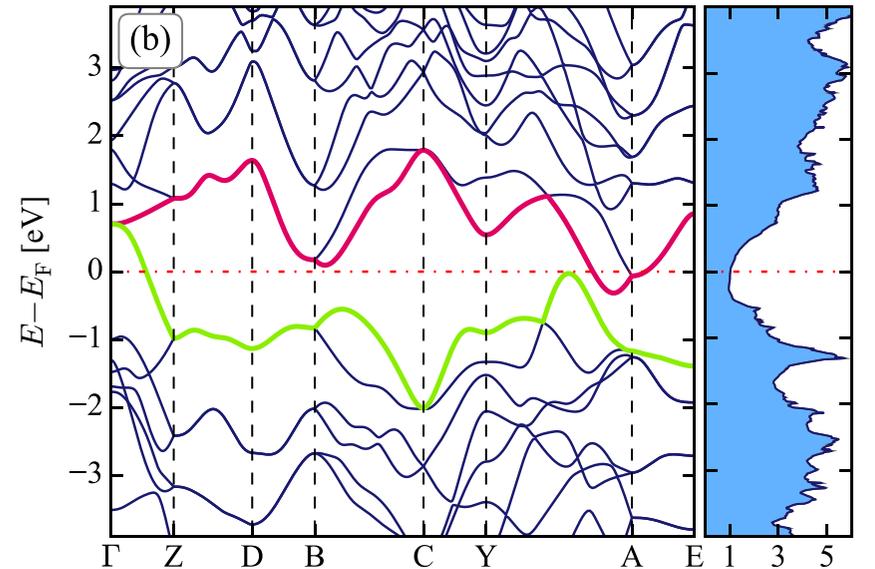
High-pressure layered structure of carbon disulfide

S. Shahab Naghavi,[1,2,3] Yanier Crespo,[4,5] Roman Martoňák,[6] and Erio Tosatti[1,2,4]

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Solid CS_2 is superficially similar to CO_2, with the same *Cmca* molecular crystal structure at low pressures, which has suggested similar phases also at high pressures. We carried out an extensive first-principles evolutionary search in order to identify the zero-temperature lowest-enthalpy structures of CS_2 for increasing pressure up to 200 GPa. Surprisingly, the molecular *Cmca* phase does not evolve into β-cristobalite as in CO_2 but transforms instead into phases HP2 and HP1, both recently described in high-pressure SiS_2. HP1 in particular, with a wide stability range, is a layered $P2_1/c$ structure characterized by pairs of edge-sharing tetrahedra and is theoretically more robust than all other CS_2 phases discussed so far. Its predicted Raman spectrum and pair correlation function agree with experiment better than those of β-cristobalite, and further differences are predicted between their respective IR spectra. The band gap of HP1-CS_2 is calculated to close under pressure, yielding an insulator-metal transition near 50 GPa, in agreement with experimental observations. However, the metallic density of states remains modest above this pressure, suggesting a different origin for the reported superconductivity.

SiS$_2$ at ambient pressure
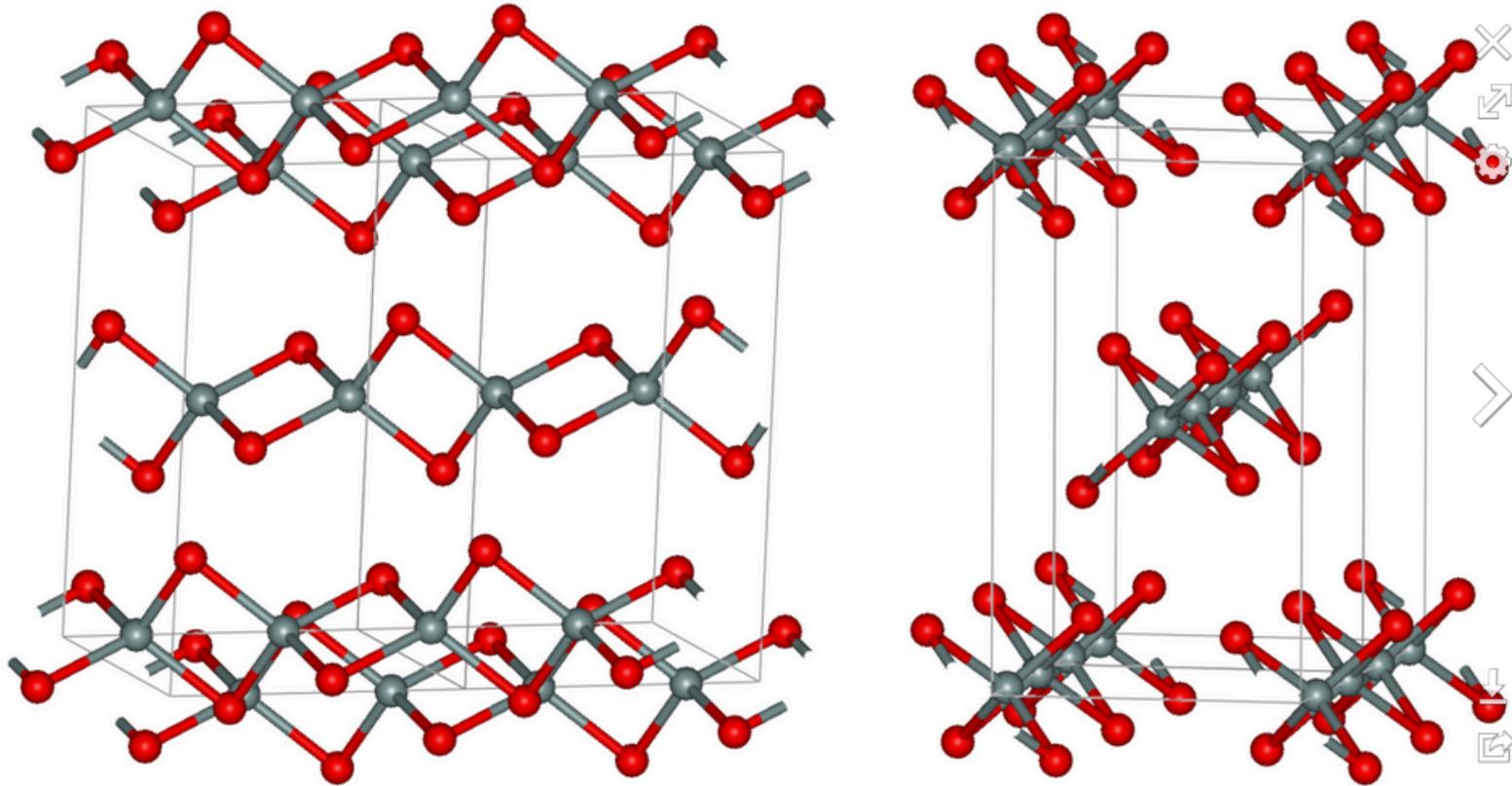
1D chains of edge-sharing tetrahedra

SiS$_2$ at high pressure

Two High-Pressure Phases of SiS$_2$ as Missing Links between the Extremes of Only Edge-Sharing and Only Corner-Sharing Tetrahedra

Jürgen Evers,* Peter Mayer, Leonhard Möckl, and Gilbert Oehlinger

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Ralf Köppe and Hansgeorg Schnöckel*

