Pressure-Induced Spin-Crossover Features in $Fe(Pm\text{-}Bia)_2(NCS)_2$: Implications for Barocaloric Applications

- February 2024 I Hend SHAHED
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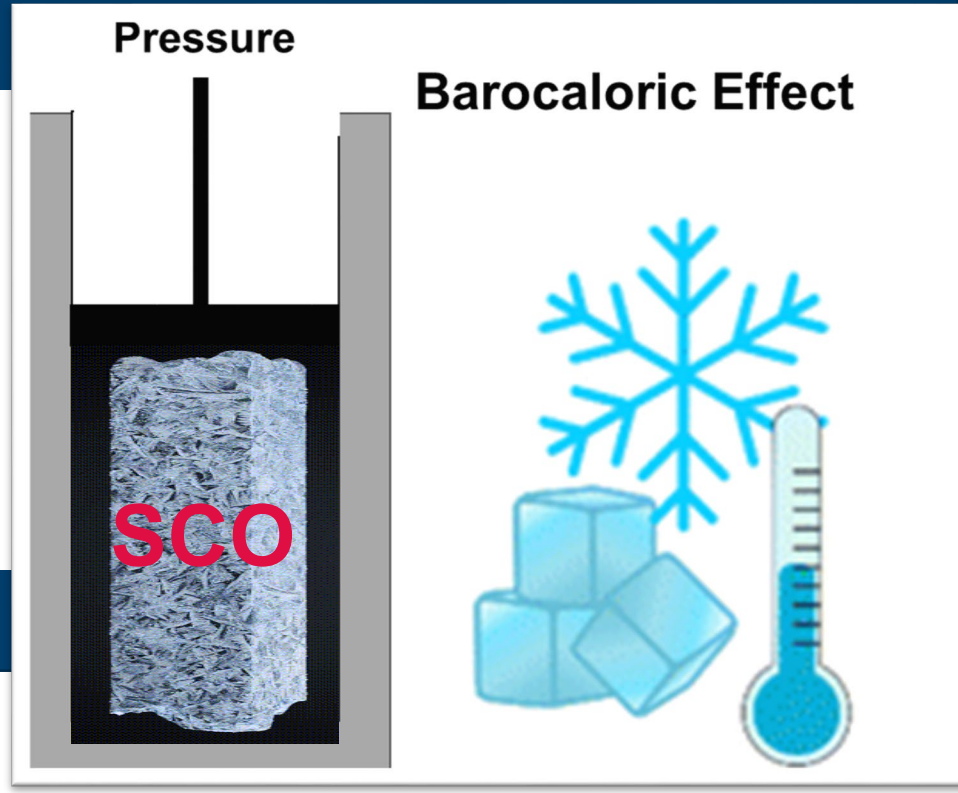
- **SCO Group:** Karen Friese, Andrzej Grzechnik, Manuel Angst, Jörg Voigt, Pulkit Prakash, Ji Qi, Jörg Persson



1

Bulk modulus

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Outline

JÜLICH
Forschungszentrum

1

Bulk modulus

2

Pressure induces spin transition?

3

Superstructure

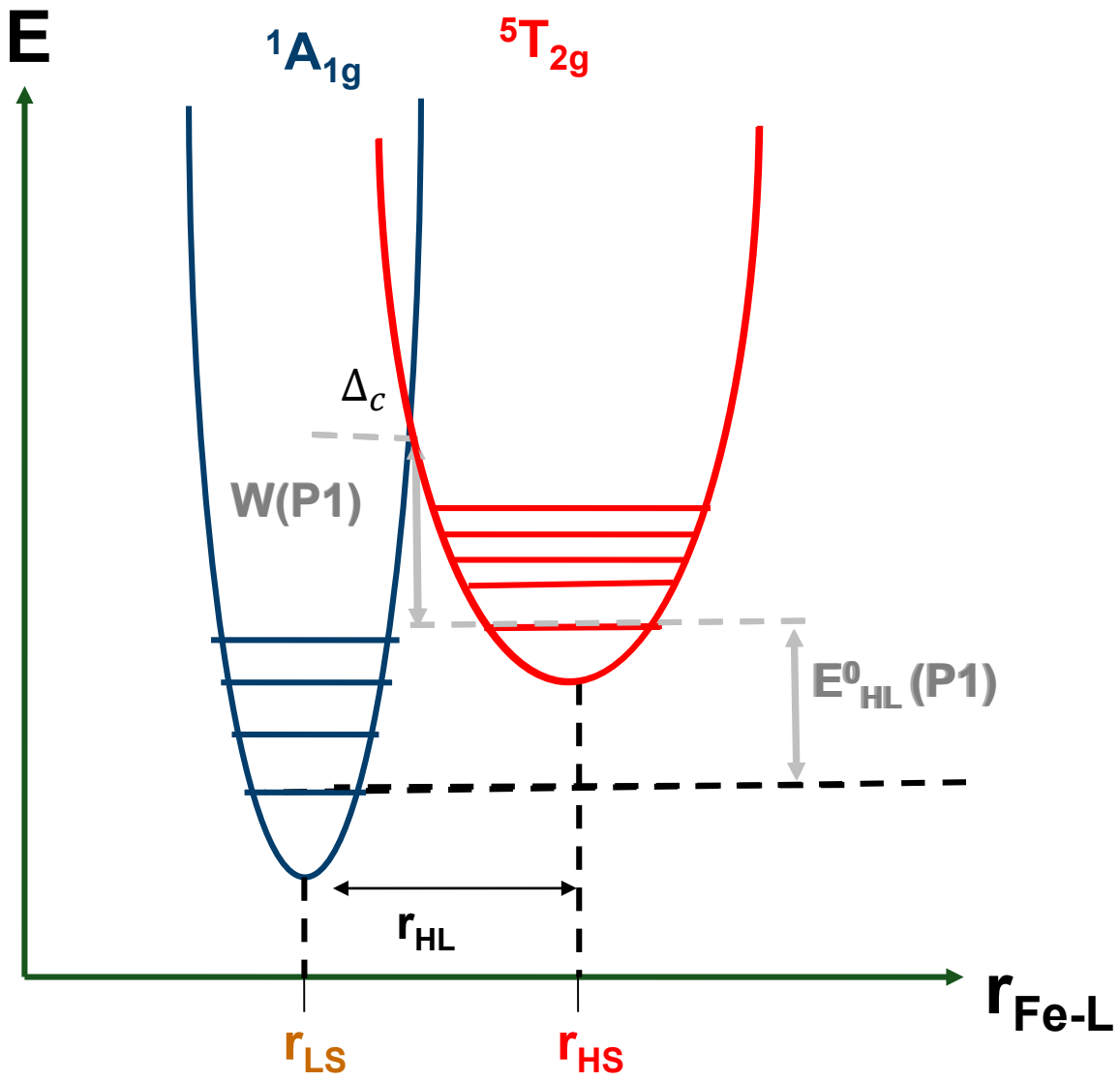
4

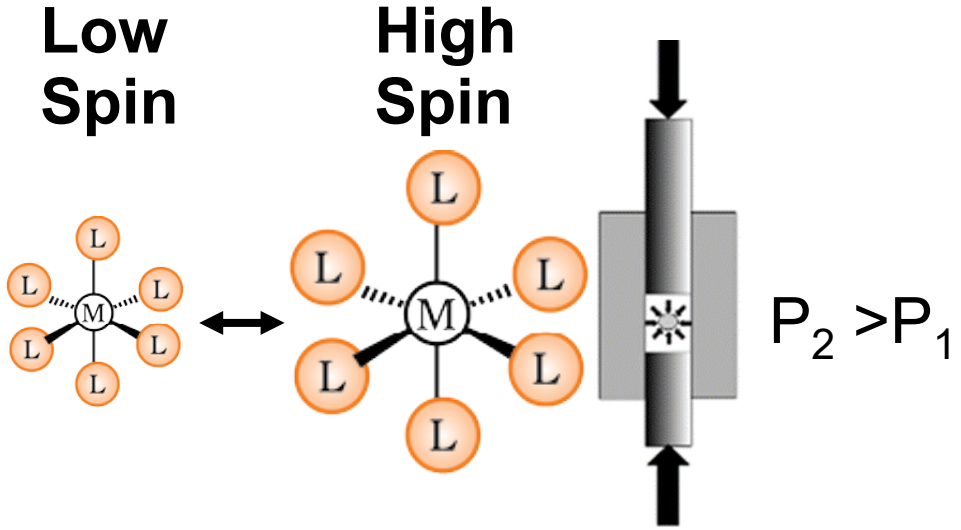
Crystal packing & Intermolecular interaction

5

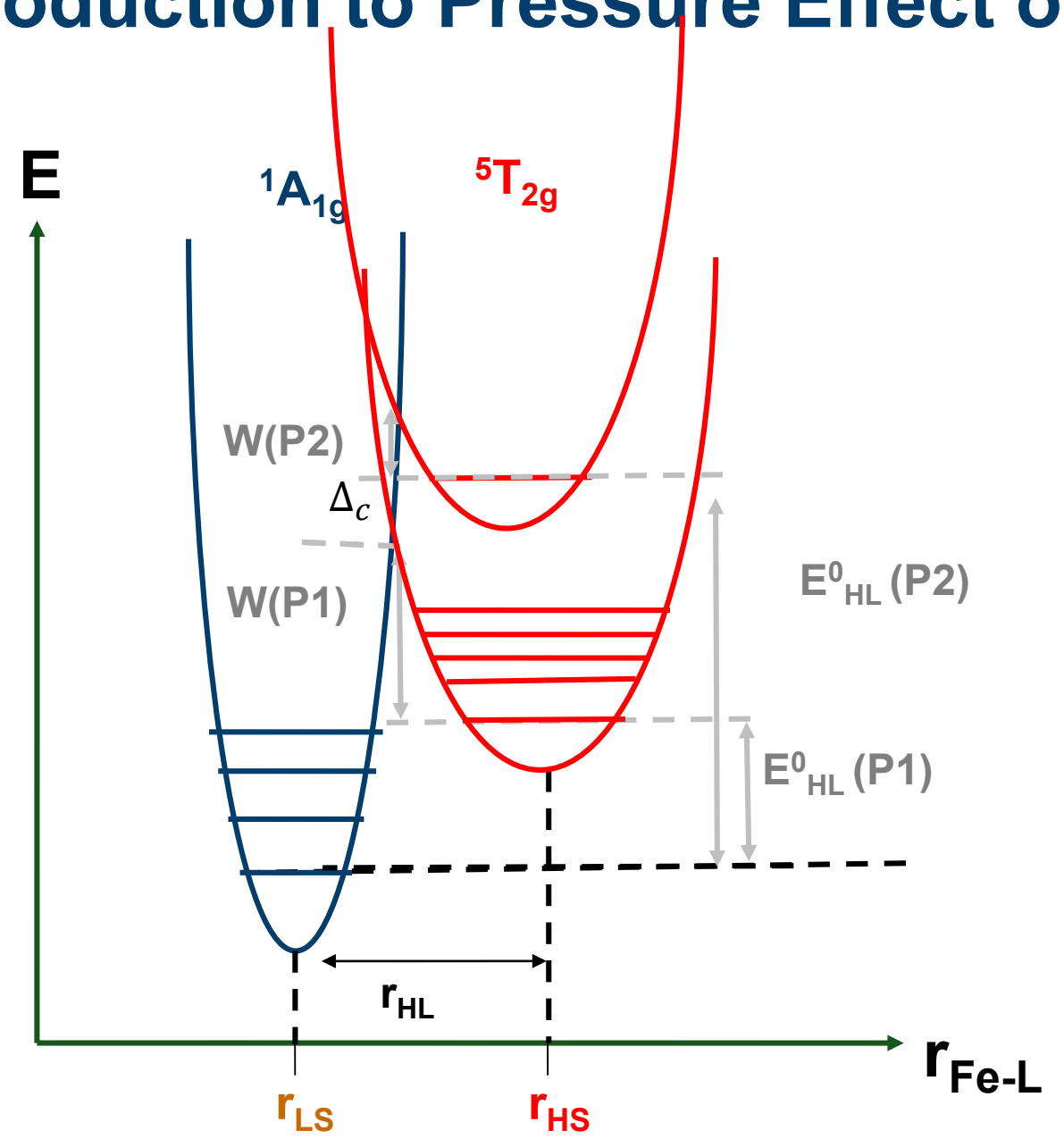
Thermal-induced spin transition Vs. Pressure-induced spin transition.

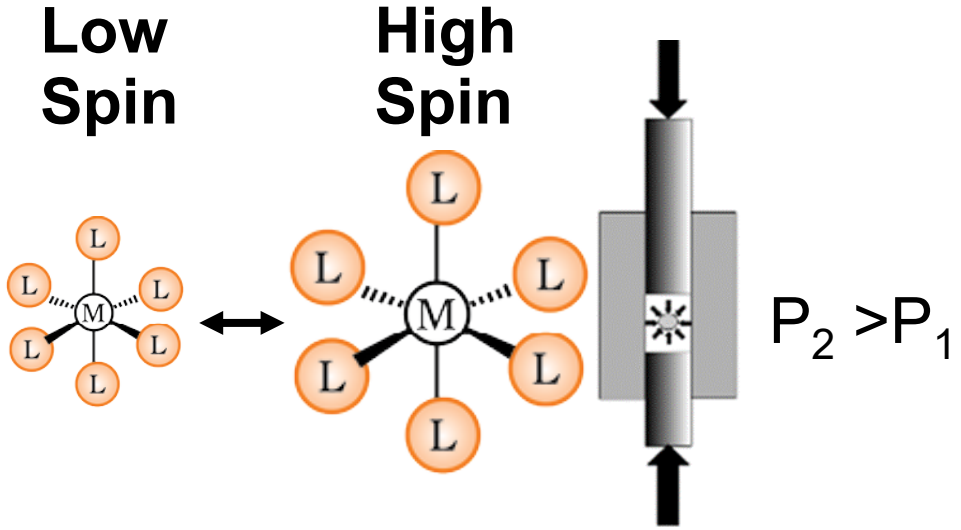
Introduction to Pressure Effect on Spin Crossover





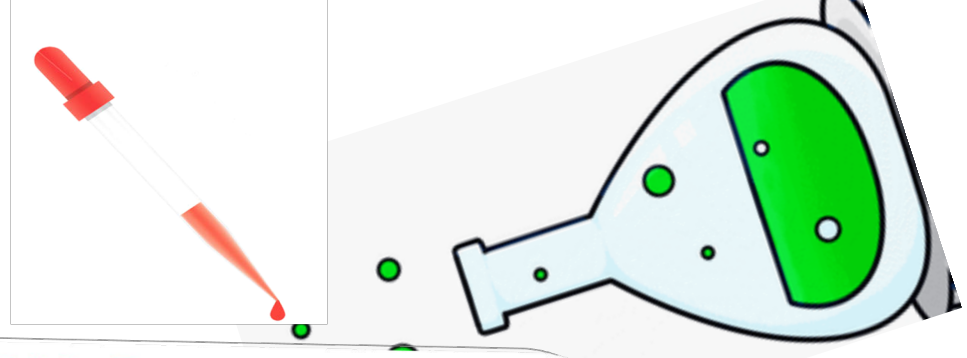
Introduction to Pressure Effect on Spin Crossover

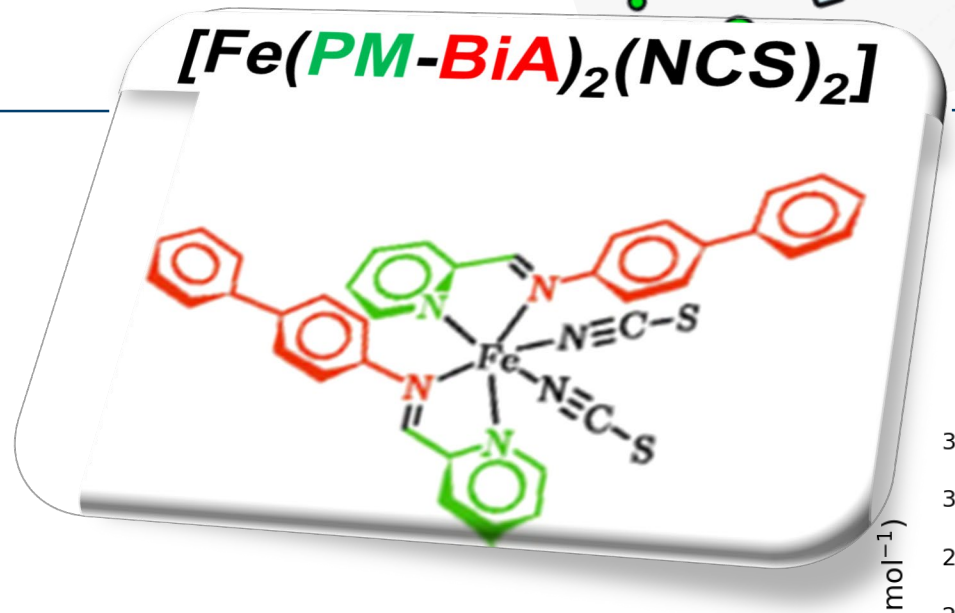




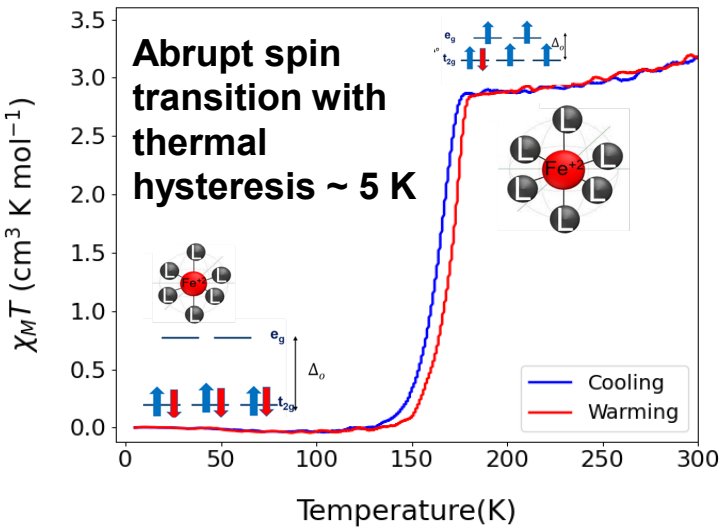
Investigated compound

$Fe(C_{18}H_{14}N_2)_2(NCS)_2$
(PM-BIA=(*N*-(2'-pyridylmethylene)
-4-amino-bi-phenyl)
NCS^- =Thiocyanate Group

