Effect of pressure and chemical substitution on the structural, magnetic and superconducting properties of iron based arsenides and chalcogenides

P. Toulemonde, S. Karlsson, D. Santos-Cottin, D. Freitas, M. Núñez Regueiro, P. Strobel, A. Sulpice, J. Marcus, S. Pairis, F. Lévy-Bertrand **Institut Néel, Grenoble**

C. Marcenat **INAC, CEA, Grenoble**

G. Garbarino **ESRF, Grenoble**

V. Nassif, Th. Hansen, J.A. Rodríguez Velamazán **ILL, Grenoble**

F. Morales **IIM, Universidad Nacional Autónoma de México, México**

Outline

- **Introduction: some key parameters of iron based superconductors**

Some words about our previous work:

- **Isovalent substitution of As by P in the SmFeAsO compound**
  & comparison with the high pressure study *Garbarino et al. Phys. Rev. B 84, 024510 (2011)*

- **Isovalent substitution of As by Sb in the LaFeAsO compound**
Karlsson et al. Phys. Rev. B 84, 104523 (2011)

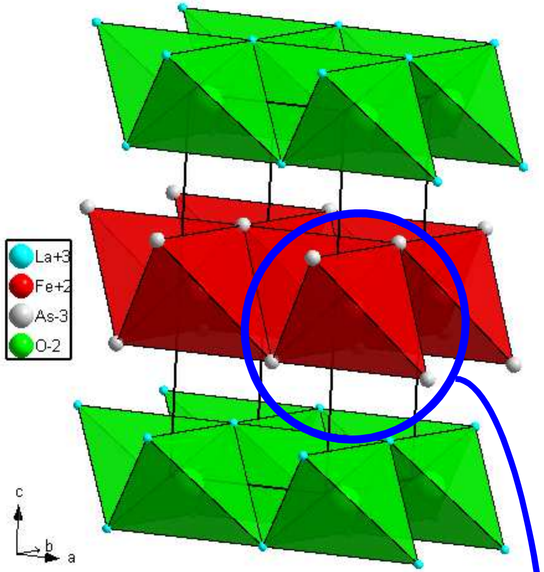
In more details in this talk:

- **Isovalent substitution of Se by S (or Te) in the $Tl_{1-y}Fe_{2-z}Se_2$ compound**
Toulemonde et al. JPCM (2013)