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S *Supporting Information*

ABSTRACT: The ambient pressure phase of silicon disulfide (NP-SiS$_2$), published in 1935, is orthorhombic and contains chains of distorted, edge-sharing SiS$_4$ tetrahedra. The first high pressure phase, HP3-SiS$_2$, published in 1965 and quenchable to ambient conditions, is tetragonal and contains distorted corner-sharing SiS$_4$ tetrahedra. Here, we report on the crystal structures of two monoclinic phases, HP1-SiS$_2$ and HP2-SiS$_2$, which can be considered as missing links between the orthorhombic and the tetragonal phase. Both monoclinic phases contain edge- as well as corner-sharing SiS$_4$ tetrahedra. With increasing pressure, the volume contraction ($-\Delta V/V$)

and the density, compared to the orthorhombic NP-phase, increase from only edge-sharing tetrahedra to only corner-sharing tetrahedra. The lattice and the positional parameters of NP-SiS$_2$, HP1-SiS$_2$, HP2-SiS$_2$, and HP3-SiS$_2$ were derived in good agreement with the experimental data from group−subgroup relationships with the CaF$_2$ structure as aristotype. In addition, the Raman spectra of SiS$_2$ show that the most intense bands of the new phases HP1-SiS$_2$ and HP2-SiS$_2$ (408 and 404 cm^{-1}, respectively) lie between those of NP-SiS$_2$ (434 cm^{-1}) and HP3-SiS$_2$ (324 cm^{-1}). Density functional theory (DFT) calculations confirm these observations.
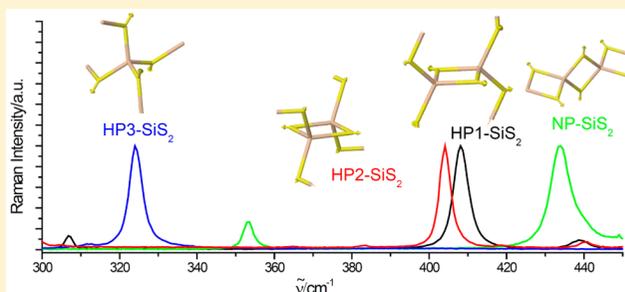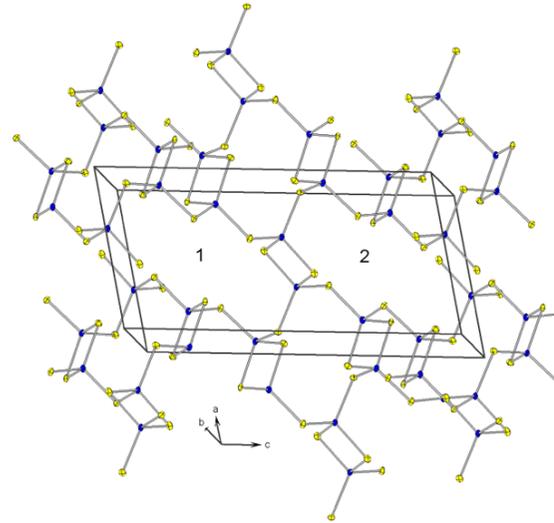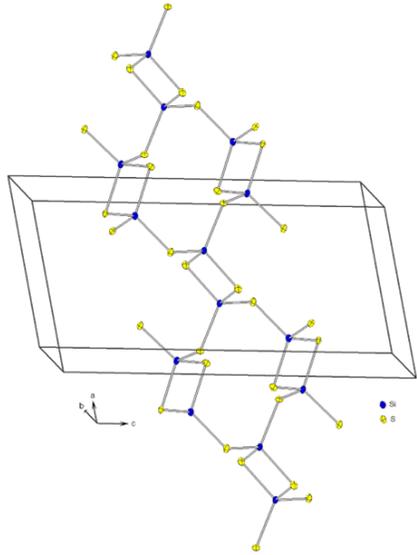
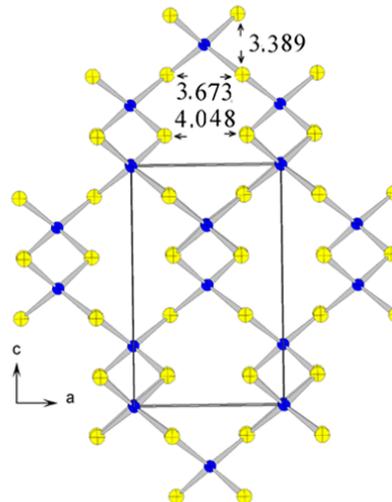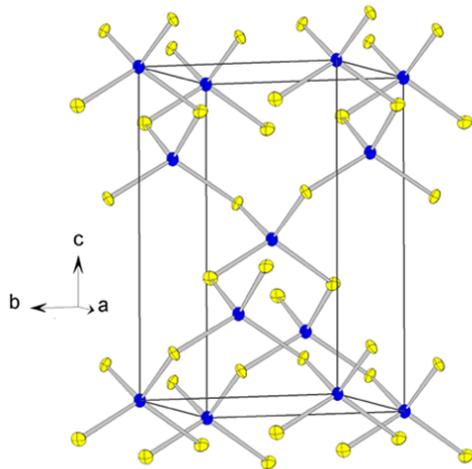# SiS₂ at high pressure (Evers et al.)
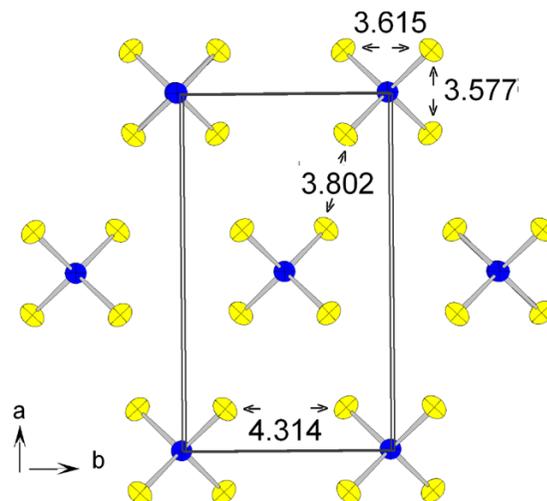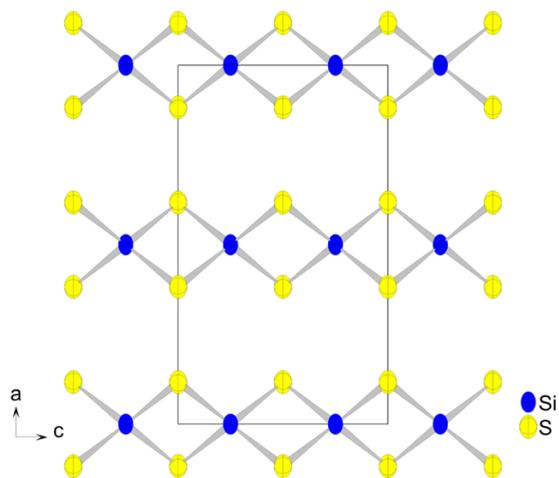
NP *Ibam*
0 GPa
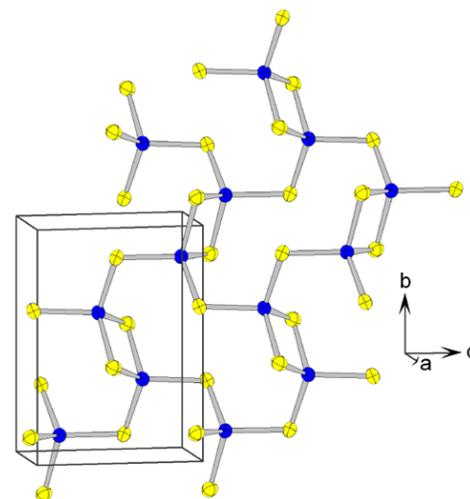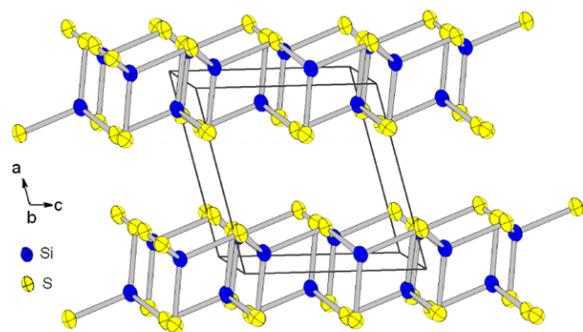
HP1 *P2₁/c*
2.8 GPa

surprise: HP1 is identical to shahabite!