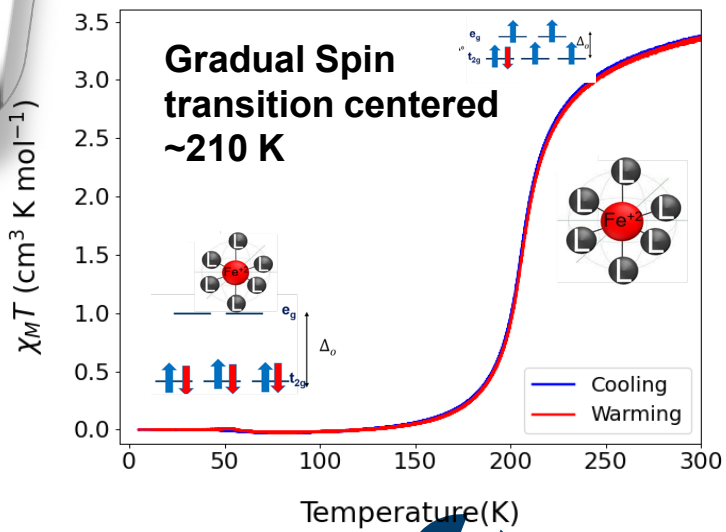




Orthorhombic
Pccn



Monoclinic
P2$_1$/c



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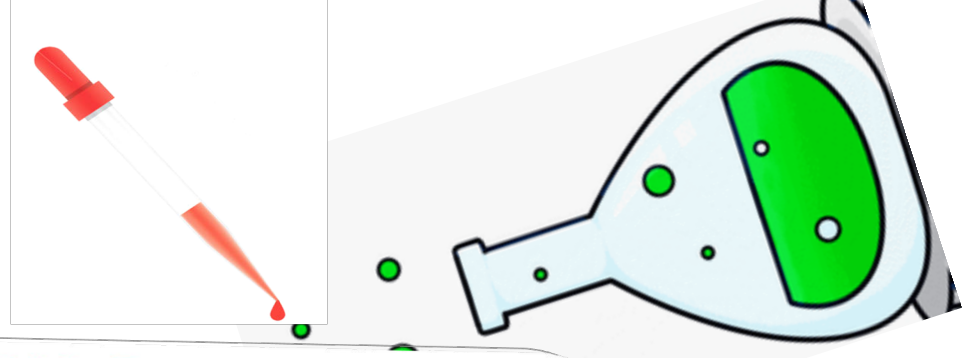
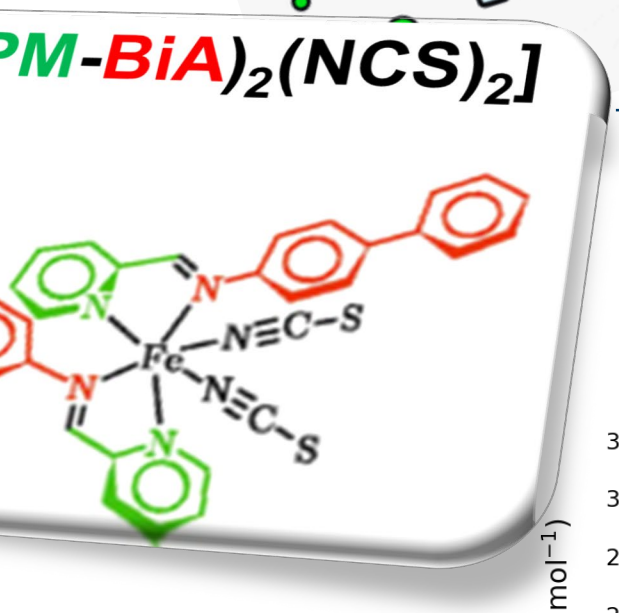
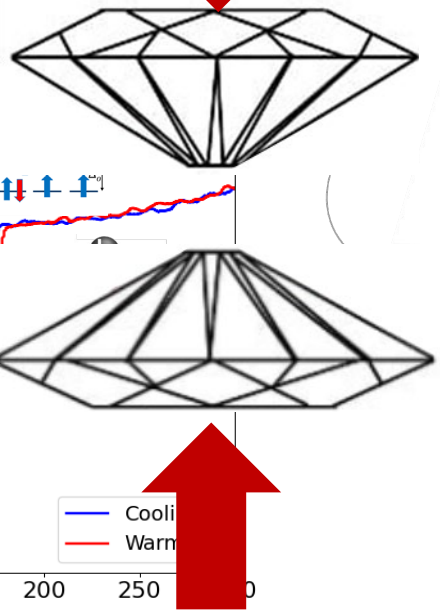
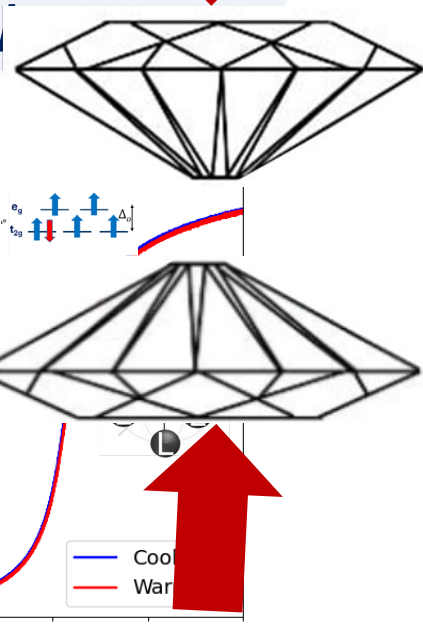




Orthorhombic
Pccr



Monoclinic
P2$_1$

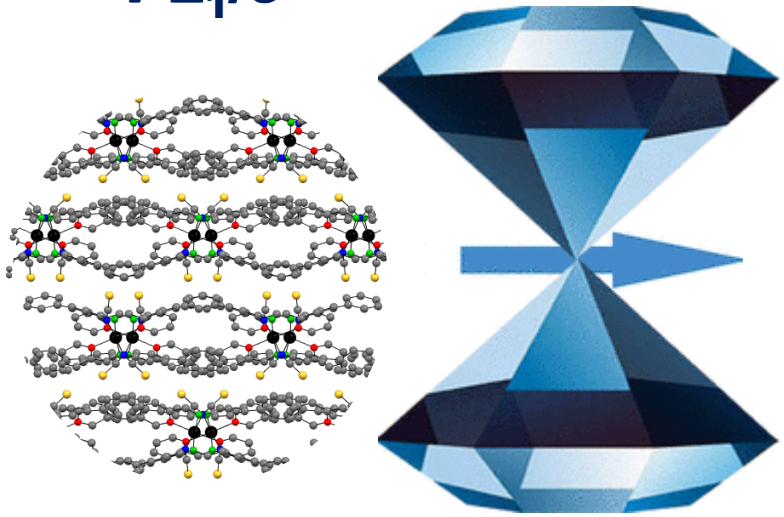


Pressure-dependent Crystal Structure

Single crystal X-ray diffraction

Monoclinic

P*2$_1$/*c

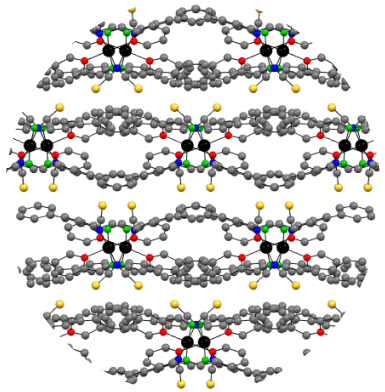


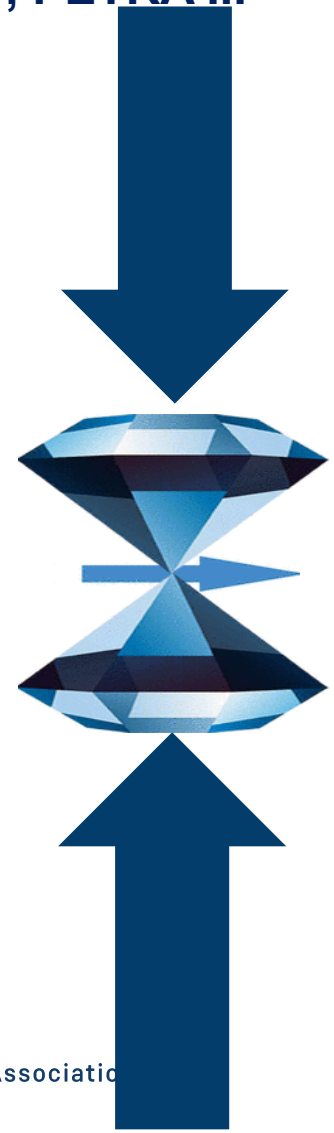
Pressure-dependent Crystal Structure

High-pressure single crystal diffraction at ambient temperature

@ P24, DESY, PETRA III

Monoclinic
P*2$_1$/*c





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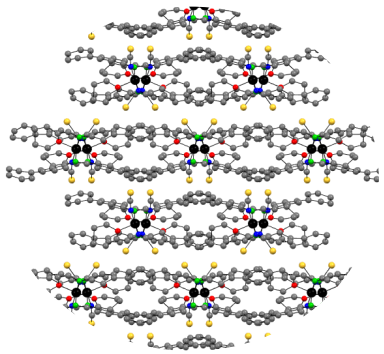
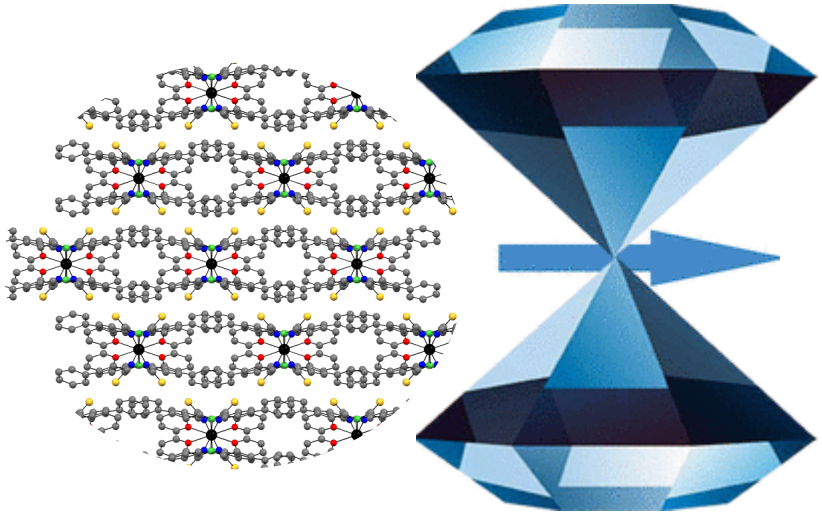


1.36 GPa

Orthorhombic
Pccn



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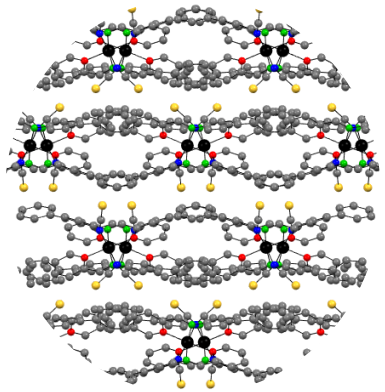
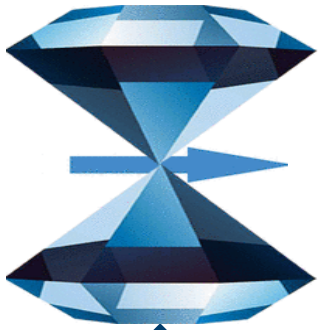
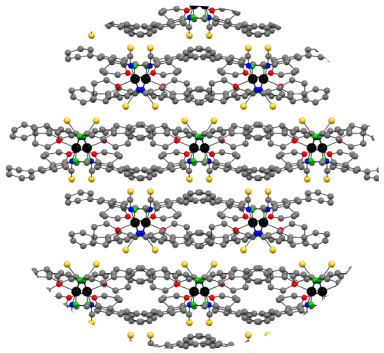




Monoclinic
P*2$_1$/*c



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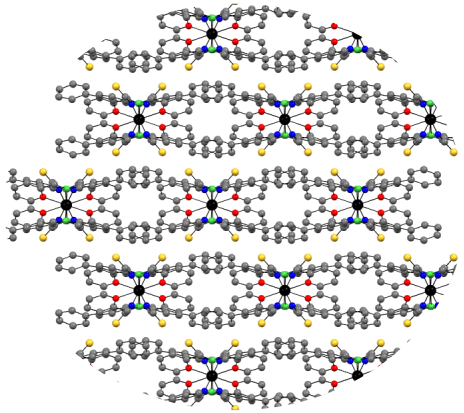

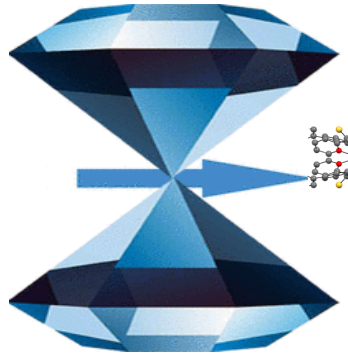

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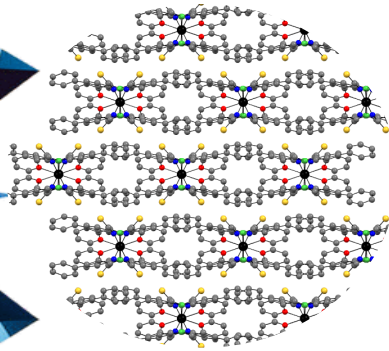
Pccn