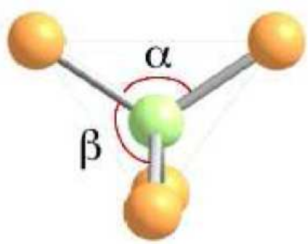
- **Conclusion**

Introduction: new iron-based superconductors

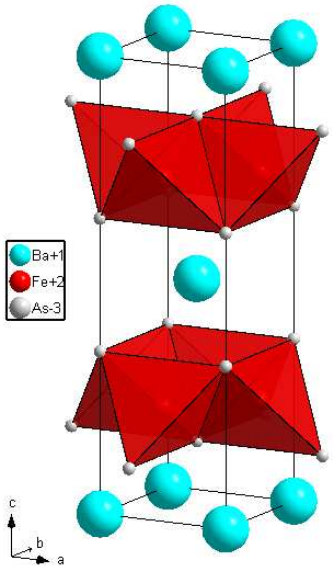
LnFeAsO
“1111”
T_c max = **55 K**



Fe-As: 2.435Å
Fe-Fe: 2.85Å & 8.74Å
α,β(As-Fe-As):
111.6° & 108.4°

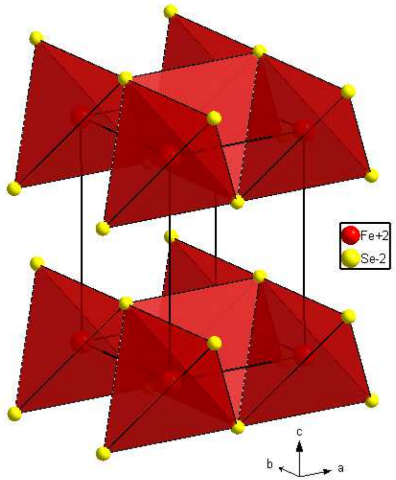


(AE,A)Fe_2As_2
“122”
T_c max = 38 K



Fe-As: 2.40Å
Fe-Fe: 2.80Å & 6.51Å
As-Fe-As:
111.1° & 108.7°

$Fe_{1+\delta}(Se_{1-x}Te_x)$
“11”
T_c = 8K to 15K



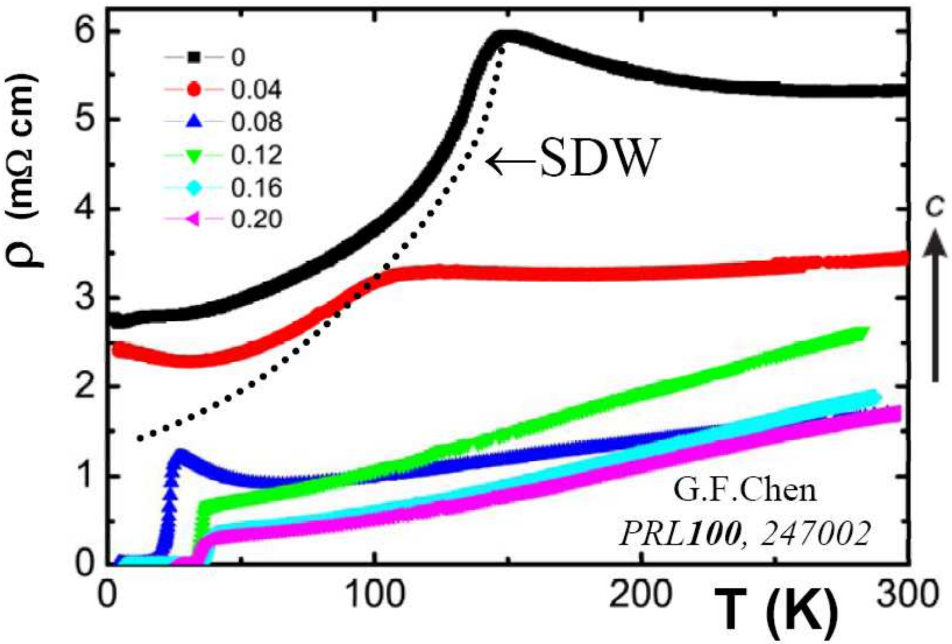
Fe-Se: 2.367 Å
Fe-Fe: 2.66 Å & 5.52 Å
Se-Fe-Se:
111.6° & 105.4°

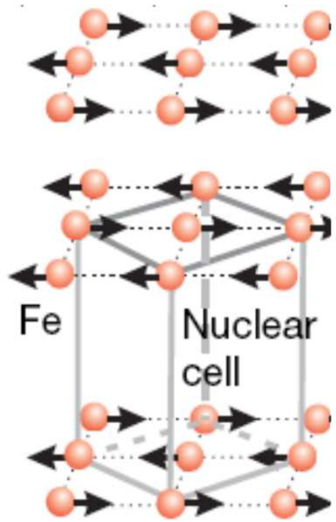
Introduction: from AntiFerroMagnetism to SuperConductivity

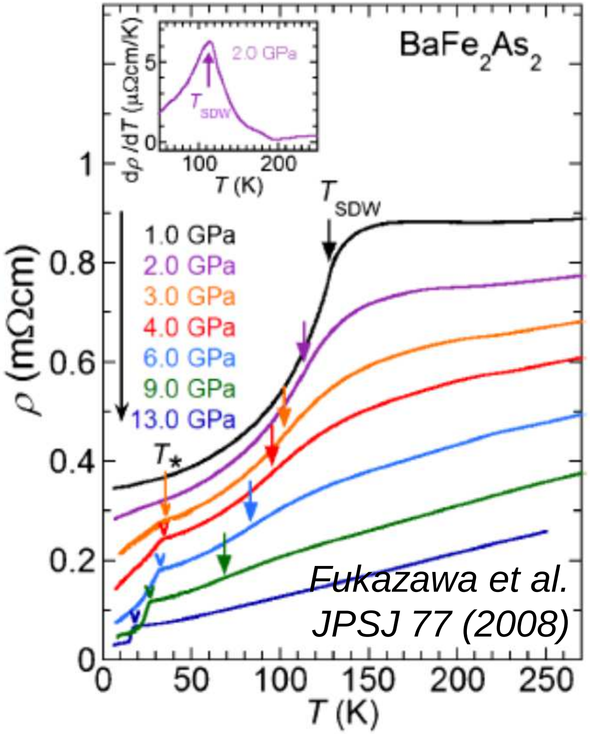
The non superconducting parent compound:

Long range AFM order (Spin Density Wave) below $T_{Néel}$

$LnFeAs(O_{1-x}F_x)$





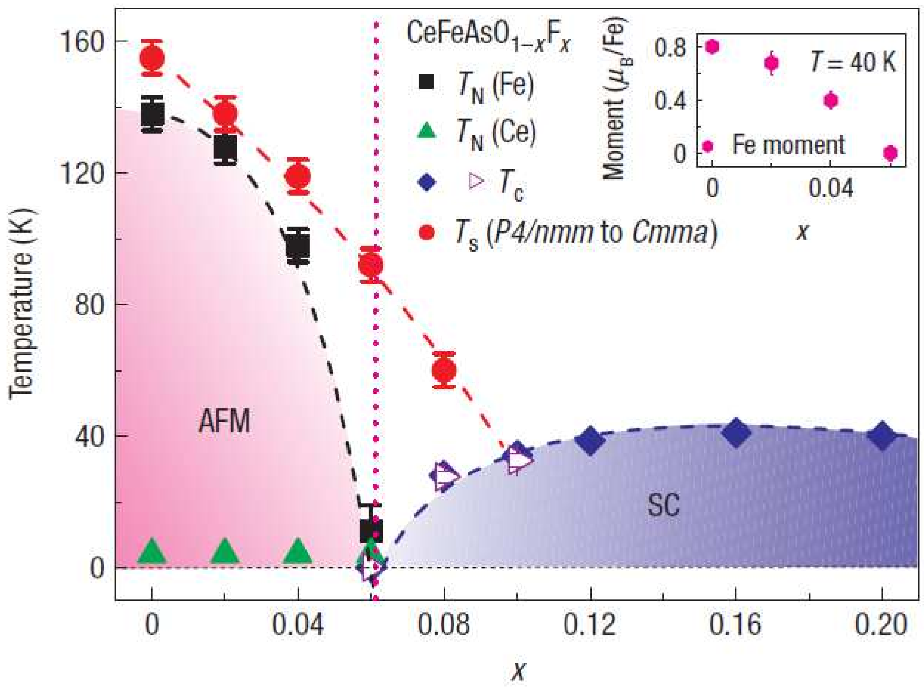


➔ Superconductivity (SC) appears when AFM order is destabilized by **chemical doping** or **mechanical pressure**

Introduction: phase diagram T vs composition or T vs pressure

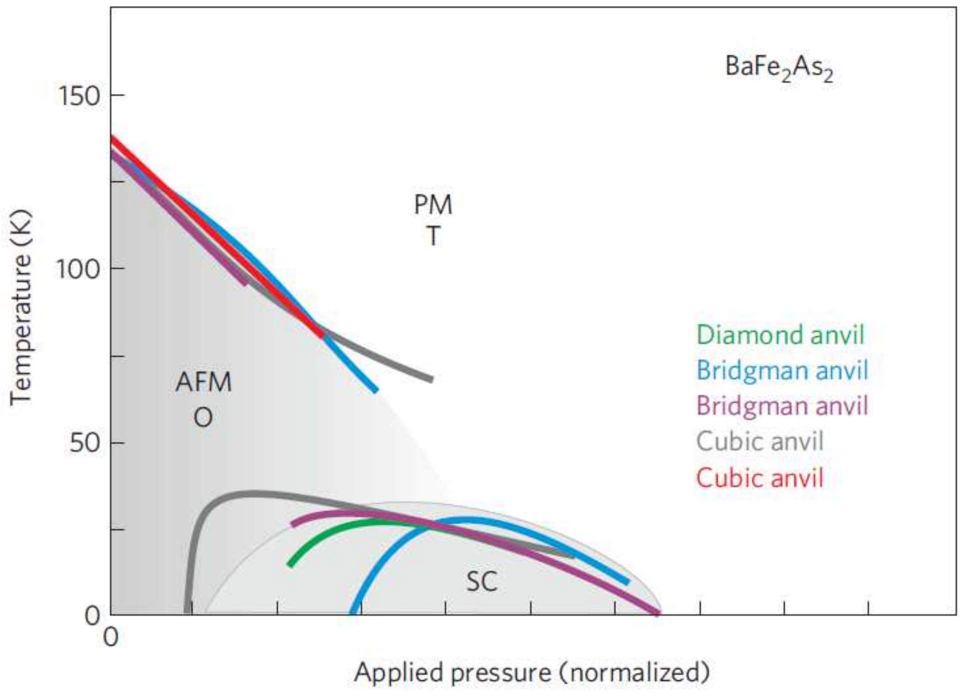
1111($O_{1-x}F_x$)