SiS$_2$ at high pressure (Evers et al.)

HP2 $P2_1/c$
3.5 GPa

HP3 $I\bar{4}2d$
4 GPa
β-cristobalite-like
same as CO_2 at
40 GPa

What happens in SiS$_2$ at even higher pressure?
A denser tetrahedral phase or an octahedral one?

Evolutionary structure search for SiS_2

- Xtalopt code and VASP used
- 6 and 12 atoms in unit cell
- p = 10, 30, 60, 100 GPa
- more than 1000 structures at each pressure
- 3 low-enthalpy layered octahedral polytypes were found, *P-3m1*, *P6$_3$mc*, *R-3m*
- the most stable one is *P-3m1,* CdI2-type structure, one layer per unit cell
- becomes thermodynamically stable at 4 GPa, densification by 19 %
- the same structure is found at p=0 in SnS_2, $SiTe_2$

Layered octahedral structures of SiS₂
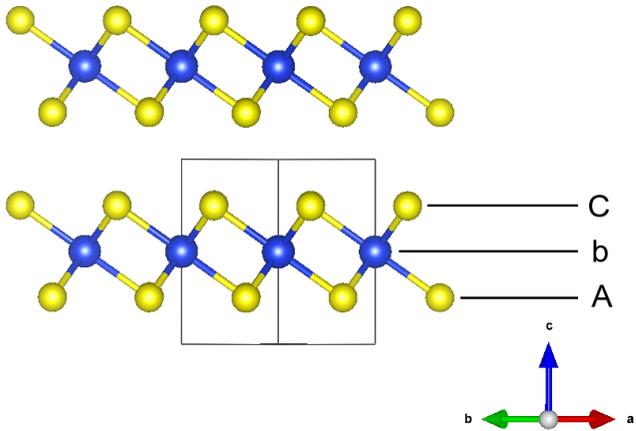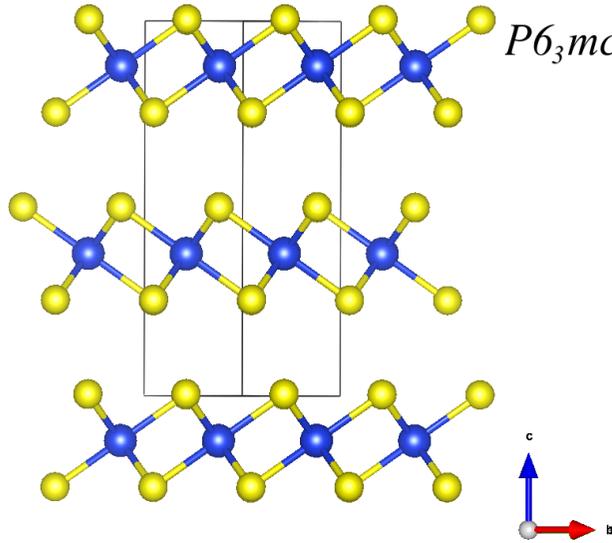
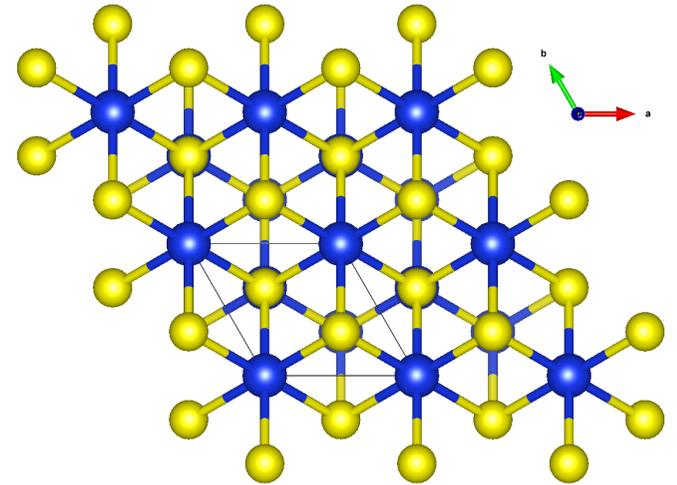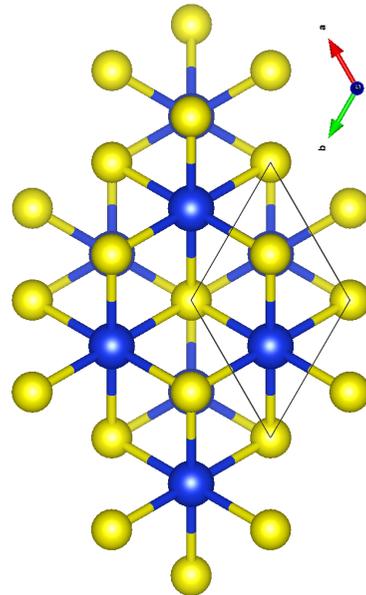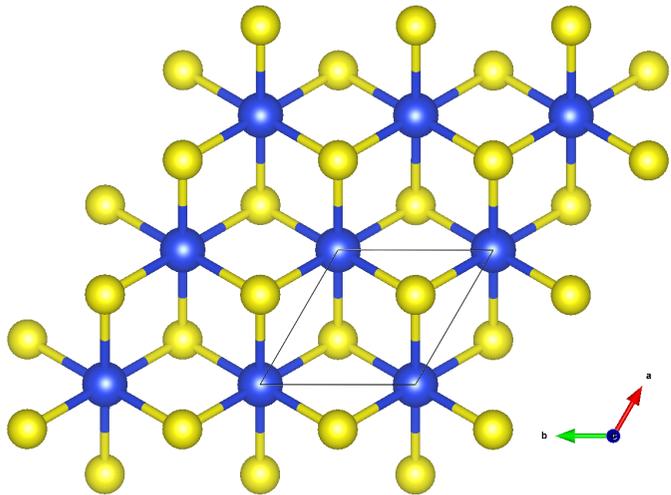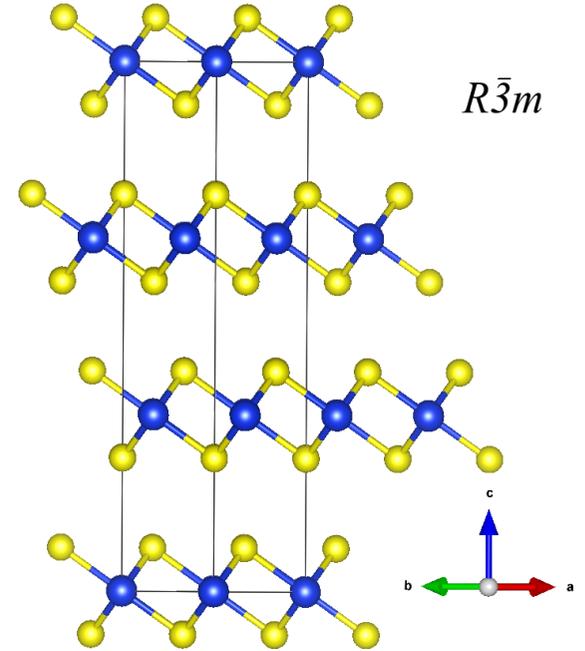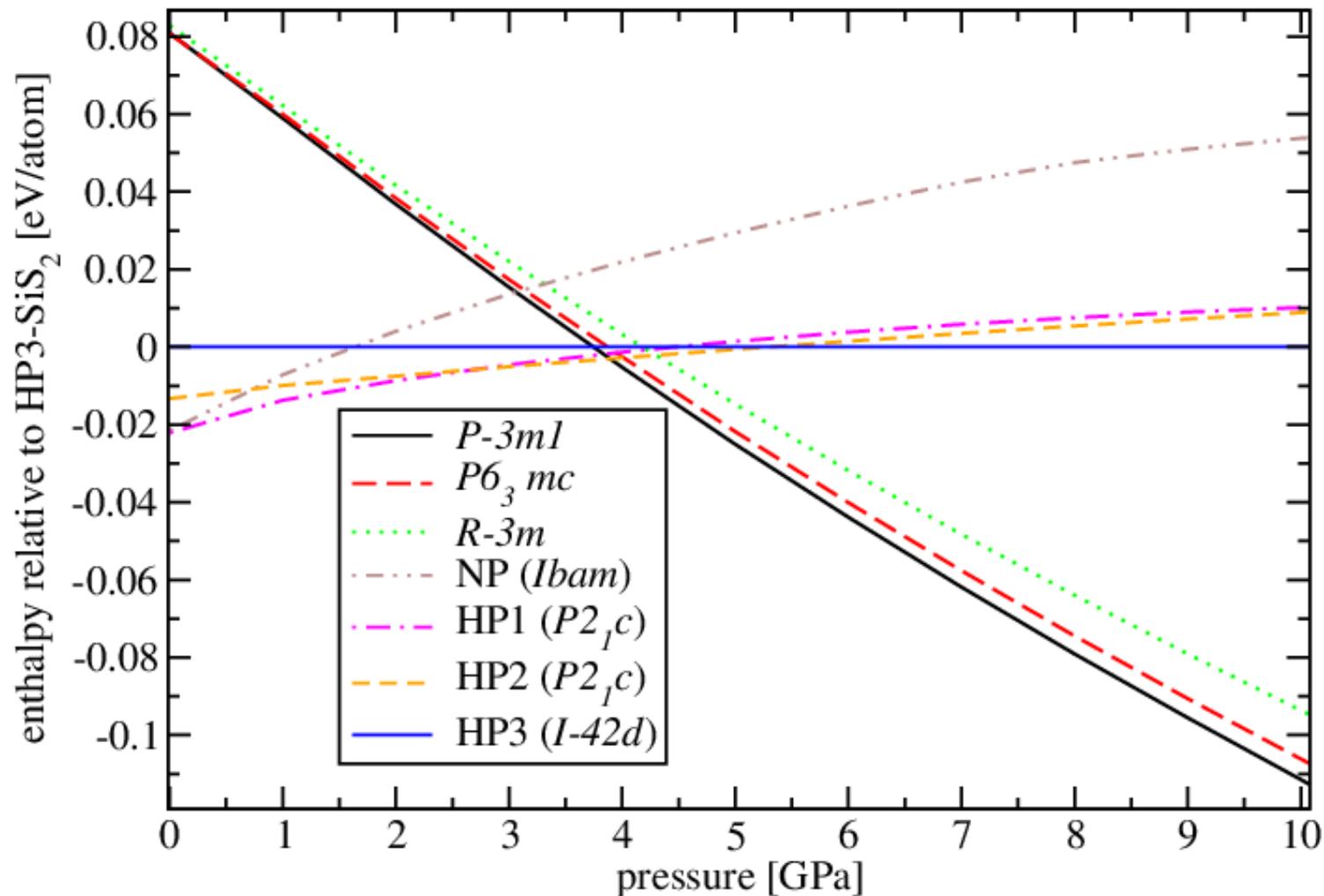# Thermodynamical stability of phases