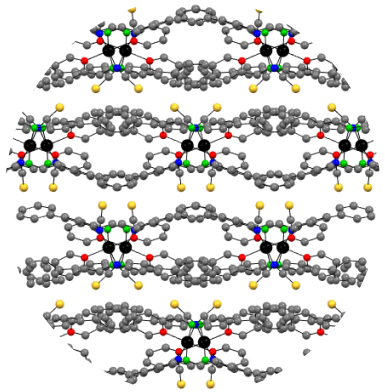
1.34 GPa

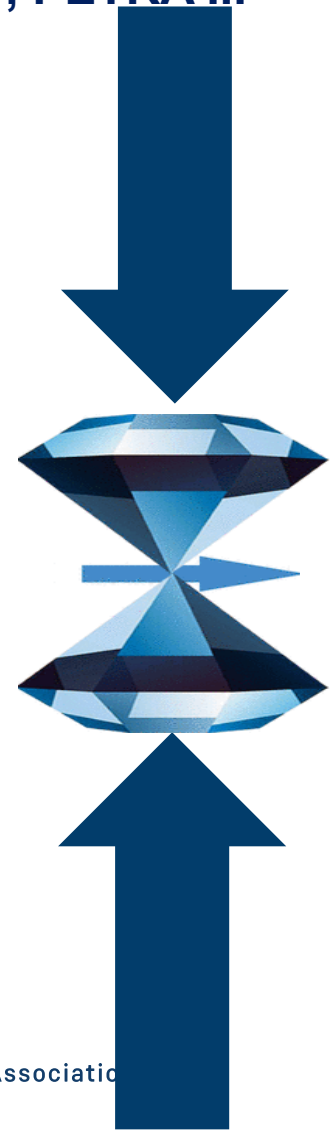
Pressure-dependent Crystal Structure

High-pressure single crystal diffraction at ambient temperature

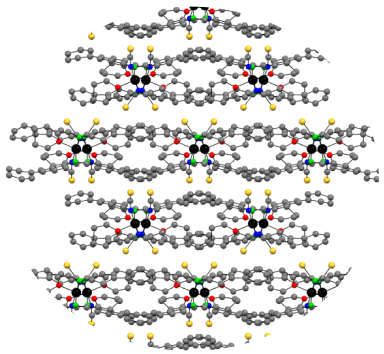
@ P24, DESY, PETRA III

Monoclinic
P*2$_1$/*c



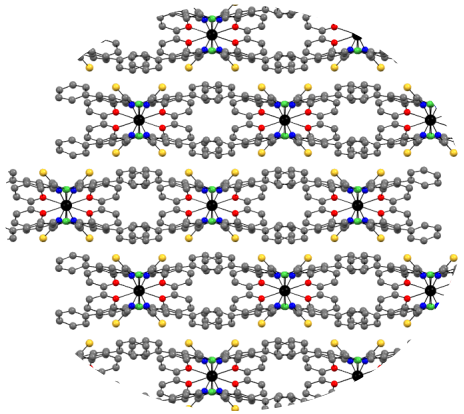


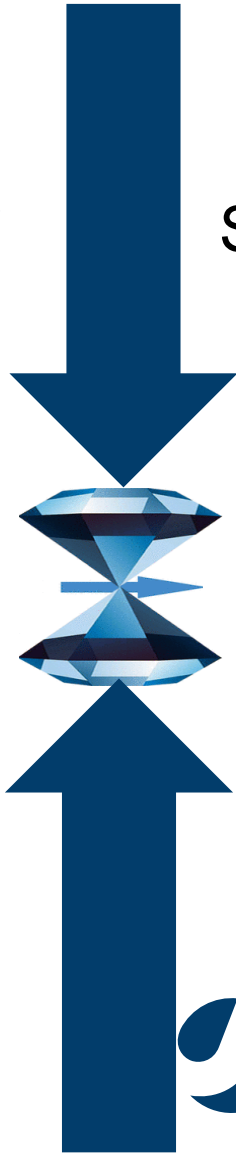
Monoclinic
P*2$_1$/*c



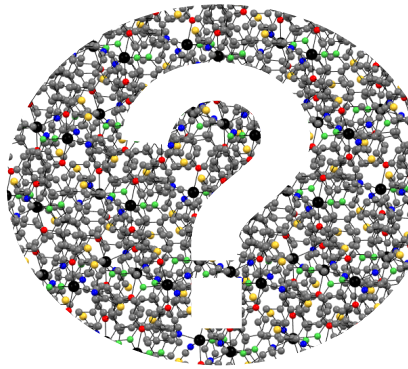
1.36 GPa

Orthorhombic
Pccn





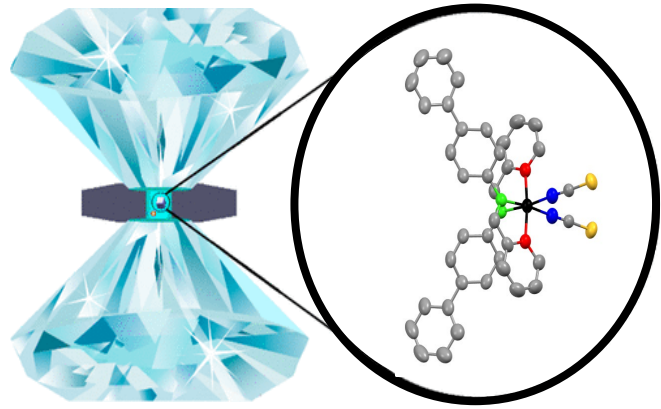
Superstructure



2.02 GPa

Bulk Modulus (K_0)

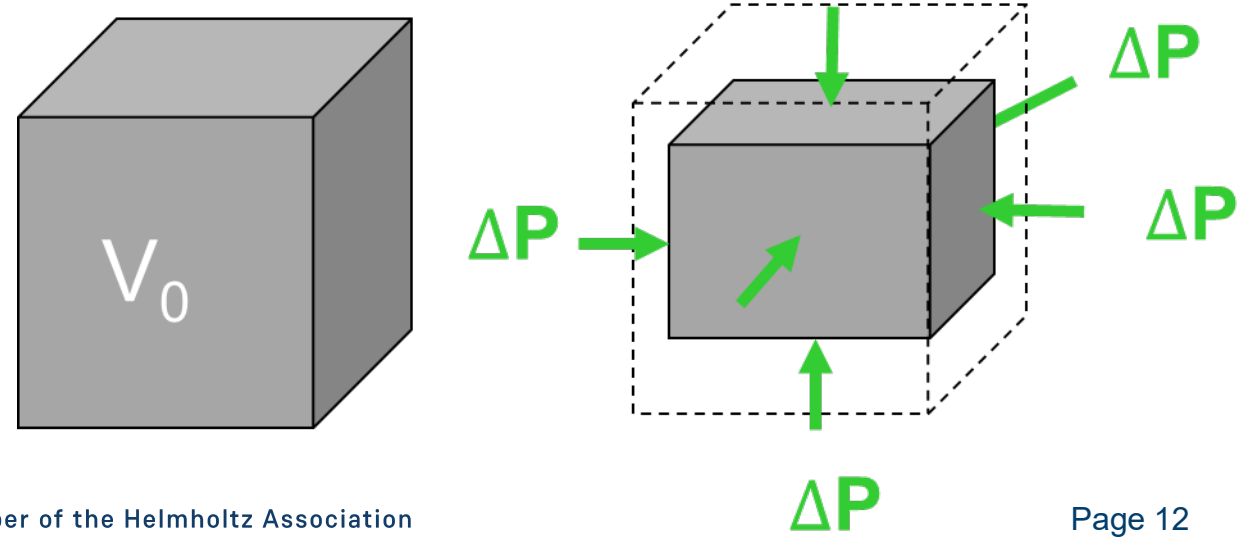
High-pressure single crystal diffraction

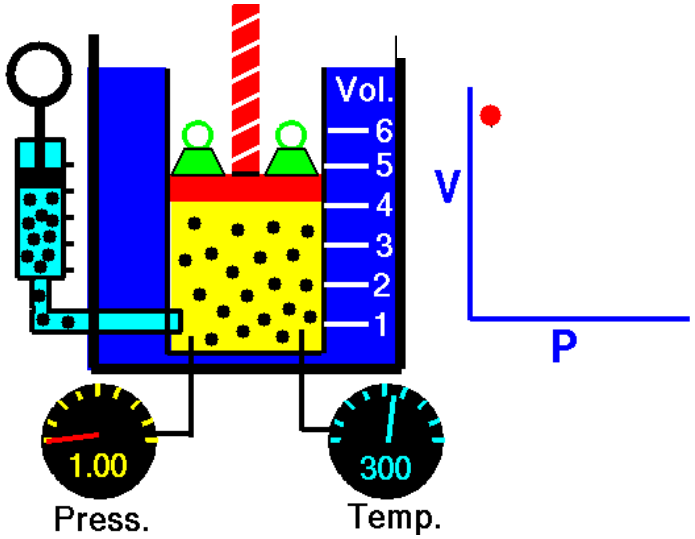


Third-order Birch-Murnaghan equation of state

P= -

=





Bulk Modulus (K_0)

High-pressure single crystal diffraction

Third-order Birch-Murnaghan equation of state

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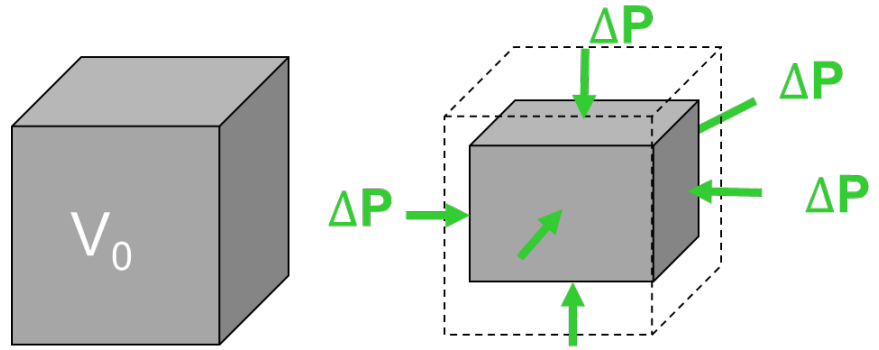
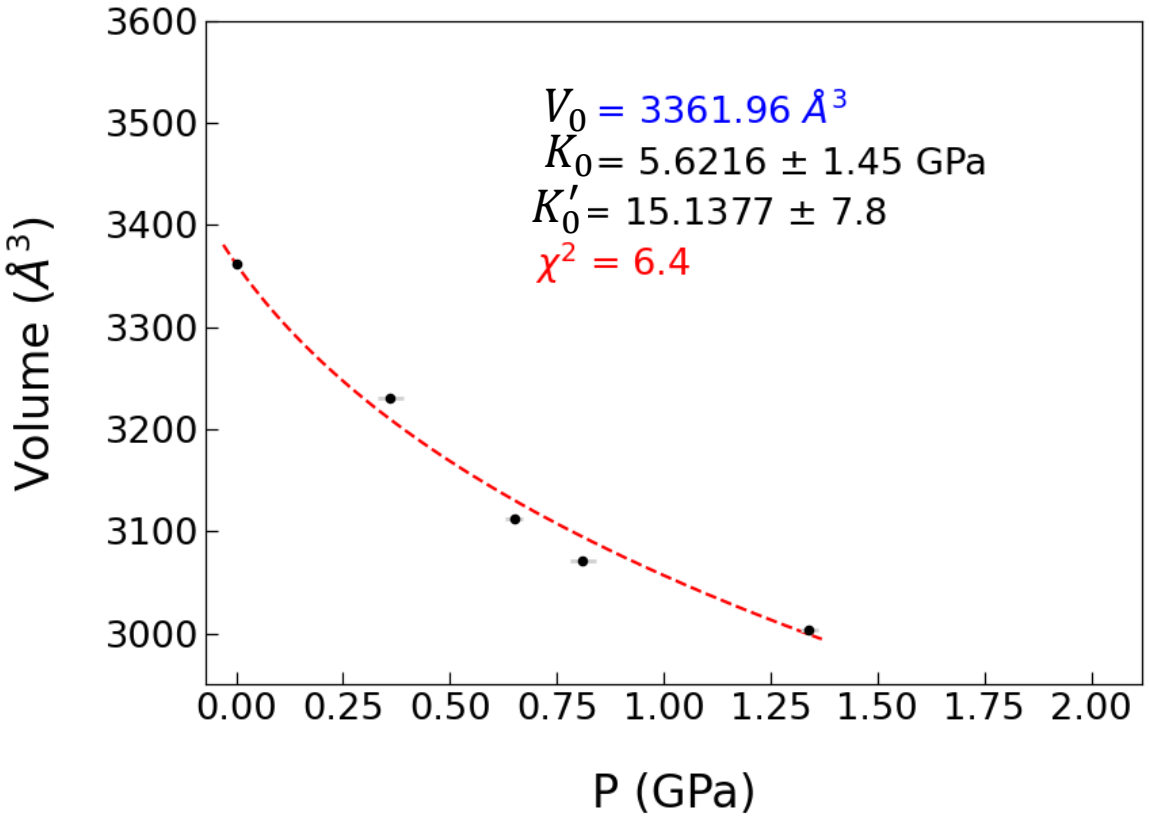
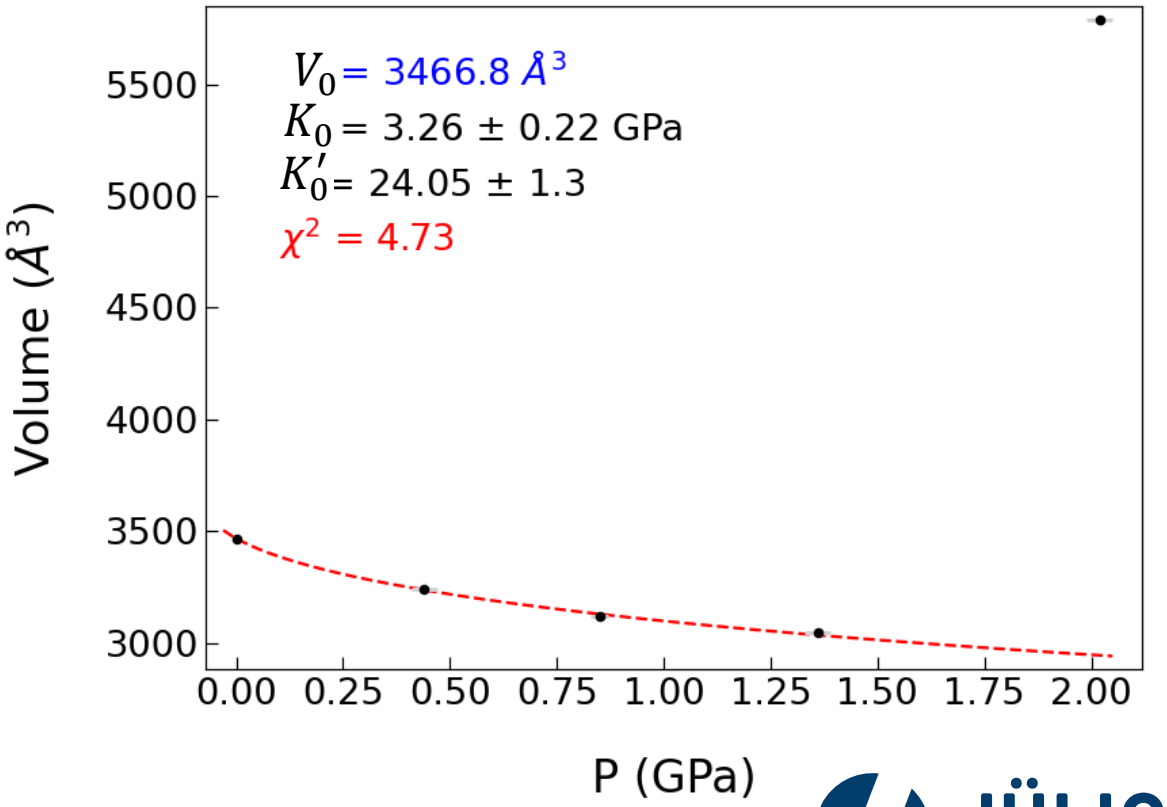