Zhao et al. Nat. Mat. (2008)



122/**HP**

Paglione & Green. Nat. Phys. (2010)



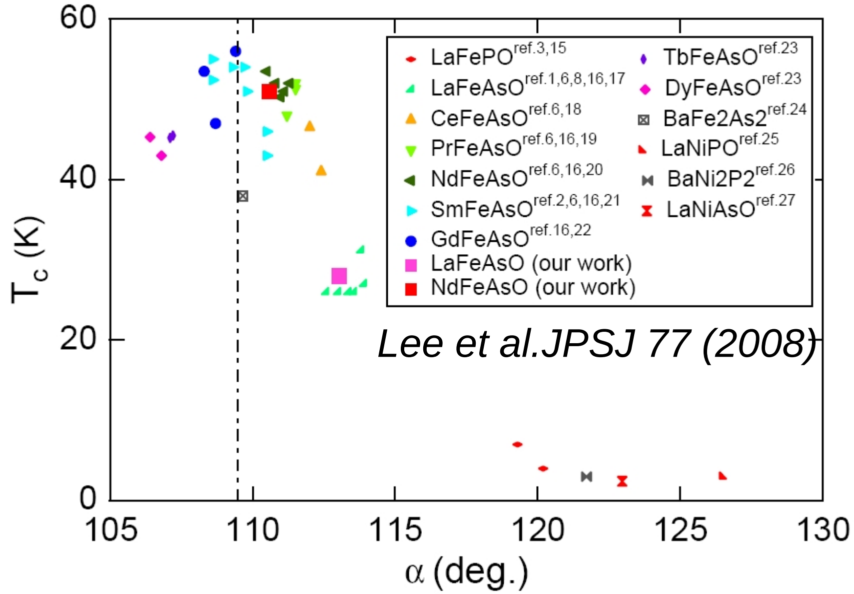
➔ Superconductivity (SC) appears when AFM order is destabilized by **chemical doping** or **mechanical pressure**

Introduction: Crystal structure – SC relationship ?