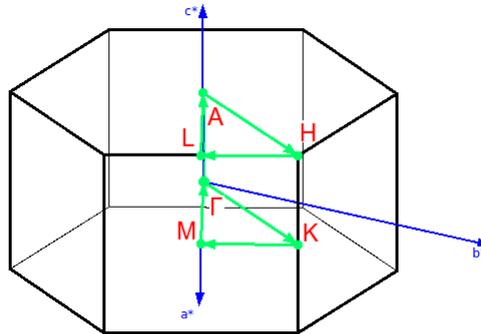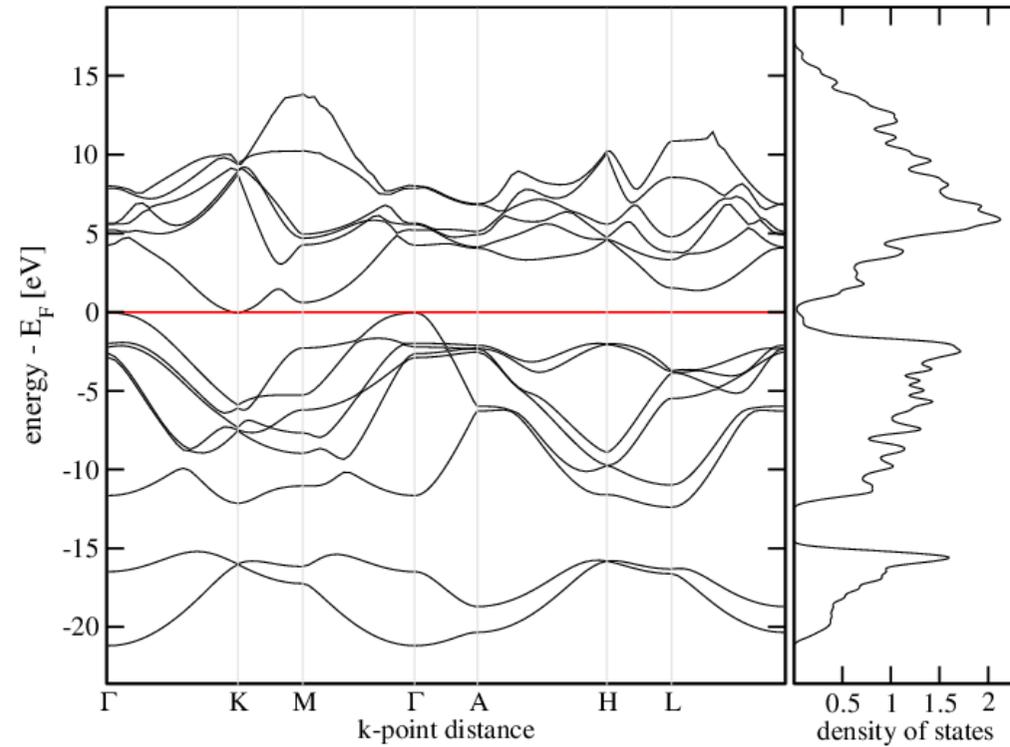- vdW calculated within the Tkatchenko-Scheffler scheme
- HP3 appears metastable, could be a kinetic effect
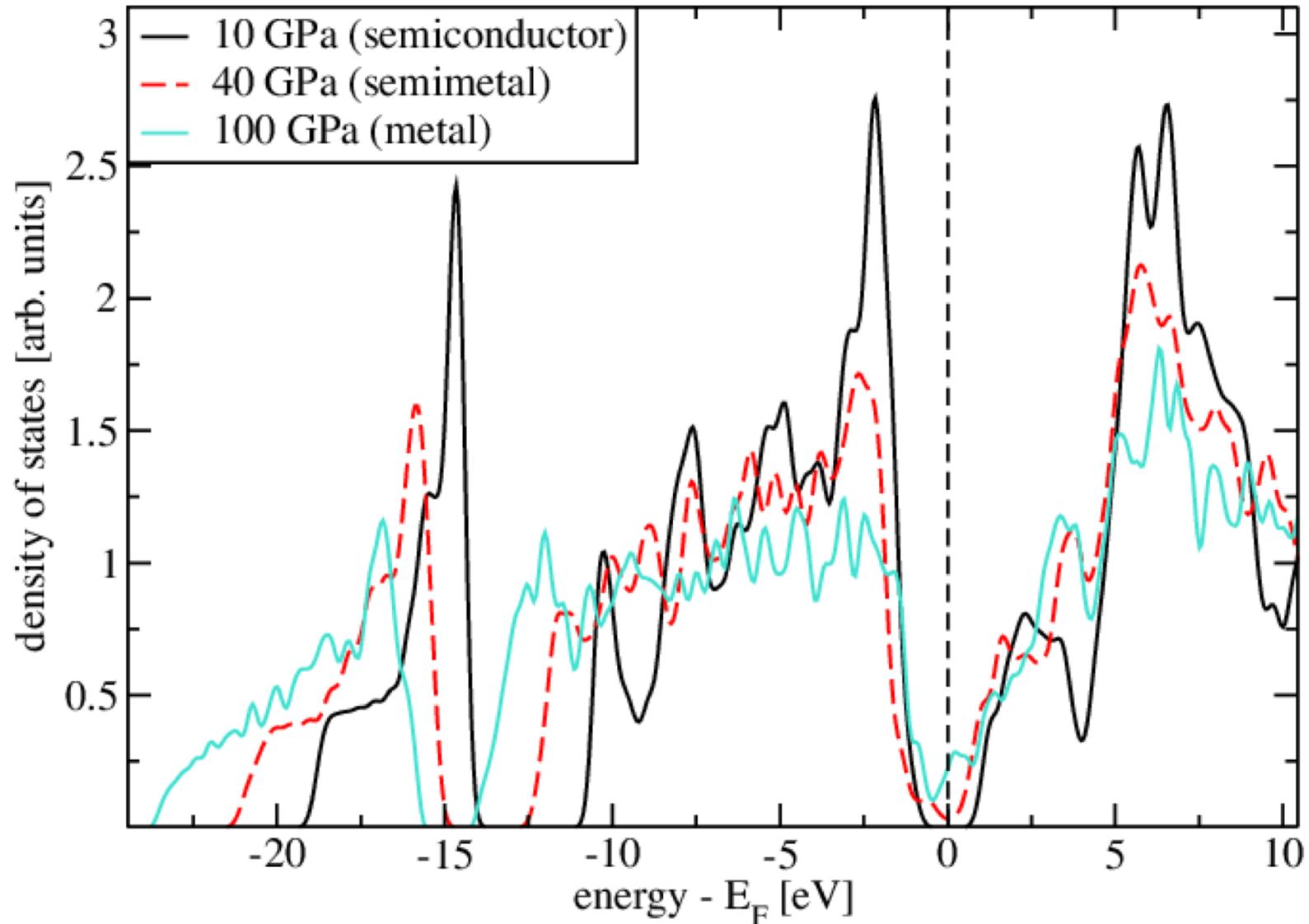- at p=0 NP and HP1 appear nearly degenerate