Monoclinic



Orthorhombic

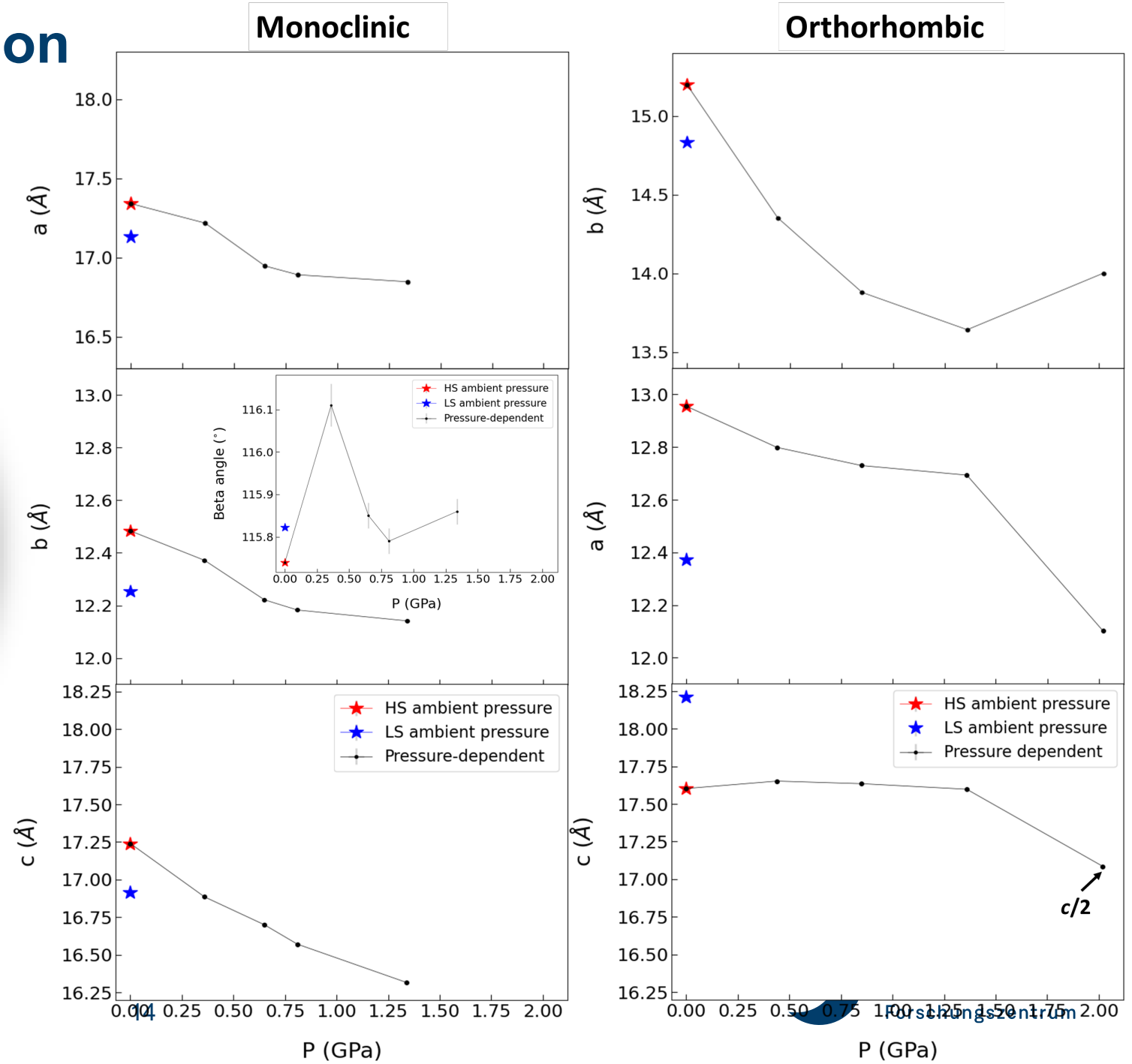


Orthorhombic is more compressible than monoclinic

Lattice Parameter Compression

Subline

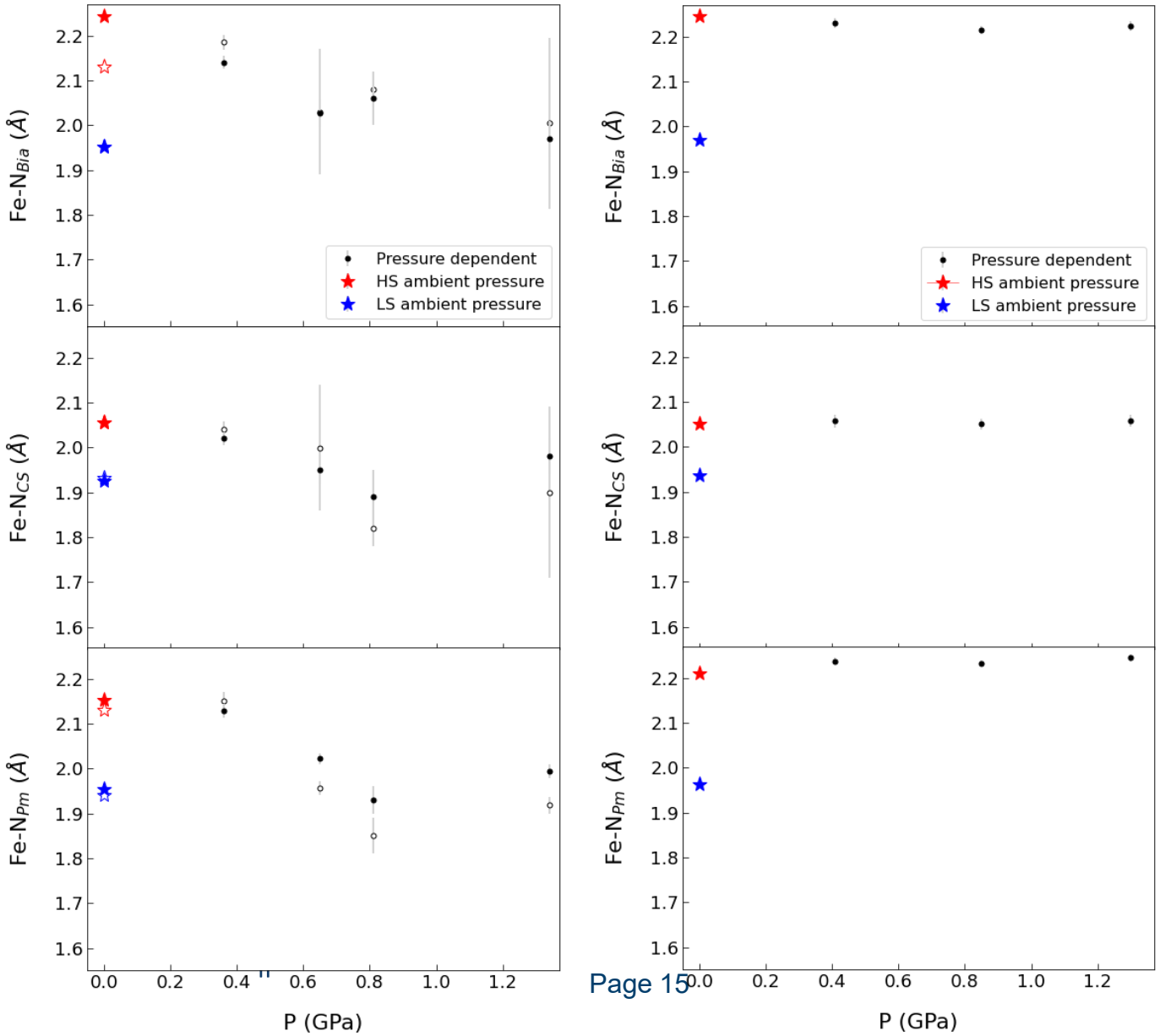
- Anisotropic unit cell compression under pressure



Pressure-Induced Spin transition?

High-pressure single crystal diffraction at ambient temperature @ P24, DESY, PETRA III

Monoclinic **Orthorhombic**

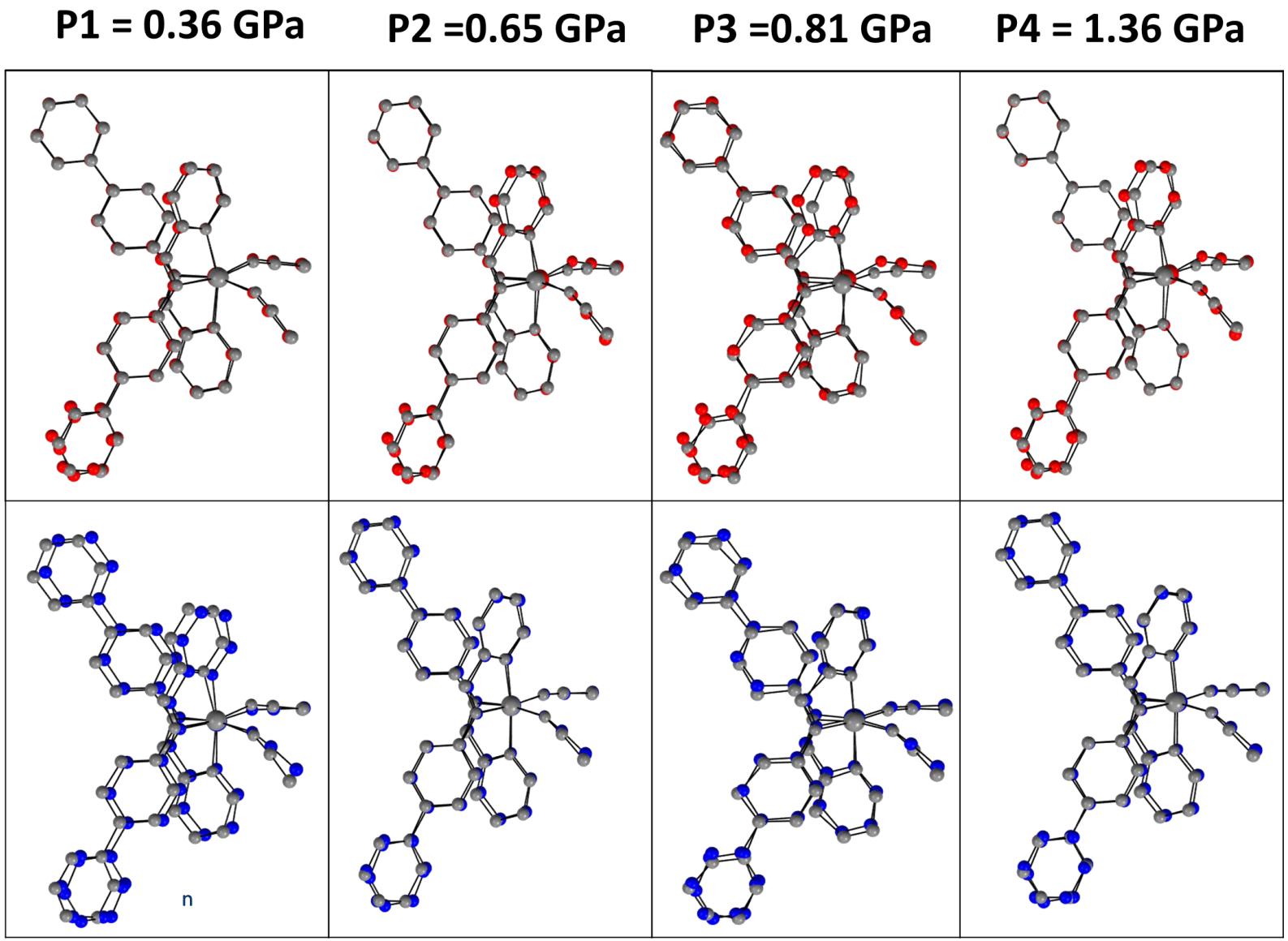


- Monoclinic undergoes an incomplete spin transition to the LS state up to 1.34 GPa.
- Orthorhombic remains in the HS state up to 1.36 GPa

Pressure-Induced Spin transition?

High-pressure single crystal diffraction at ambient temperature @ P24, DESY, PETRA III

Monoclinic



HS

Pressure dependent

LS

Pressure dependent

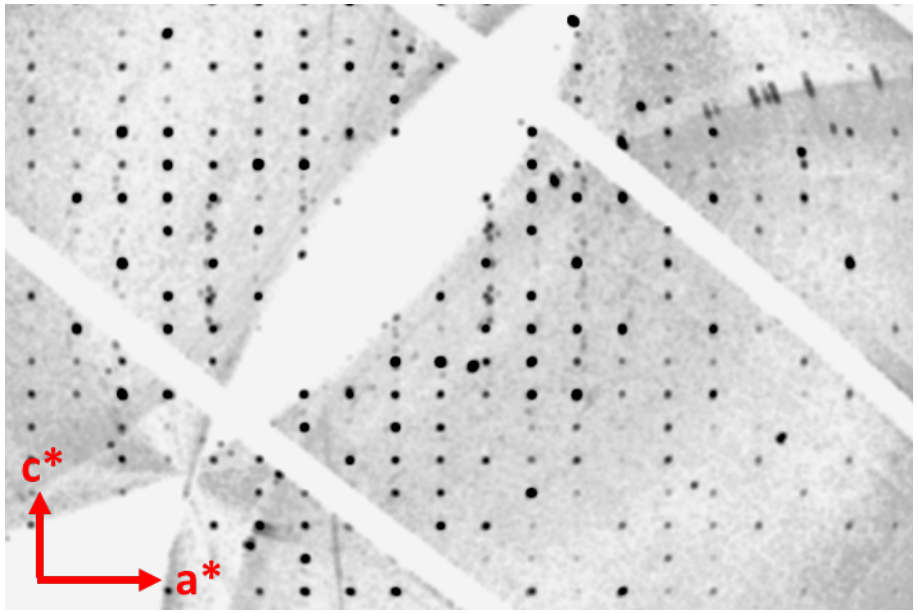
Superstructure at Critical Pressure

Orthorhombic

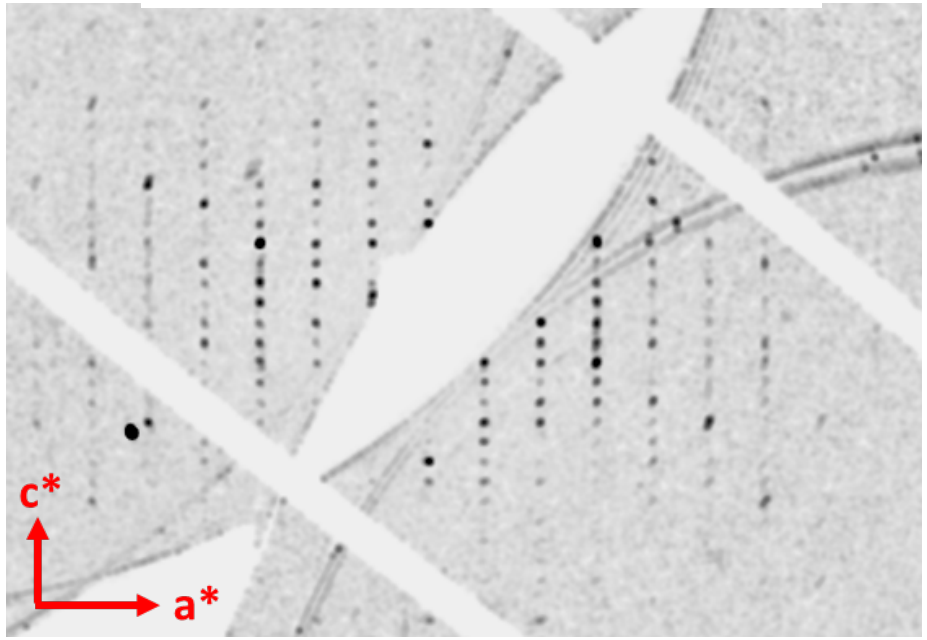
Sublime

h1l

P_2=0.85 GPa



P_4=2.02 GPa

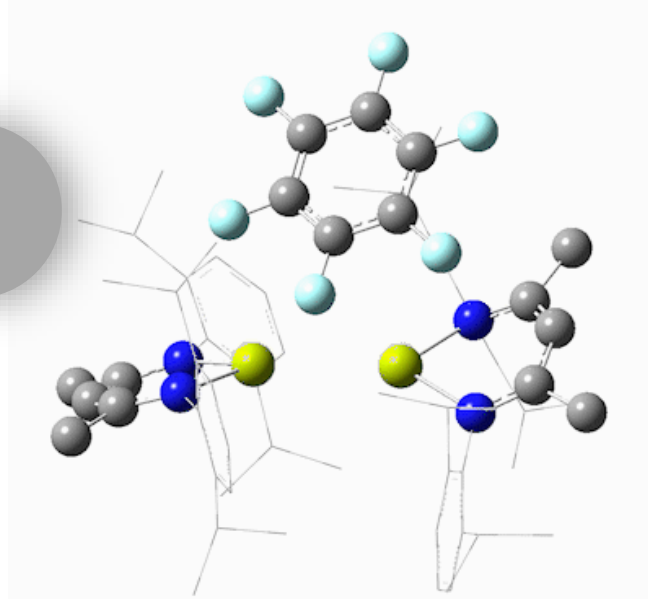


The crystal structure is not yet solved!

Intermolecular Interactions

Monoclinic

Orthorhombic

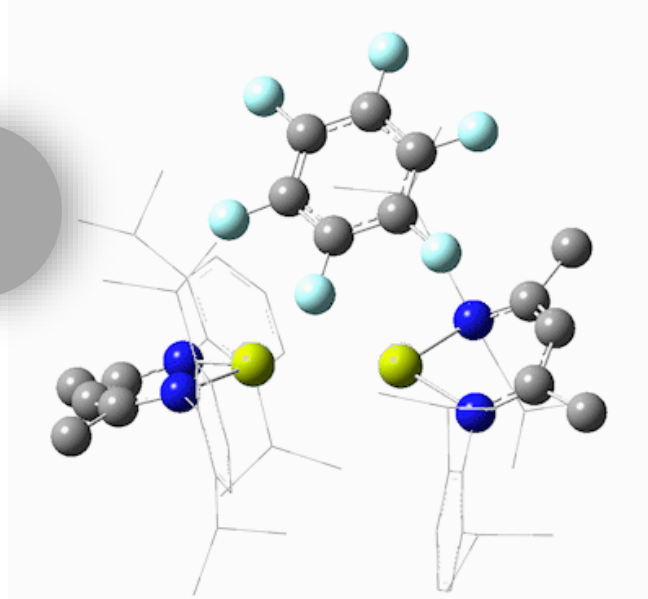


Intermolecular Interactions

Monoclinic

- interactions
- Van der Waals
- H-bonding

Orthorhombic



Intermolecular Interactions

Monoclinic

- ✓ interactions
- ✓ Van der Waals
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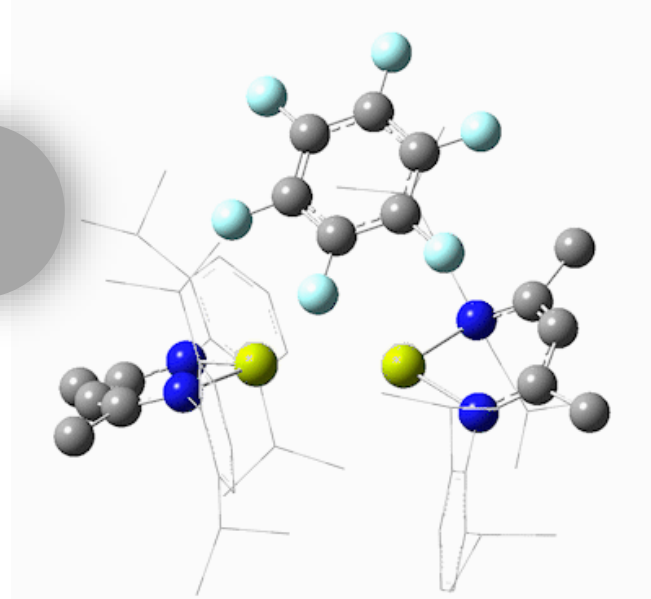
Orthorhombic