- T_c max when $Fe(As/Se)_4$ tetrahedron is regular

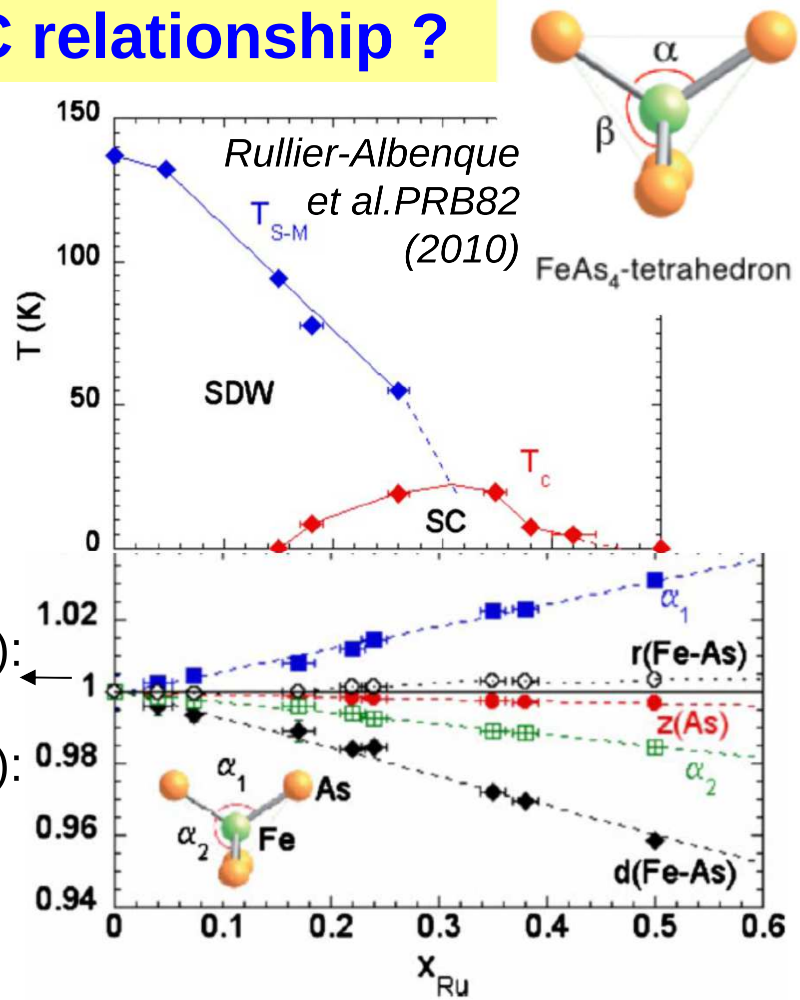
i.e. @ optimized h(As/Se) and c/a values

$$\alpha = 2\tan^{-1}\left(\frac{a/2}{hAs}\right) = 2\tan^{-1}\left[\frac{(a/c)}{2\,zAs - 1}\right]$$



True in compounds doped outside of the FePn layers:
LnFeAs(O,F), (AE,A)Fe_2As_2

α_1(x=0): 111.2°
α_2(x=0): 108.62

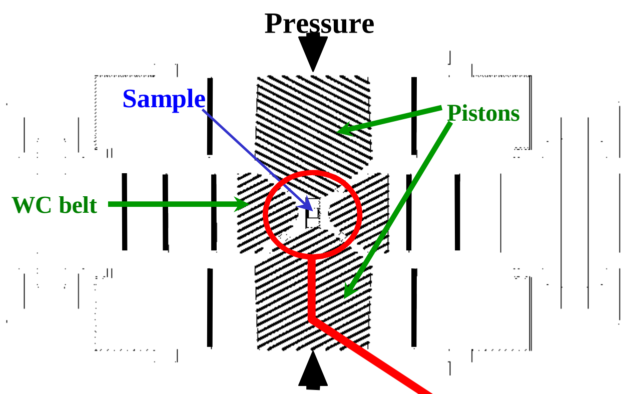


False in compounds substituted **isoelectronically** inside the FePn layers:
$AE(Fe_{1-x}Ru_x)_2As_2$
$AEFe_2(As_{1-x}P_x)_2$

Our previous study: isovalent substitution of As by P (chemical pressure) or Sb in LnFeAsO (Ln=Sm,La)?
➔ *Garbarino et al. Phys. Rev. B 84, 024510 (2011).*
& *Karlsson et al. Phys. Rev. B 84, 104523 (2011).*