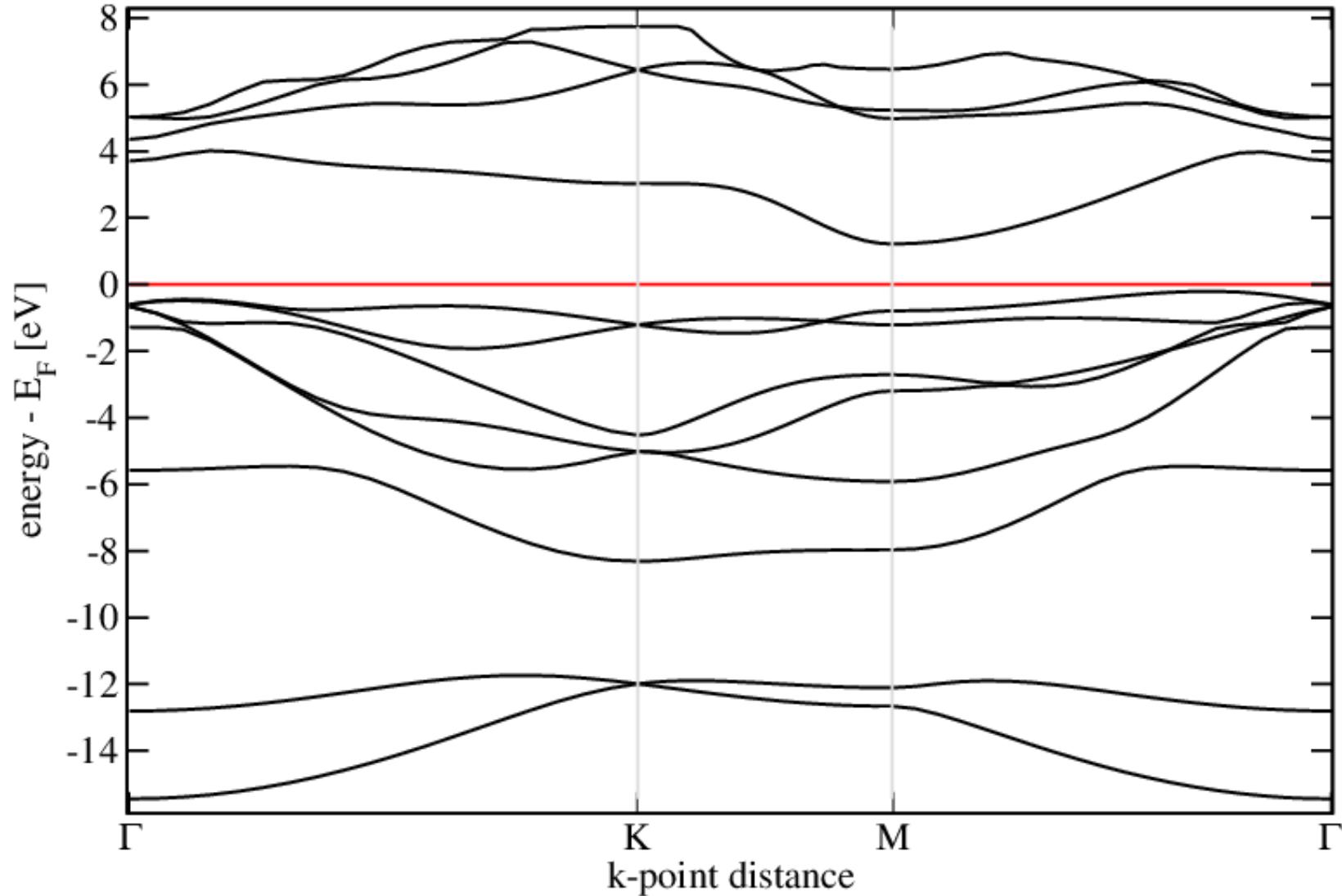# Band structure of the *P-3m1* phase
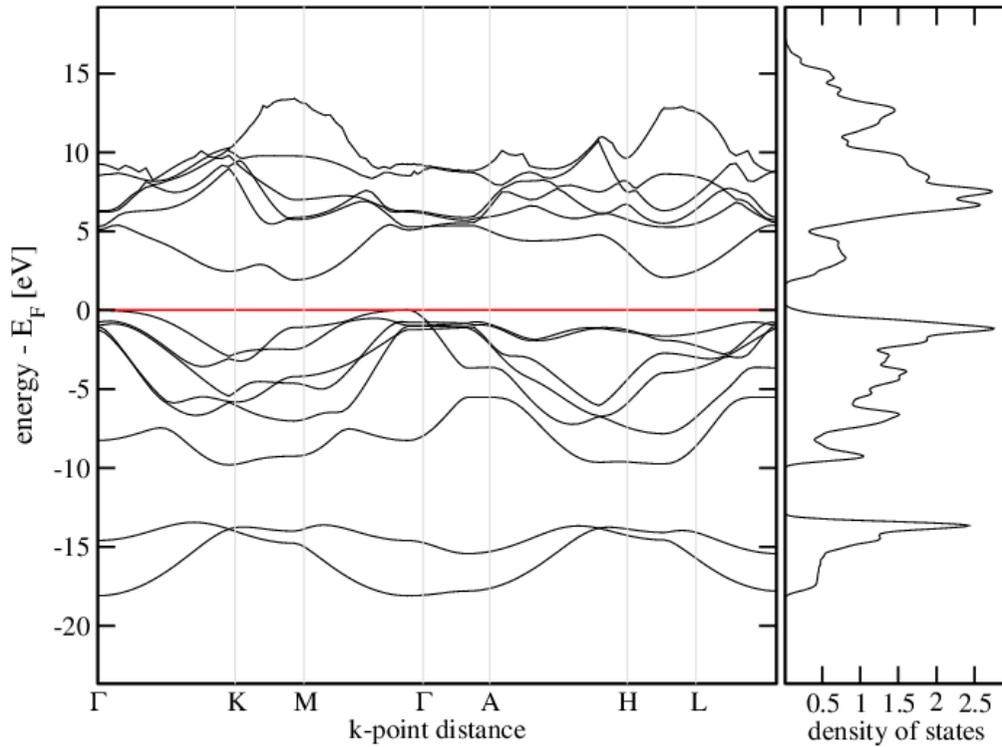
indirect gap semiconductor, metallizes at 40 GPa