- ✗ interactions
- ✓ Van der Waals
- ✓ H-bonding



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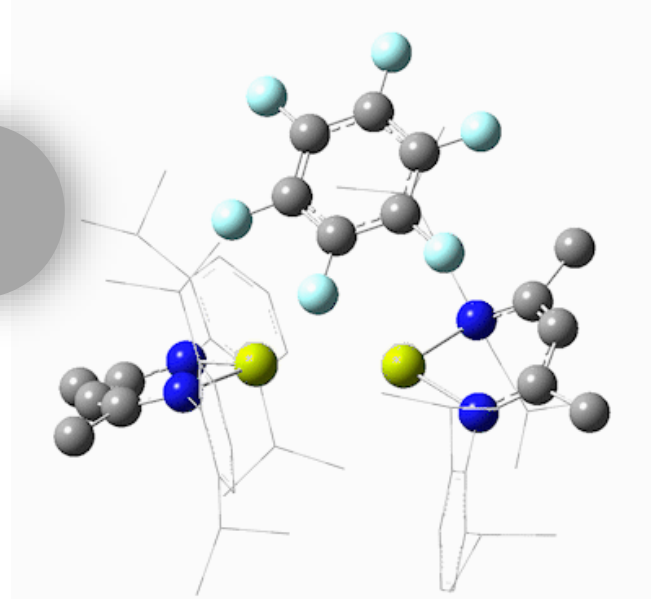

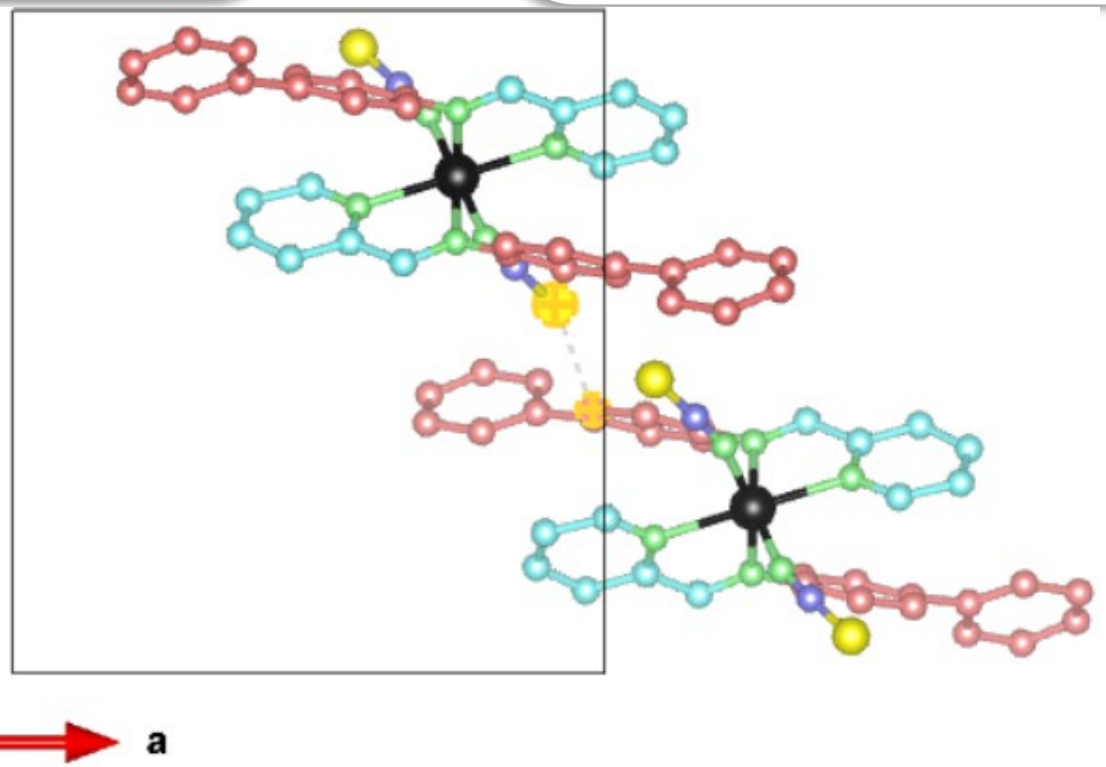

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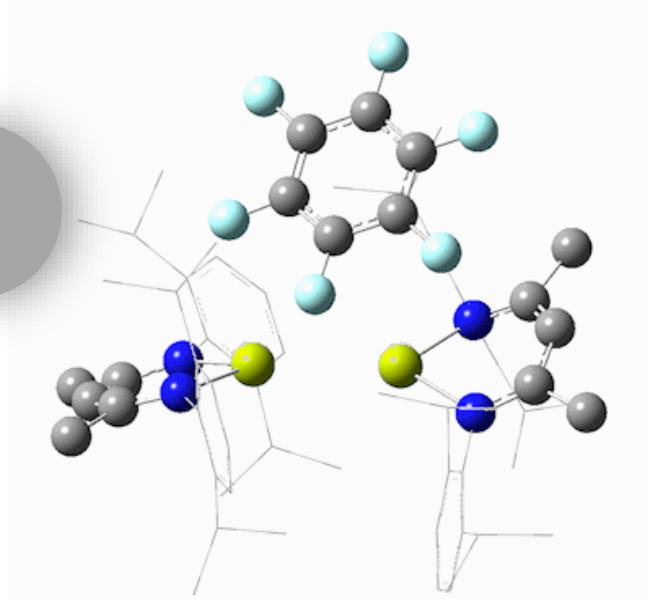
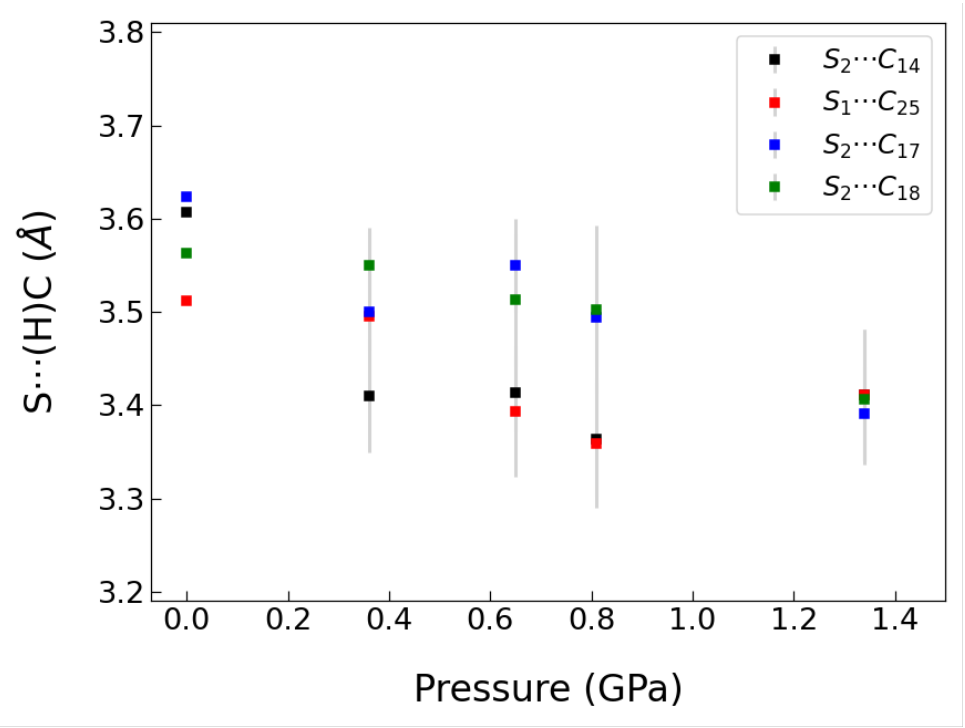
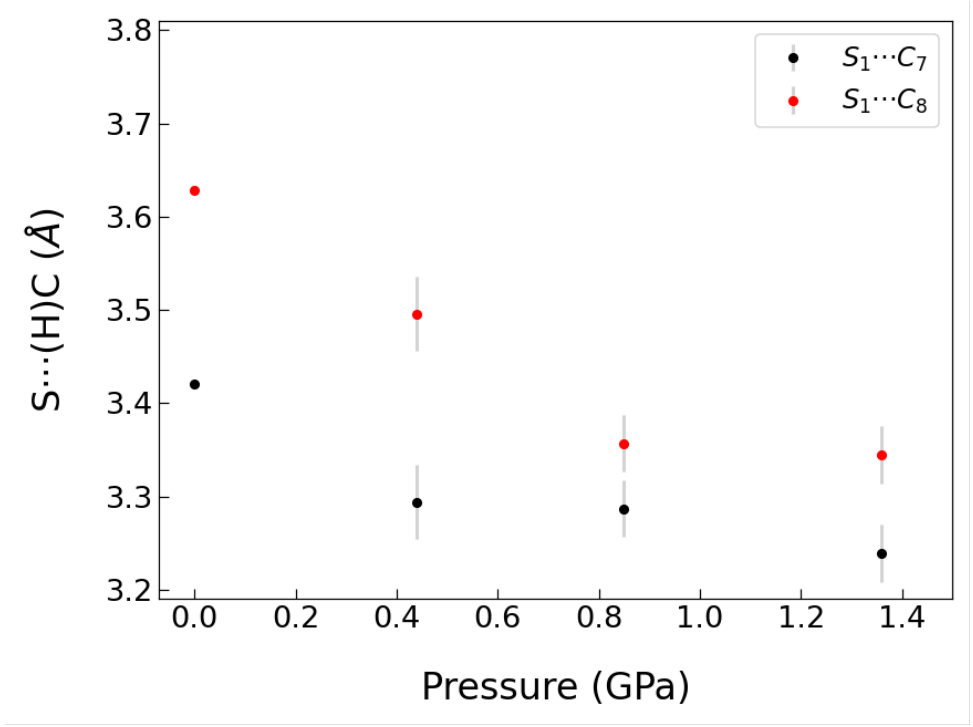
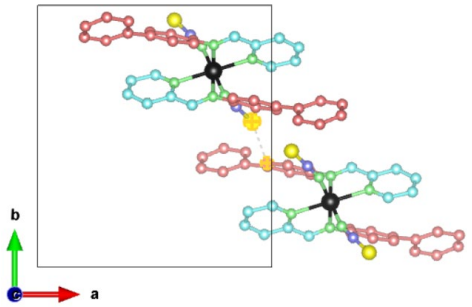