Isovalent substitution of As by P in SmFeAsO

$SmFe(As_{1-x}P_x)O$: mechanical pressure VS chemical pressure

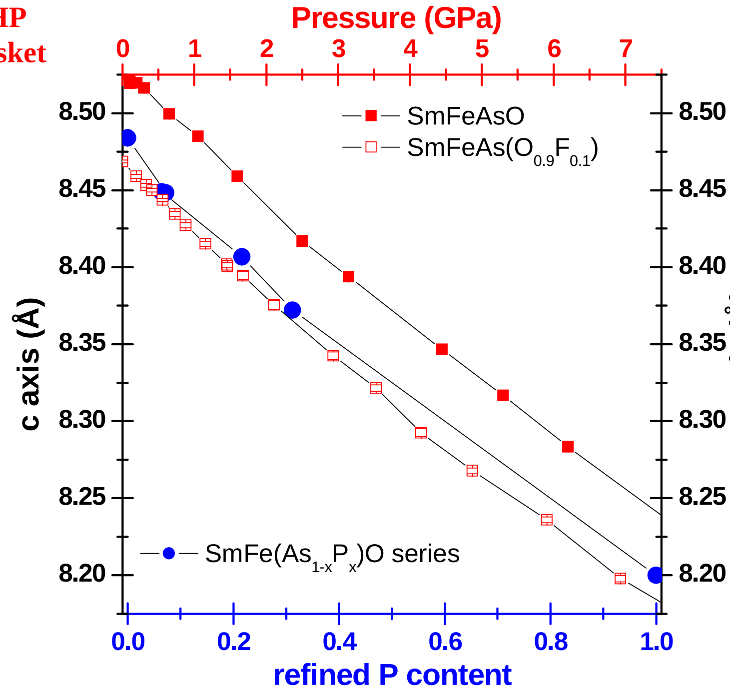


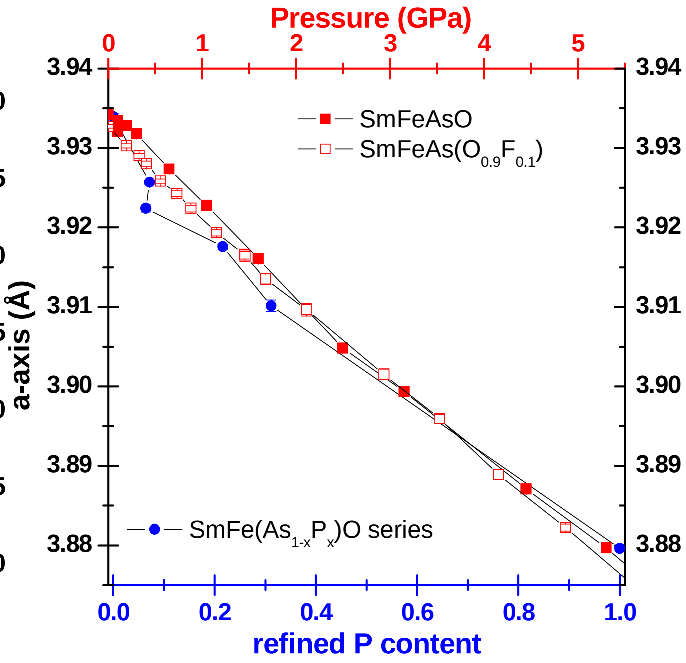
belt

High pressure – high temperature synthesis
« belt » system
(Institut Néel)
6GPa - 1100°C