Pressure evolution of e-DOS at E_F

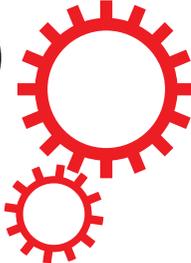remains poor metal even at high pressure

Octahedral monolayer SiS$_2$ band structure

1 eV indirect band gap semiconductor

SCIENTIFIC REPORTS

Creating new layered structures at high pressures: SiS$_2$

Dušan Plašienka[1], Roman Martoňák[1] & Erio Tosatti[2,3]

Old and novel layered structures are attracting increasing attention for their physical, electronic, and frictional properties. SiS$_2$, isoelectronic to SiO$_2$, CO$_2$ and CS$_2$, is a material whose phases known experimentally up to 6 GPa exhibit 1D chain-like, 2D layered and 3D tetrahedral structures. We present highly predictive ab initio calculations combined with evolutionary structure search and molecular dynamics simulations of the structural and electronic evolution of SiS$_2$ up to 100 GPa. A highly stable CdI2-type layered structure, which is octahedrally coordinated with space group $P\bar{3}m1$ surprisingly appears between 4 and up to at least 100 GPa. The tetrahedral-octahedral switch is naturally expected upon compression, unlike the layered character realized here by edge-sharing SiS$_6$ octahedral units connecting within but not among sheets. The predicted phase is semiconducting with an indirect band gap of about 2 eV at 10 GPa, decreasing under pressure until metallization around 40 GPa. The robustness of the layered phase suggests possible recovery at ambient pressure, where calculated phonon spectra indicate dynamical stability. Even a single monolayer is found to be dynamically stable in isolation, suggesting that it could possibly be sheared or exfoliated from bulk $P\bar{3}m1$-SiS$_2$.

Experiment: octahedral SiS$_2$

More Than 50 Years after Its Discovery in SiO$_2$ Octahedral Coordination Has Also Been Established in SiS$_2$ at High Pressure

Jürgen Evers,[*,†][iD] Leonhard Möckl,[†] Gilbert Oehlinger,[†] Ralf Köppe,[‡] Hansgeorg Schnöckel,[*,‡] Oleg Barkalov,[§,⊥] Sergey Medvedev,[*,§] and Pavel Naumov[§,‖]

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(S) *Supporting Information*

ABSTRACT: SiO$_2$ exhibits a high-pressure−high-temperature polymorphism, leading to an increase in silicon coordination number and density. However, for the related compound SiS$_2$ such pressure-induced behavior has not been observed with tetrahedral coordination yet. All four crystal structures of SiS$_2$ known so far contain silicon with tetrahedral coordination. In the orthorhombic, ambient-pressure phase these tetrahedra share edges and achieve only low space filling and density. Up to 4 GPa and 1473 K, three phases can be quenched as metastable phases from high-pressure high-temperature to ambient conditions. Space occupancy and density are increased first by edge and corner sharing and then by corner sharing alone. The structural situation of SiS$_2$ up to the current study resembles that of SiO$_2$ in 1960: Then, in its polymorphs only Si−O$_4$ tetrahedra were known. But in 1961, a polymorph with rutile structure was discovered: octahedral Si-O$_6$ coordination was established. Now, 50 years later, we report here on the transition from 4-fold to 6-fold coordination in SiS$_2$, the sulfur analogue of silica.
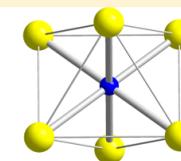
HP4-SiS$_2$ 12.7 GPa
Si − S: 2.29(1) Å
Si − Si: 3.22(1) Å
S − S: 3.22(1), 3.24(1) Å