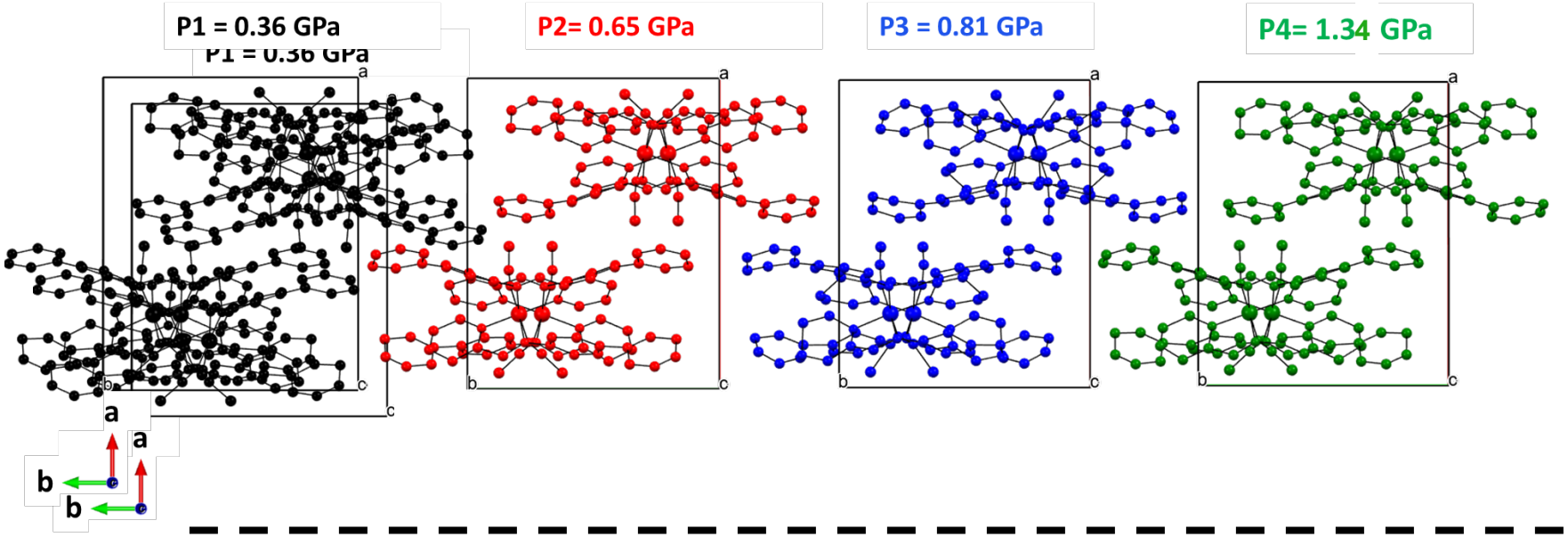




JÜLICH
Forschungszentrum

Crystal Packing

Monoclinic



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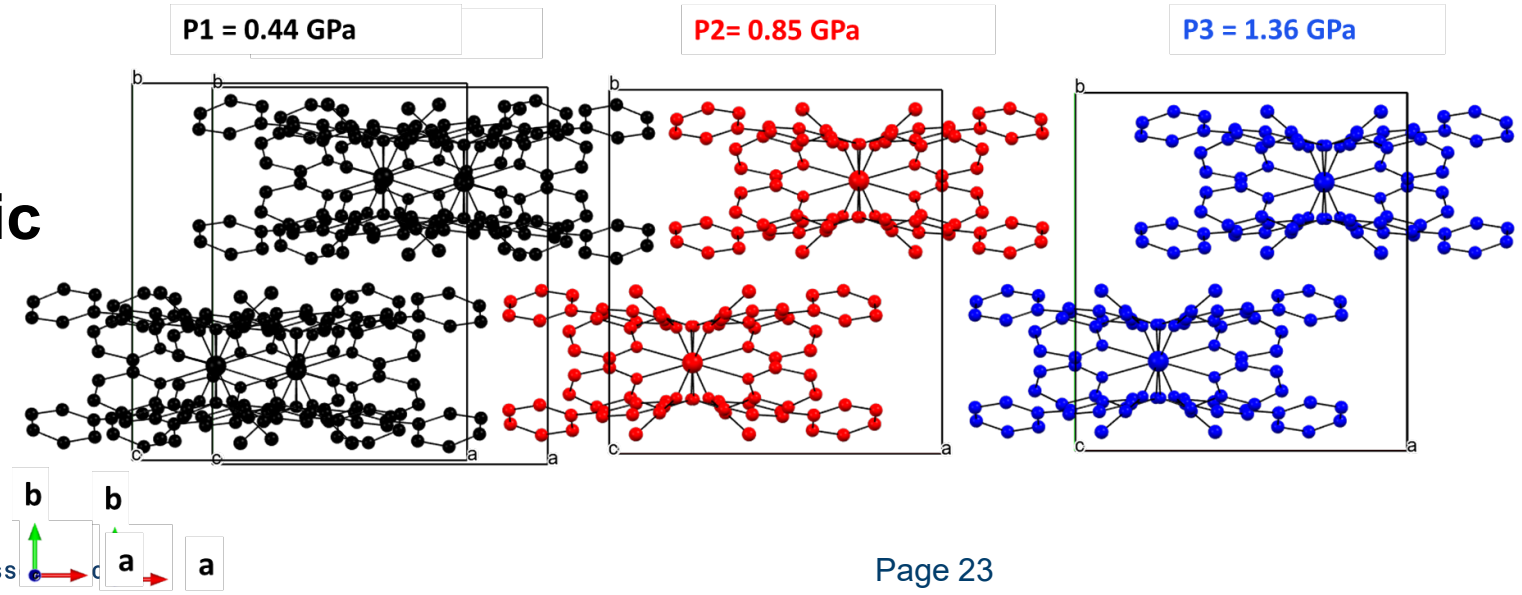
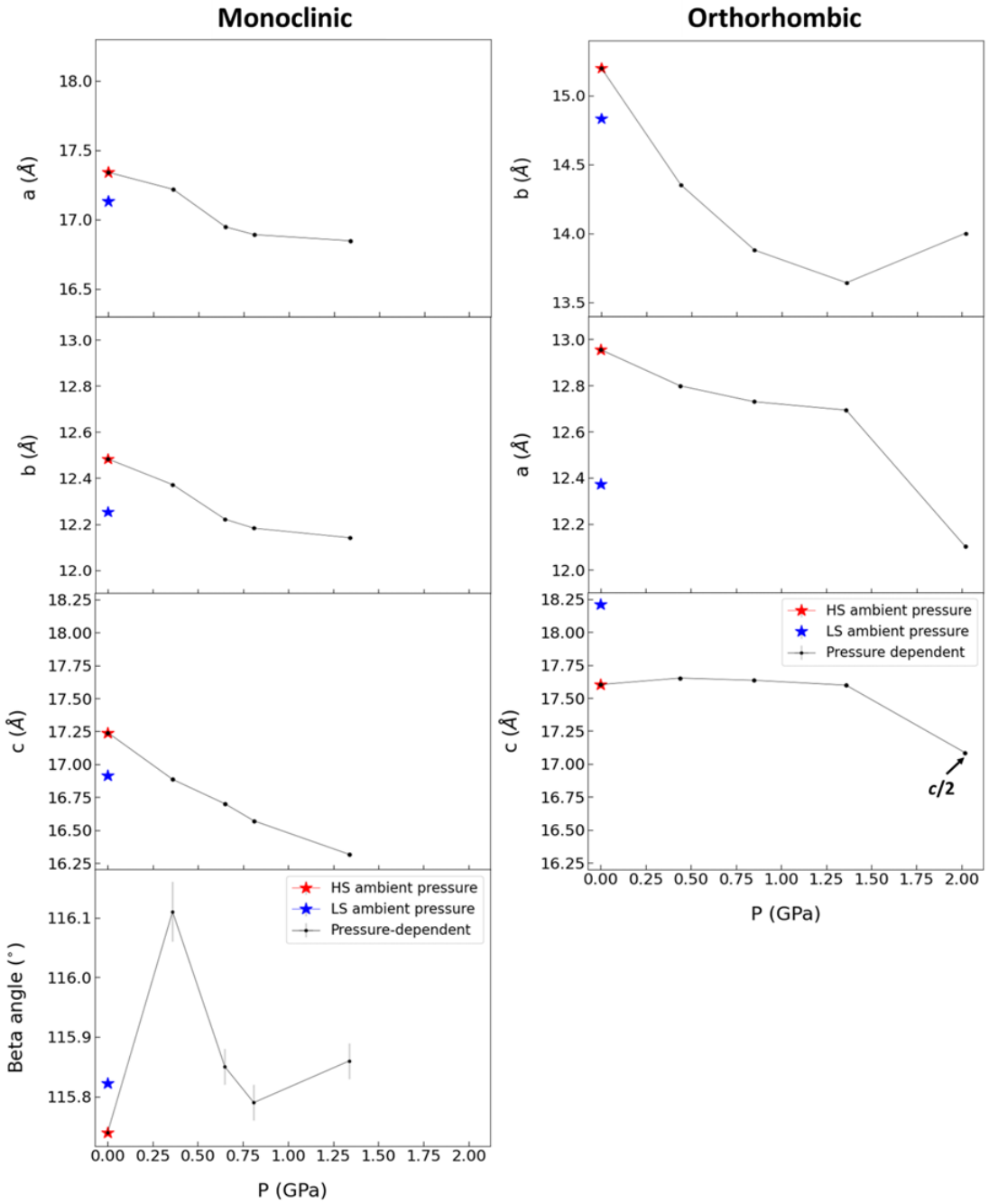
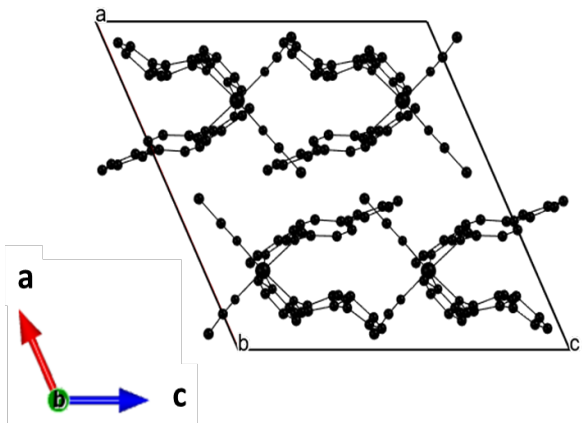
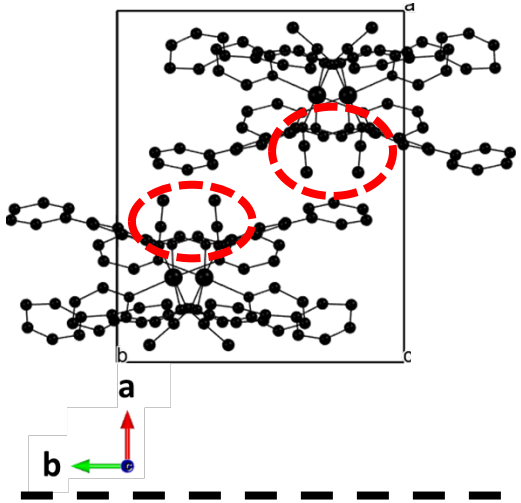


Crystal Packing

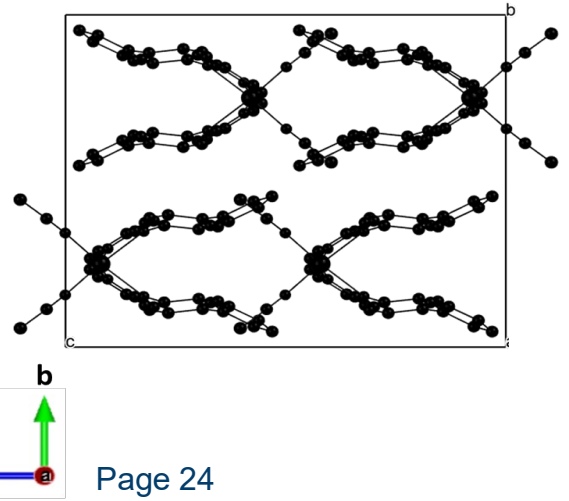


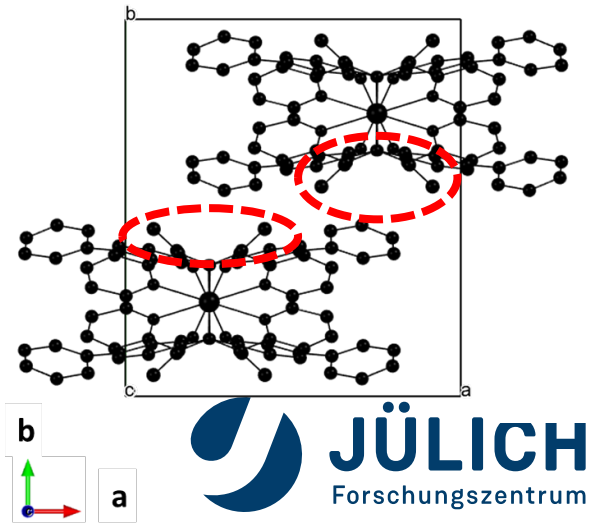


Monoclinic



Orthorhombic





JÜLICH Forschungszentrum

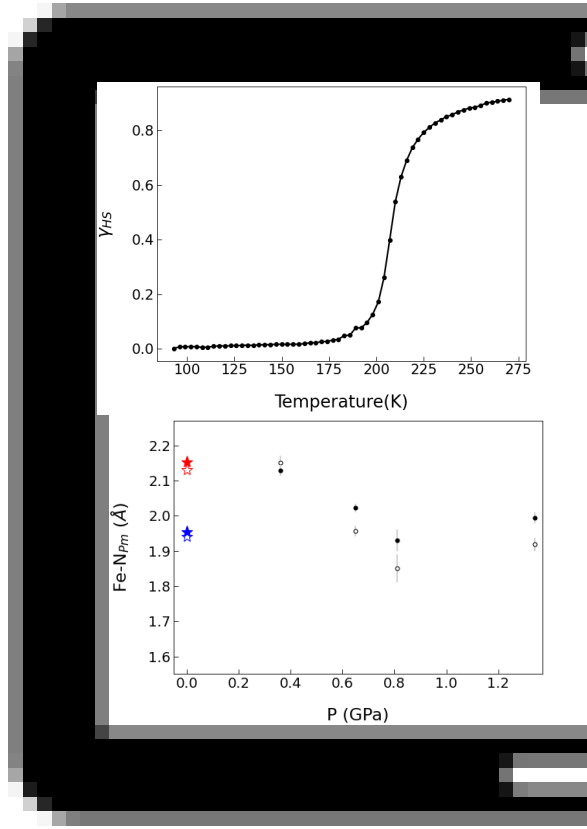
Monoclinic

Thermal transition

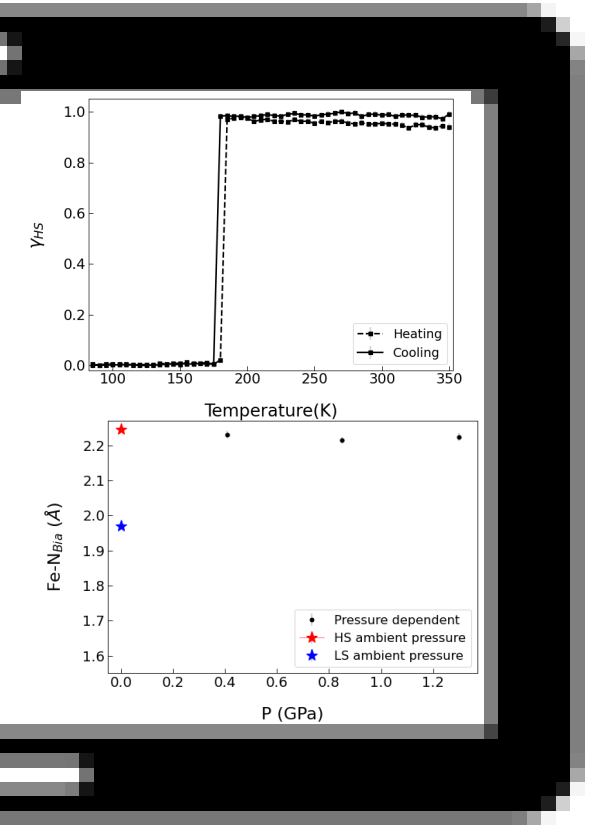
- π-π interaction

Pressure-induced spin transition

- π-π interaction
- H-bonding



Orthorhombic



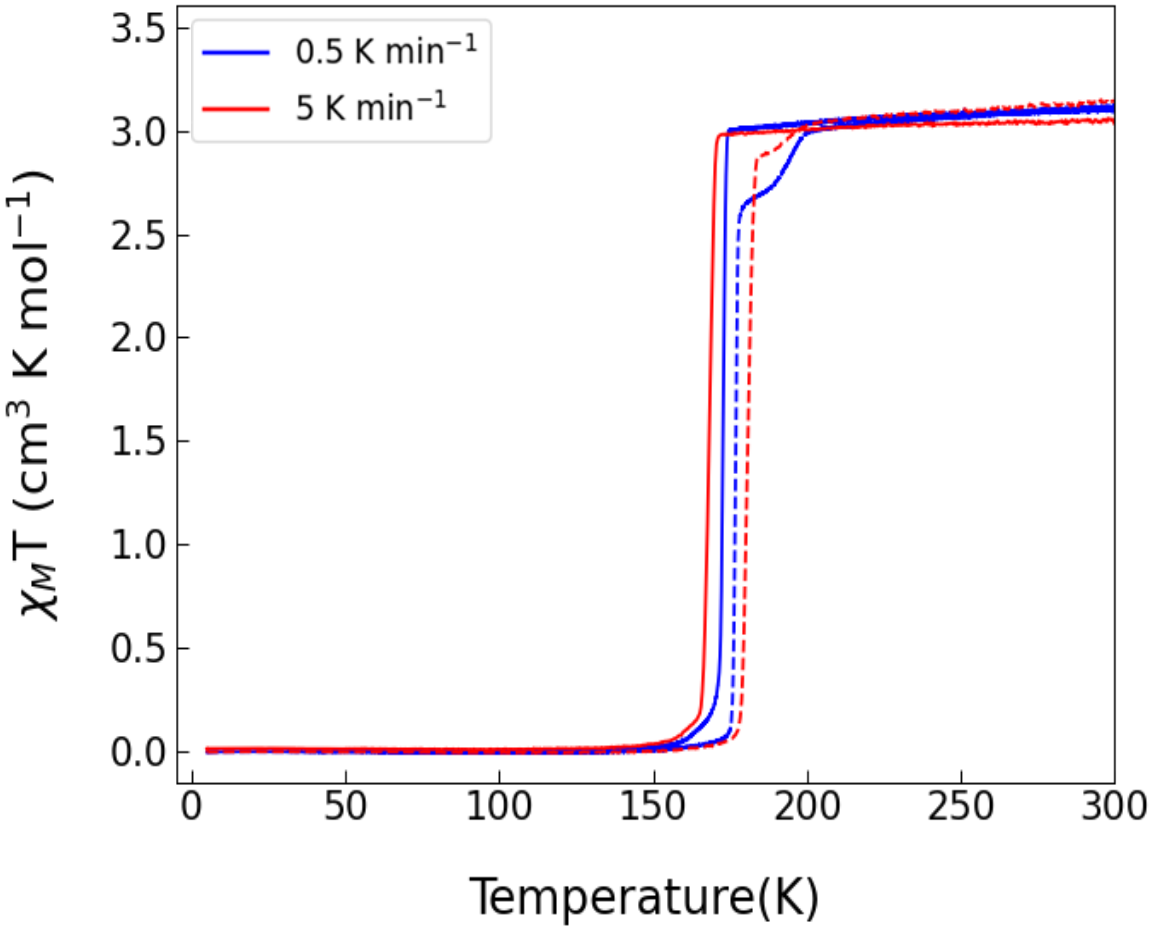
H-bonding → Thermal transition

H-bonding → Pressure-induced spin transition

Scan Rate dependence

Orthorhombic @ Dyancool PPMS

Polycrystalline



Scan Rate dependence

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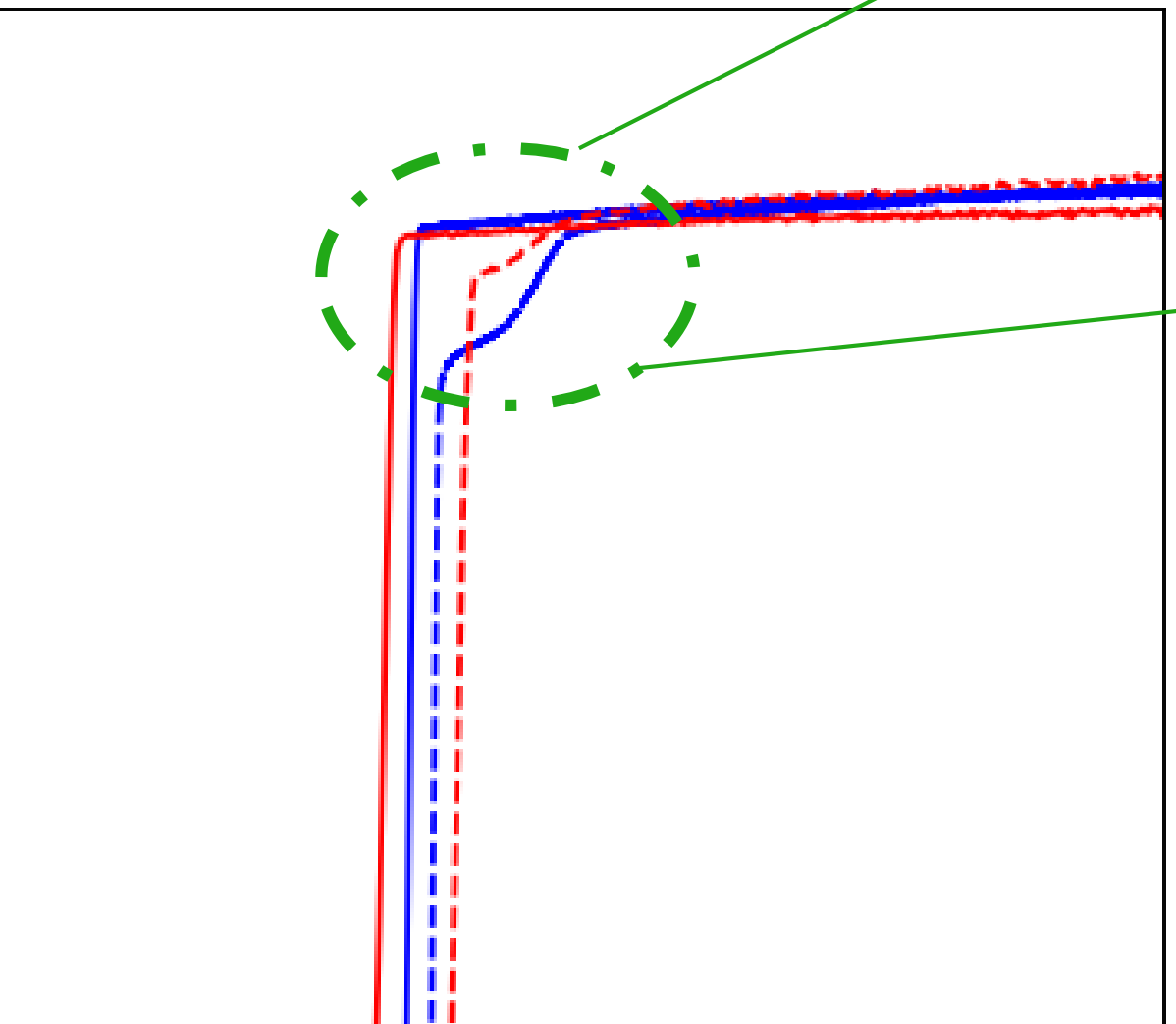
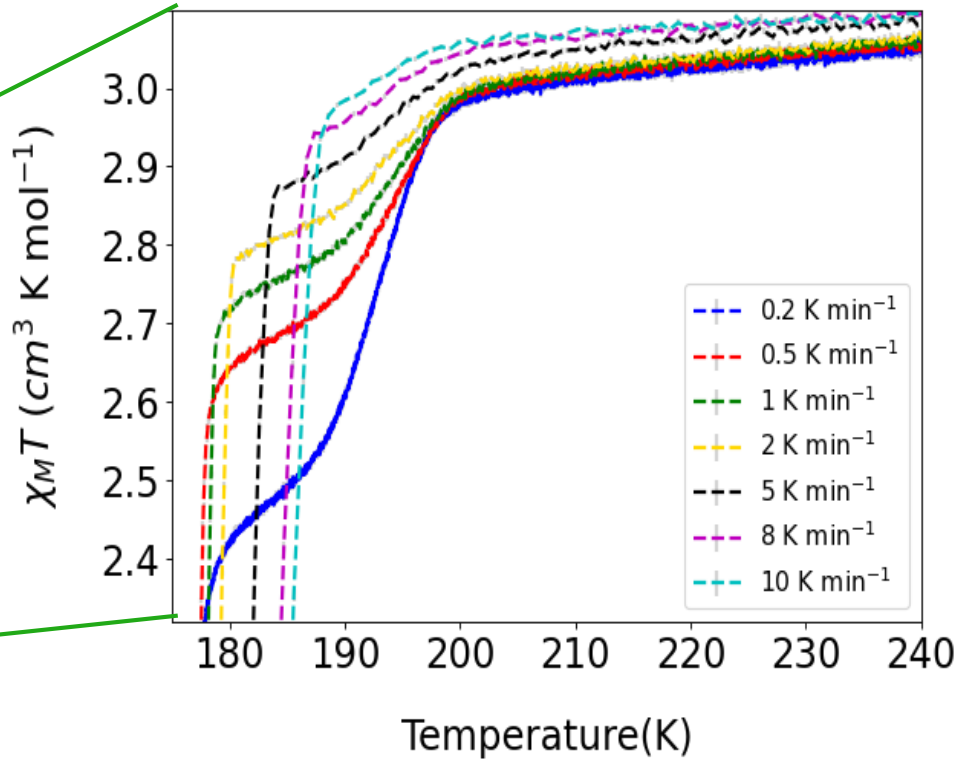