a-axis: 100% P ↔ 5.5 GPa
c-axis: 100% P ↔ 7.5 GPa

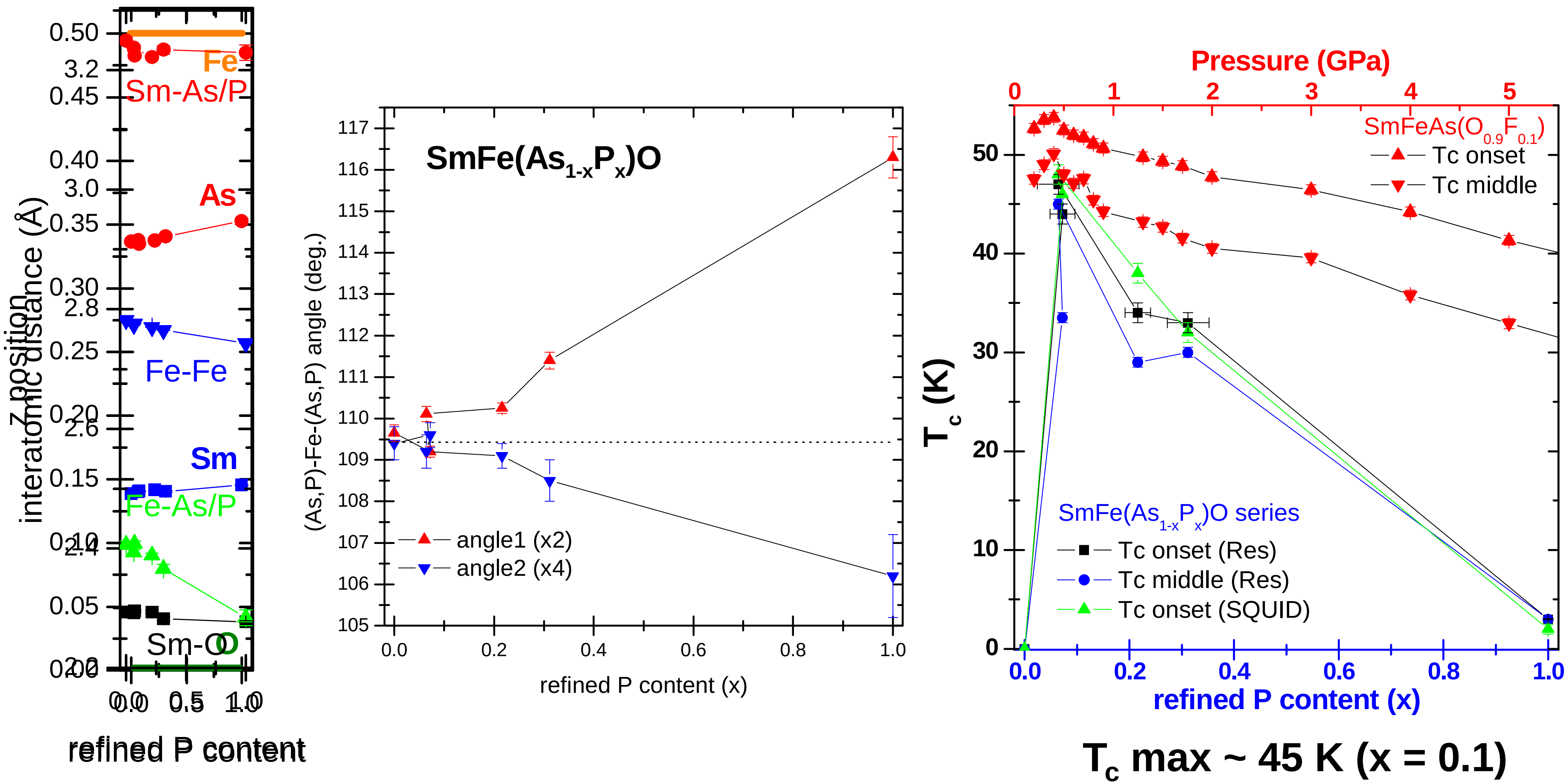
Effect of mechanical P ≠ effect of chemical subst.





Toulemonde et al, unpublished.

SmFe($As_{1-x}P_x$)O series: correlation Tc ⇔crystallo structure.



T_c max ~ 45 K (x = 0.1)

P substitution in SmFeAsO induces superconductivity with a T_c variation different from the one obtained under pressure