XRD pattern and Raman spectrum
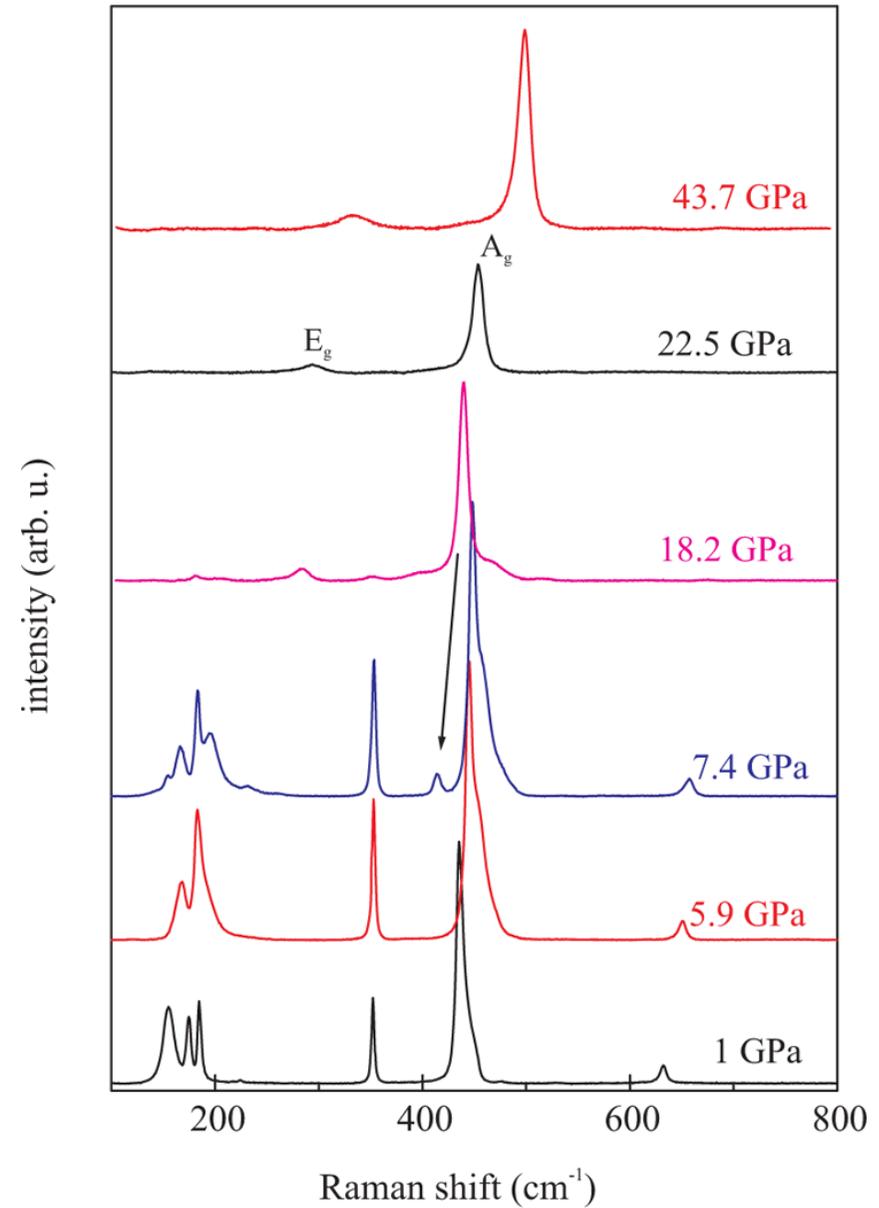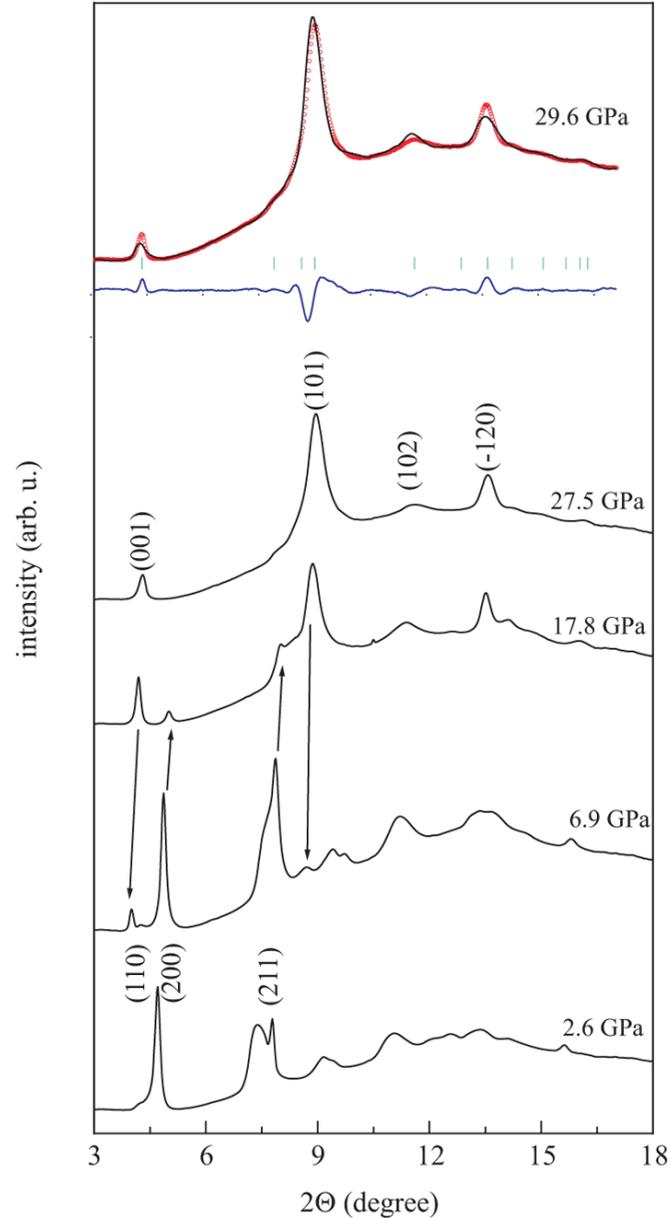
theoretical prediction of the *P-3m1* octahedral phase fully confirmed, Evers et al. (2016)

Direct synthesis of SiS2 at high pressure

Synthesis and Raman spectroscopy of a layered SiS$_2$ phase at high pressures

Yu Wang,[1,2] Shu-Qing Jiang,[1] Alexander F. Goncharov,[1,3] Federico A. Gorelli,[4] Xiao-Jia Chen,[5] Dušan Plašienka,[6] Roman Martoňák,[6] Erio Tosatti,[7,8] and Mario Santoro[4,a)]

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[3]*Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road, Washington, DC 20015, USA*
[4]*Istituto Nazionale di Ottica (CNR-INO) and European Laboratory for non Linear Spectroscopy (LENS), Via N. Carrara 1, 50019 Sesto Fiorentino, Italy*
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[7]*International School for Advanced Studies (SISSA) and CNR-IOM Democritos, Via Bonomea 265, 34136 Trieste, Italy*
[8]*The Abdus Salam International Centre for Theoretical Physics (ICTP), Strada Costiera 11, 34151 Trieste, Italy*

FIG. 1. Raman spectra of the Si/S mixture under pressure, before (elemental Si and S) and after (layered, *l*, octahedral, *o* SiS$_2$) laser heating. Inset: sample configuration. Blue and grey: diamond anvils and gasket. Yellow and black slabs: S and Si, respectively. Horizontal arrows at the top and at the bottom point to green and near IR laser beams used for Raman spectroscopy and for sample heating (double side), respectively.