JÜLICH Forschungszentrum

Temperature Scan Rate Dependent PXRD

Orthorhombic

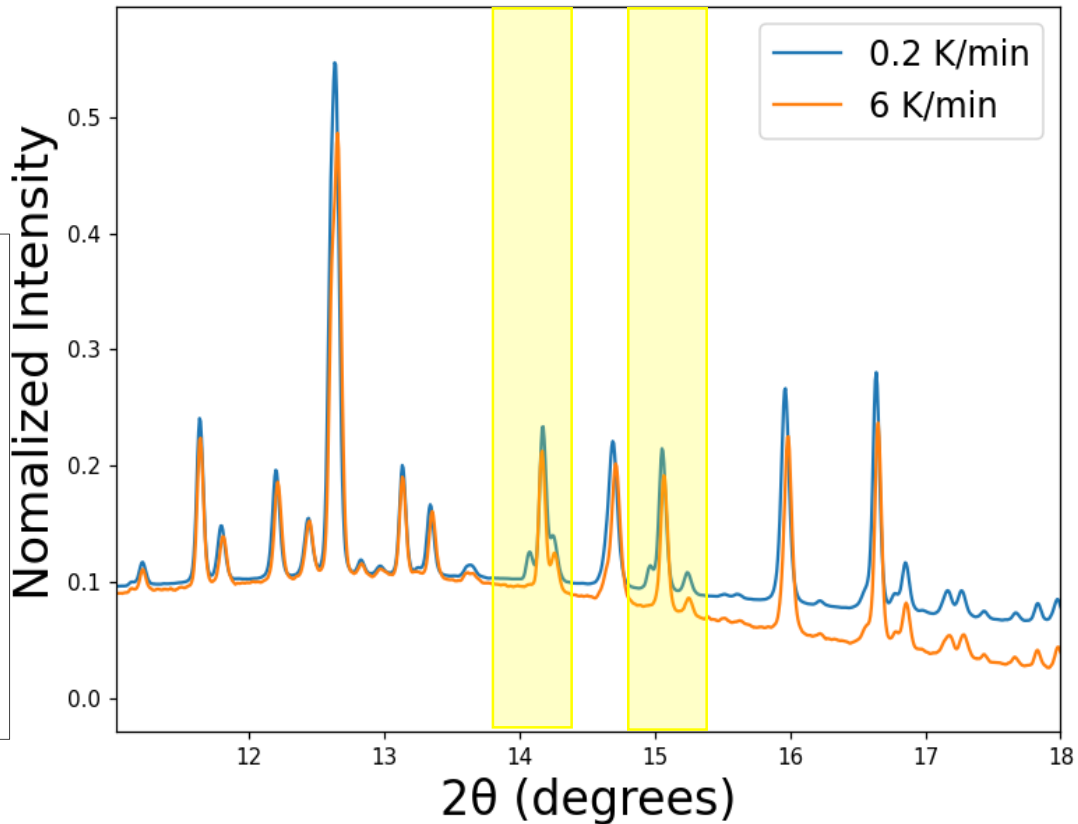
150 K250 K

6 K/min | **0.2 K/min**

@T= 185 K

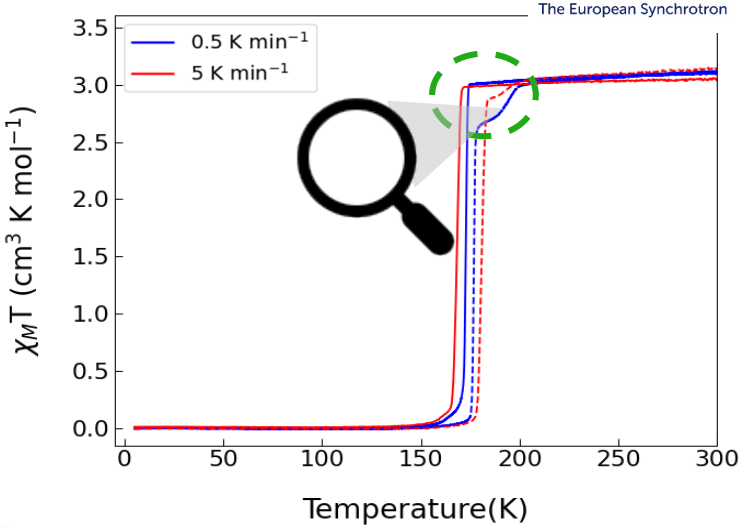
Heating

These additional peaks were fitted with a supercell!

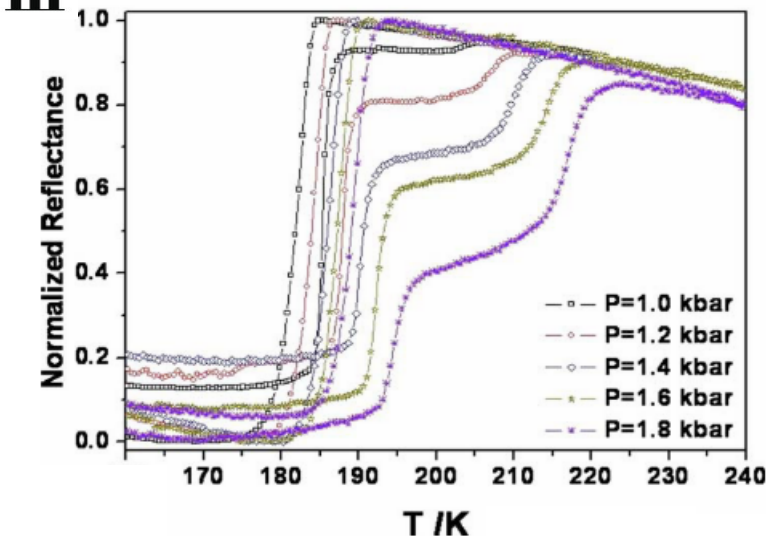


Swiss-Norwegian Beam Lines at ESRF

ESRF The European Synchrotron



P Ⅲ



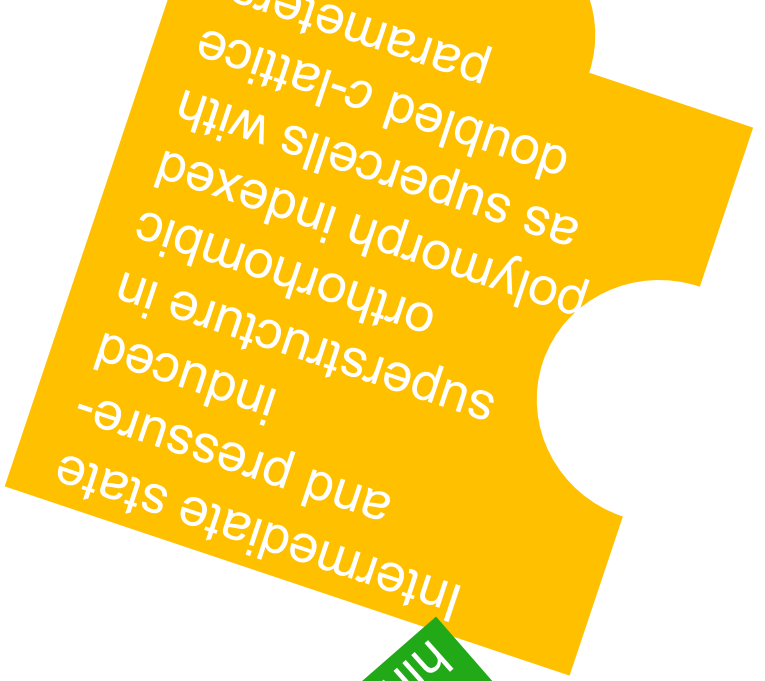
Rotaru, A., et. al, (2009). J. Appl. Phys. 106, 053515.

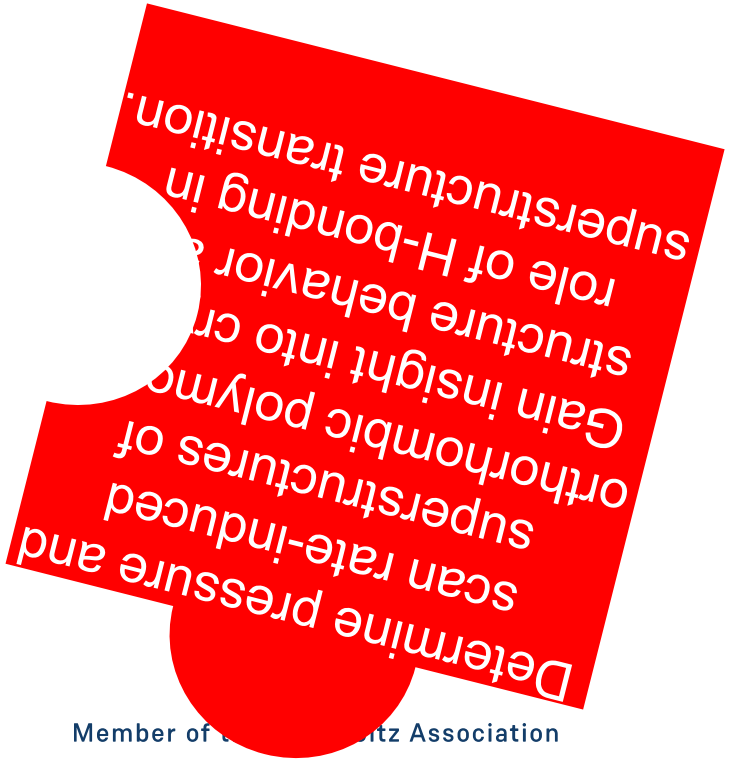
Are the investigated polymorphs suitable candidates for barocaloric applications?

Conclusion

With applying pressure:

- Monoclinic polymorph undergoes ST to LS but it is incomplete.
- Orthorhombic polymorph does not experience any spin transition to the LS.





Conclusi

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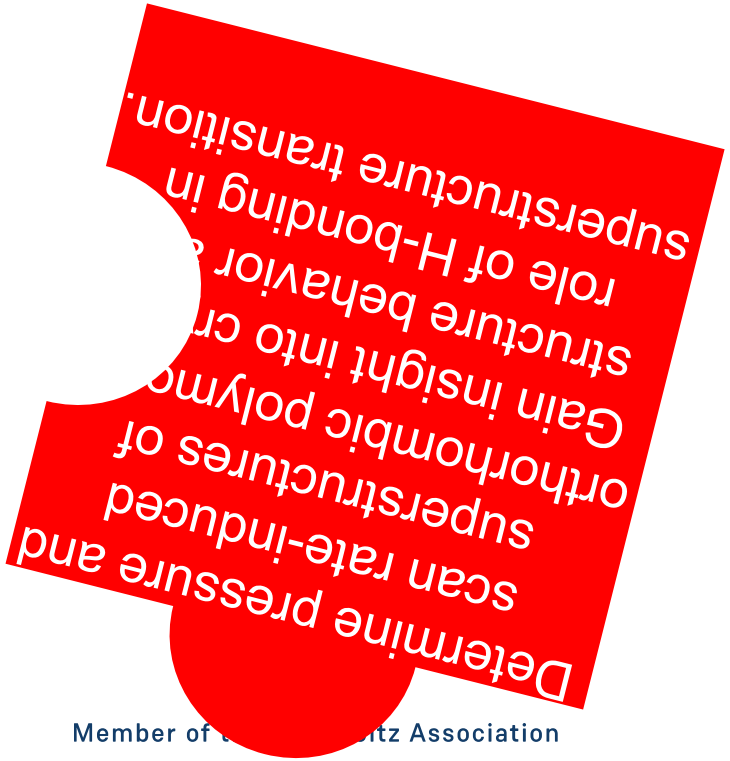
Intermediate state and pressure-induced superstructure in orthorhombic polymorph indexed as supercells with doubled *c*-lattice parameters.



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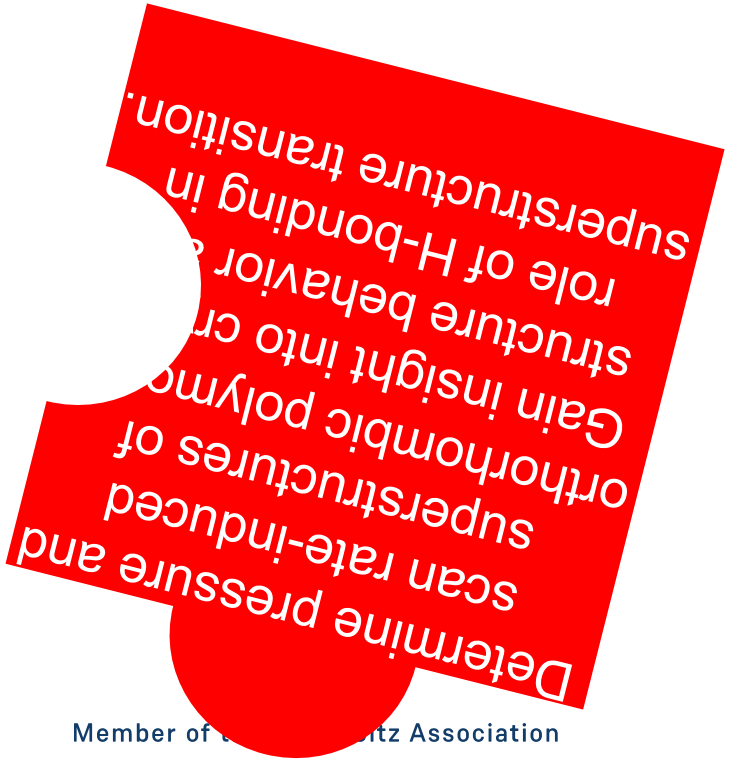
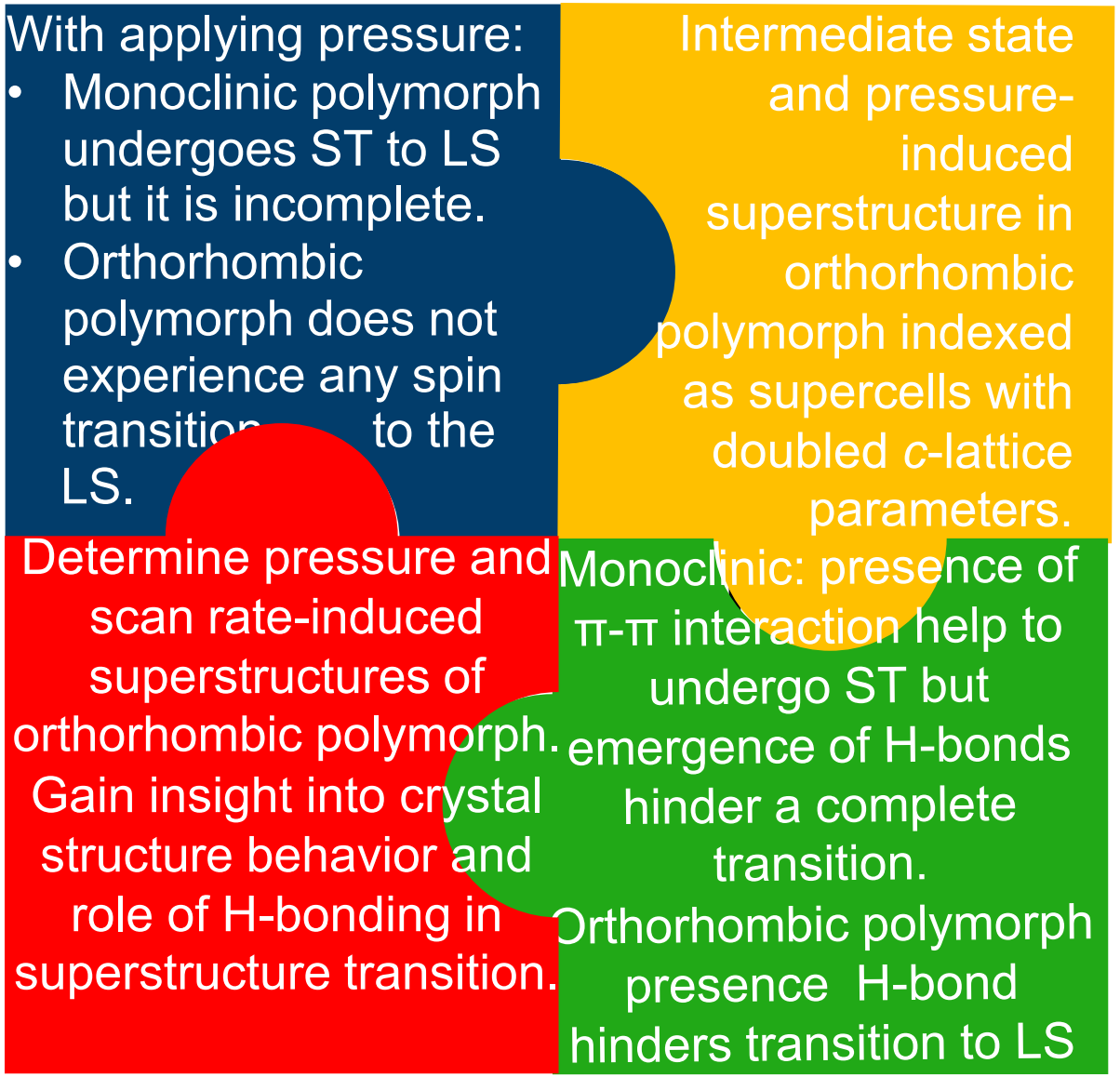
Monoclinic: presence of π-π interaction help to undergo ST but emergence of H-bonds hinder a complete transition.
Orthorhombic polymorph presence H-bond hinders transition to LS

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Intermediate state and pressure-induced superstructure in orthorhombic polymorph indexed as supercells with doubled c-lattice parameters.
Determine pressure and scan rate-induced superstructures of orthorhombic polymorph. Gain insight into crystal structure behavior and role of H-bonding in superstructure transition.
Monoclinic: presence of π-π interaction help to undergo ST but emergence of H-bonds hinder a complete transition.
Orthorhombic polymorph presence H-bond hinders transition to LS

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Dr. Carsten Paulmann

Dr. Denis Sheptyakov

Dr. Cervellino Antonio

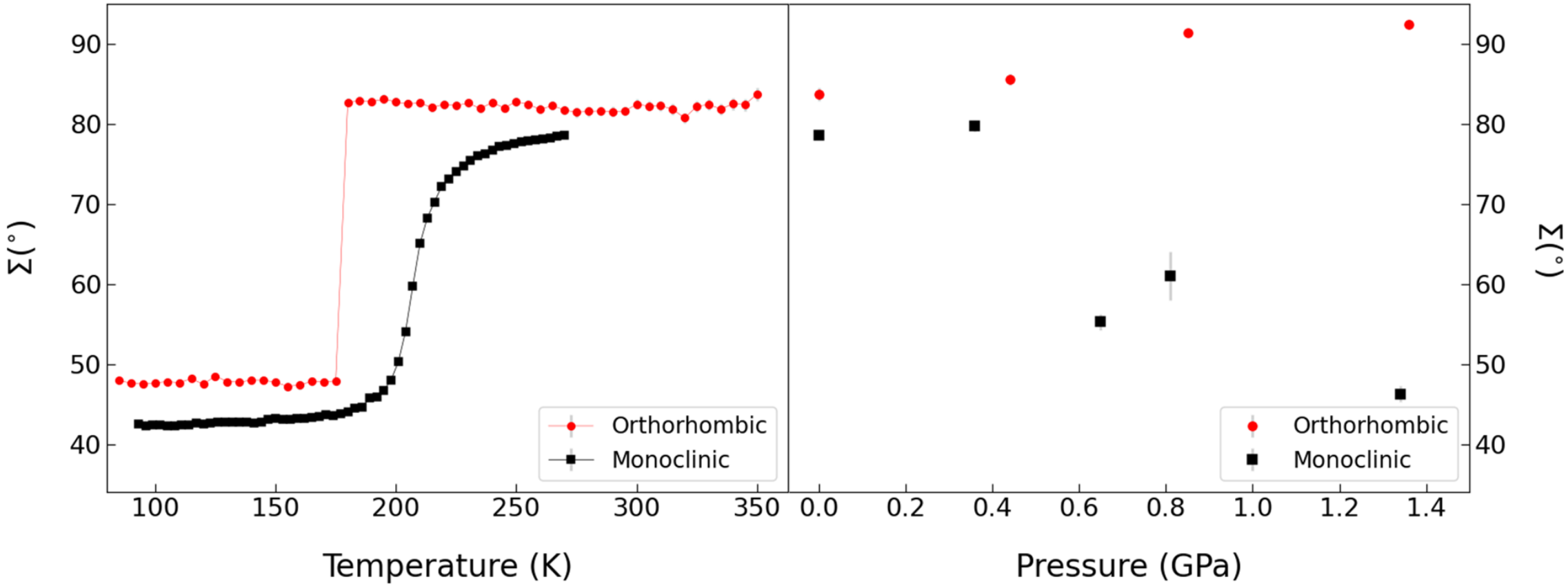
Prof. Dr. Ghassan Saffarini

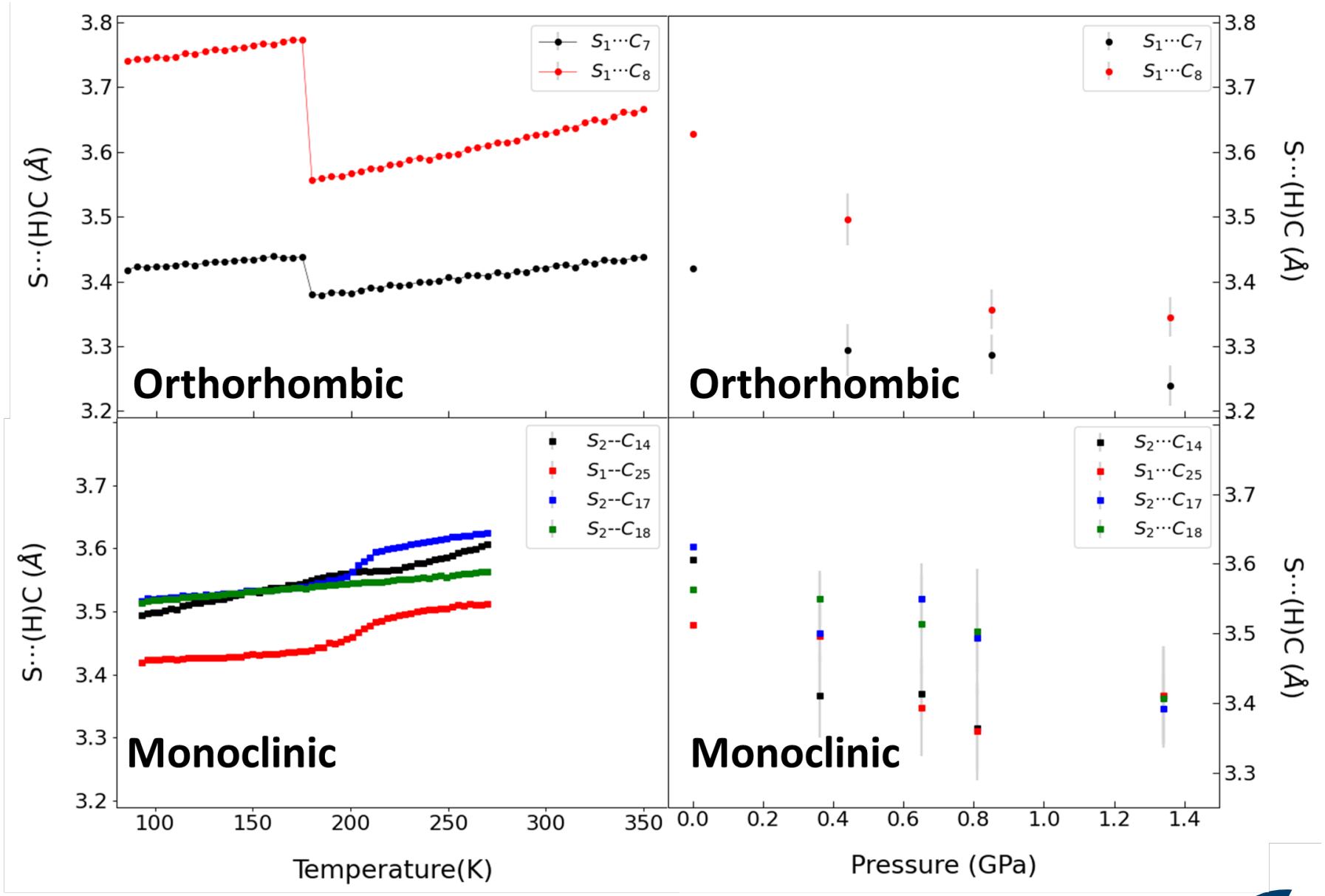
Thank you for your Attention !

Back Up Slides

Distortion Parameters

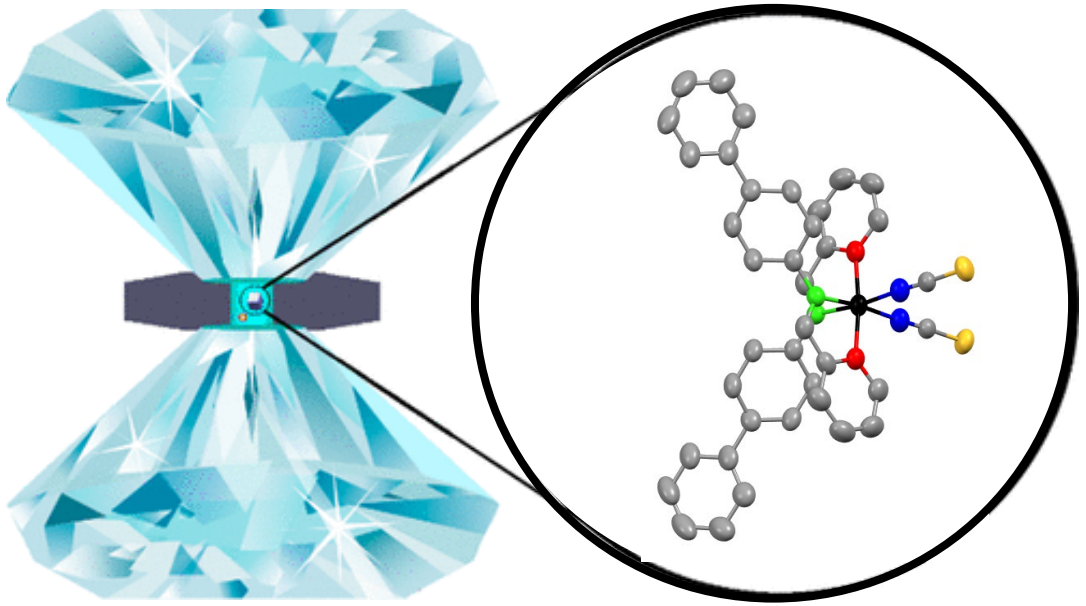
Angular distortion

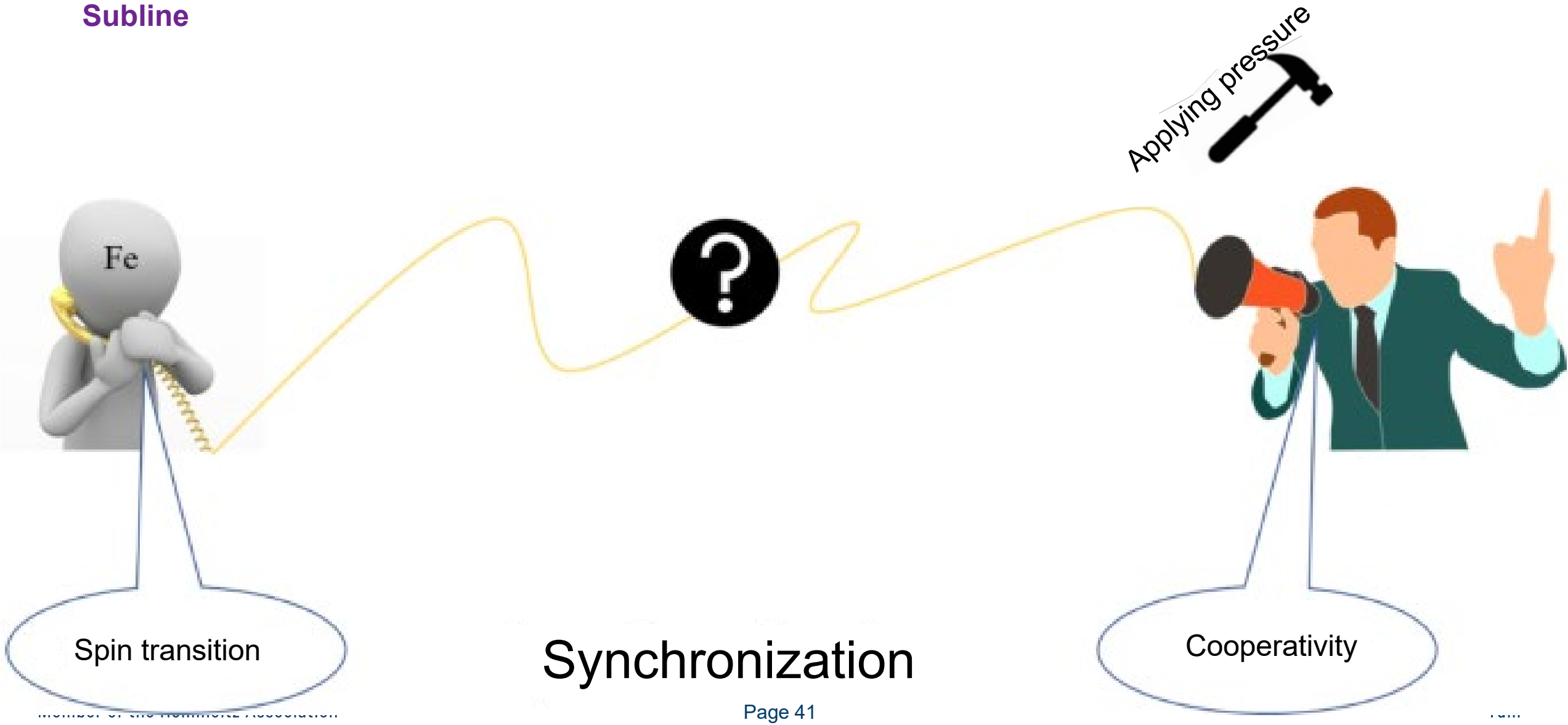



Orthorhombic
Orthorhombic
Monoclinic
Monoclinic
S···(H)C (Å)
Temperature(K)
Pressure (GPa)
$S_1\cdots C_7$
$S_1\cdots C_8$
S_2--C_{14}
S_1--C_{25}
S_2--C_{17}
S_2--C_{18}
$S_2\cdots C_{14}$
$S_1\cdots C_{25}$
$S_2\cdots C_{17}$
$S_2\cdots C_{18}$

Pressure-dependent Crystal Structure

Diamond Anvil Cell




Applying pressure
Fe
Spin transition
Synchronization
Cooperativity

Intermolecular interaction H-bonding, π-π interaction, Van der Waals

Spin transition

?

Synchronization

Applying pressure

Cooperativity