Dichalcogenides are known to exhibit layered solid phases, at ambient and high pressures, where 2D layers of chemically bonded formula units are held together by van der Waals forces. These materials are of great interest for solid-state sciences and technology, along with other 2D systems such as graphene and phosphorene. SiS$_2$ is an archetypal model system of the most fundamental interest within this ensemble. Recently, high pressure (GPa) phases with Si in octahedral coordination by S have been theoretically predicted and also experimentally found to occur in this compound. At variance with stishovite in SiO$_2$, which is a 3D network of SiO$_6$ octahedra, the phases with octahedral coordination in SiS$_2$ are 2D layered. Very importantly, this type of semiconducting material was theoretically predicted to exhibit continuous bandgap closing with pressure to a poor metallic state at tens of GPa. We synthesized layered SiS$_2$ with octahedral coordination in a diamond anvil cell at 7.5-9 GPa, by laser heating together elemental S and Si at 1300-1700 K. Indeed, Raman spectroscopy up to 64.4 GPa is compatible with continuous bandgap closing in this material with the onset of either weak metallicity or of a narrow bandgap semiconductor state with a large density of defect-induced, intra-gap energy levels, at about 57 GPa. Importantly, our investigation adds up to the fundamental knowledge of layered dichalcogenides. *Published by AIP Publishing.* https://doi.org/10.1063/1.5011333
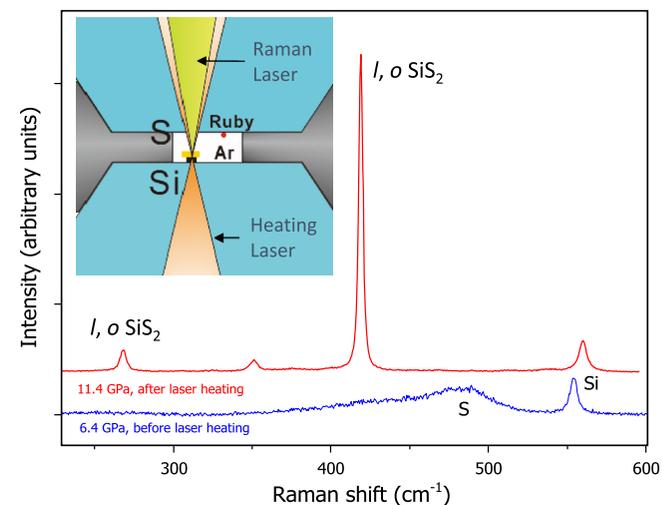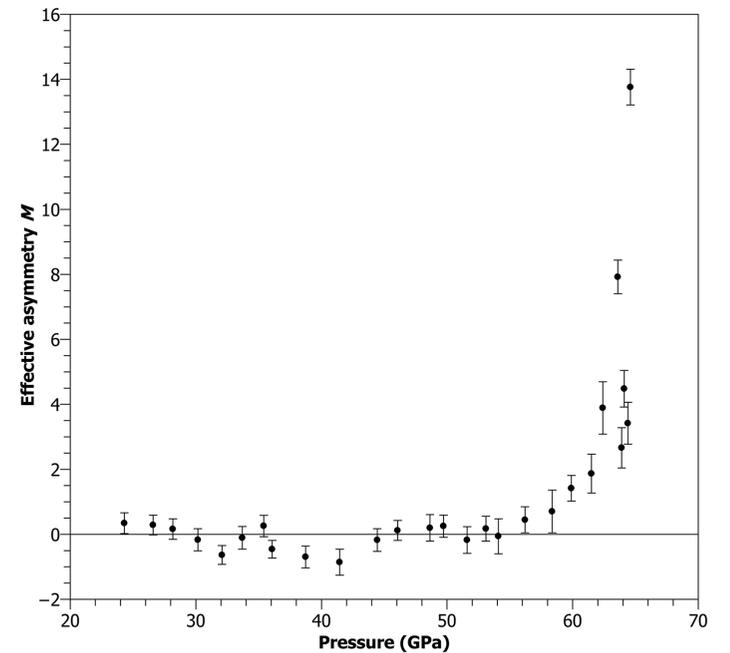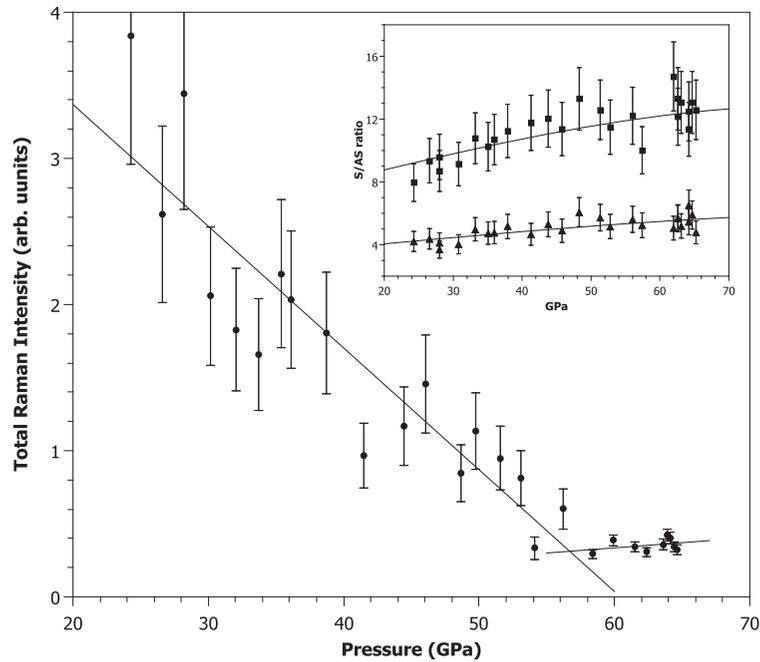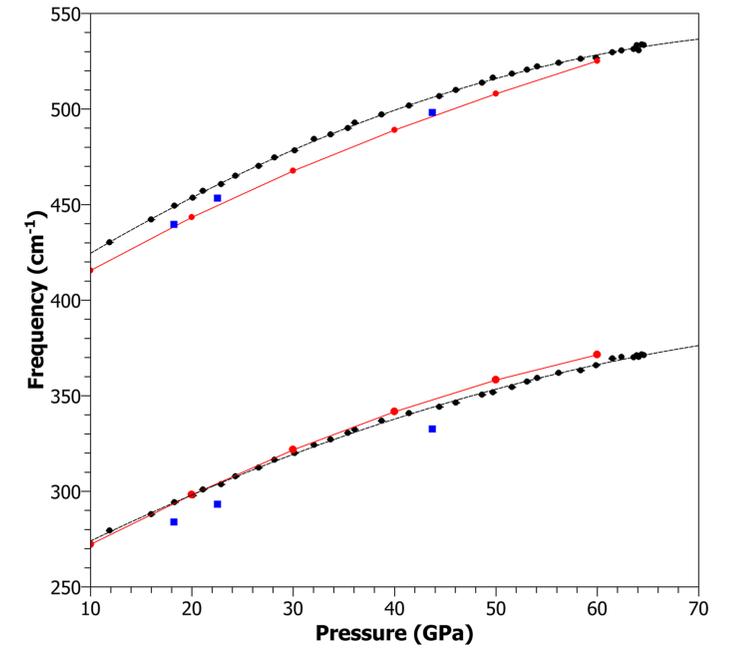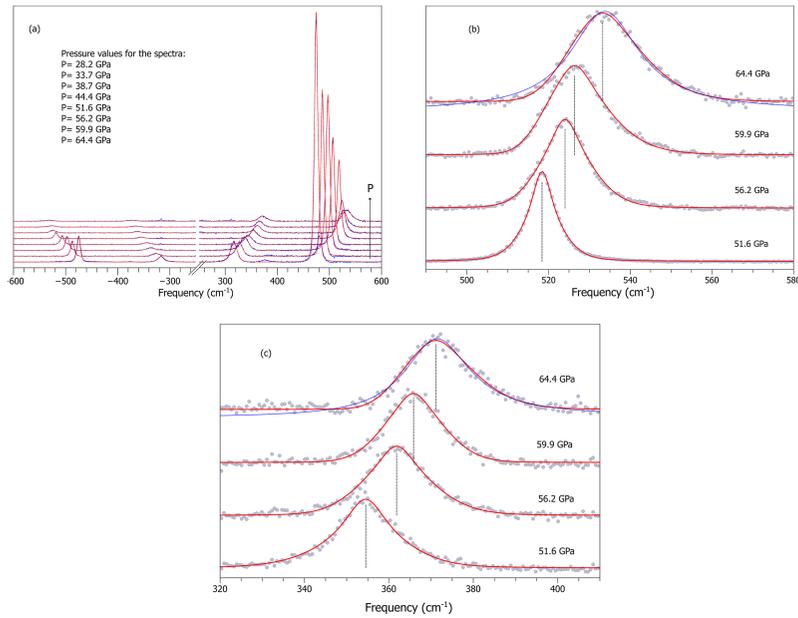
Experiment Raman

metallization at 57 GPa detected by asymmetry of Raman lines (Fano resonance)

Conclusions

- new prediction - CS_2 creates at 30 GPa a layered tetrahedral *$P2_1/c$* structure - better candidate for the phase observed by Dias et al.
- the *$P2_1/c$* phase of CS_2 is identical to the HP1 phase of SiS_2 at 3.5 GPa
- CS_2 is at low pressure similar to CO_2 and at higher pressure to SiS_2
- challenge to prepare it in more crystalline form - low temperature compression?
- new prediction - SiS_2 creates at 4 GPa a layered octahedral phase of CdI_2 type (confirmed experimentally)
- SiS_2 is similar both to CS_2 and to CO_2
- undergoes an interesting evolution in dimensionality - from 1D to 2D to 3D to 2D
- beyond SiO_2 many layered structures are found

Acknowledgements