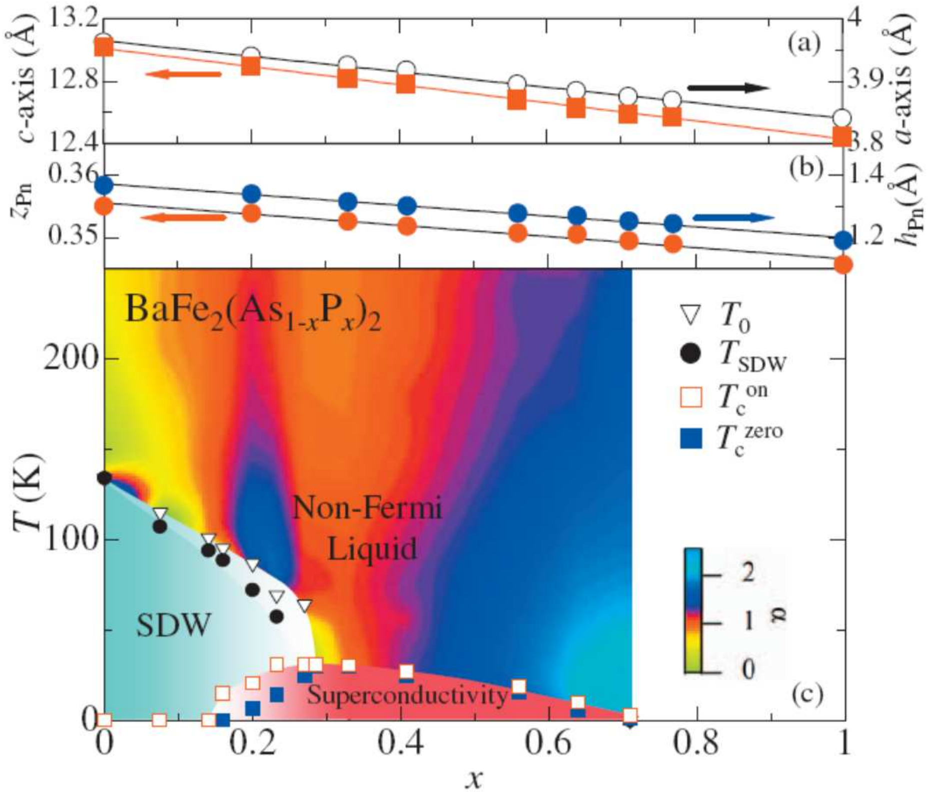
In strong contrast with $BaFe_2(As_{1-x}P_x)_2$ system !!!

➔ Explanation: electronic structure changes (nesting, N(E_F)) are different

Toulemonde et al, unpublished.

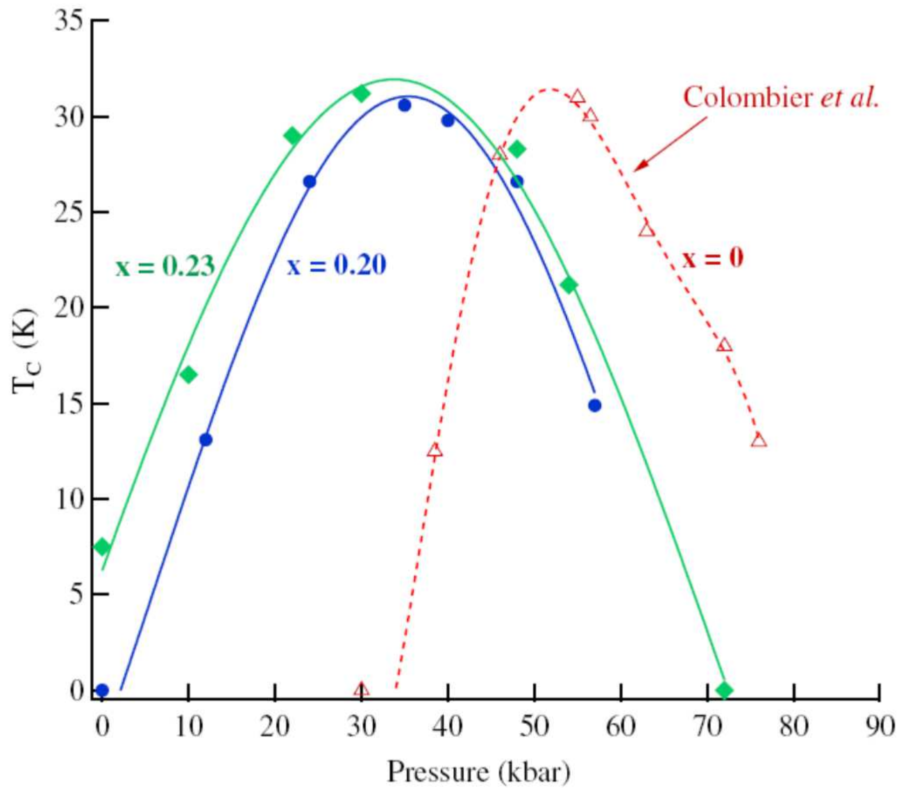
$BaFe_2(As_{1-x}P_x)_2$ series: literature

Isovalent subtitution by P induces SC with T_c max = 31K for x~0.3



Kasahara et al. PRB 81 (2010)

Pressure on $BaFe_2(As_{1-x}P_x)$ induces SC with T_c max = 31K



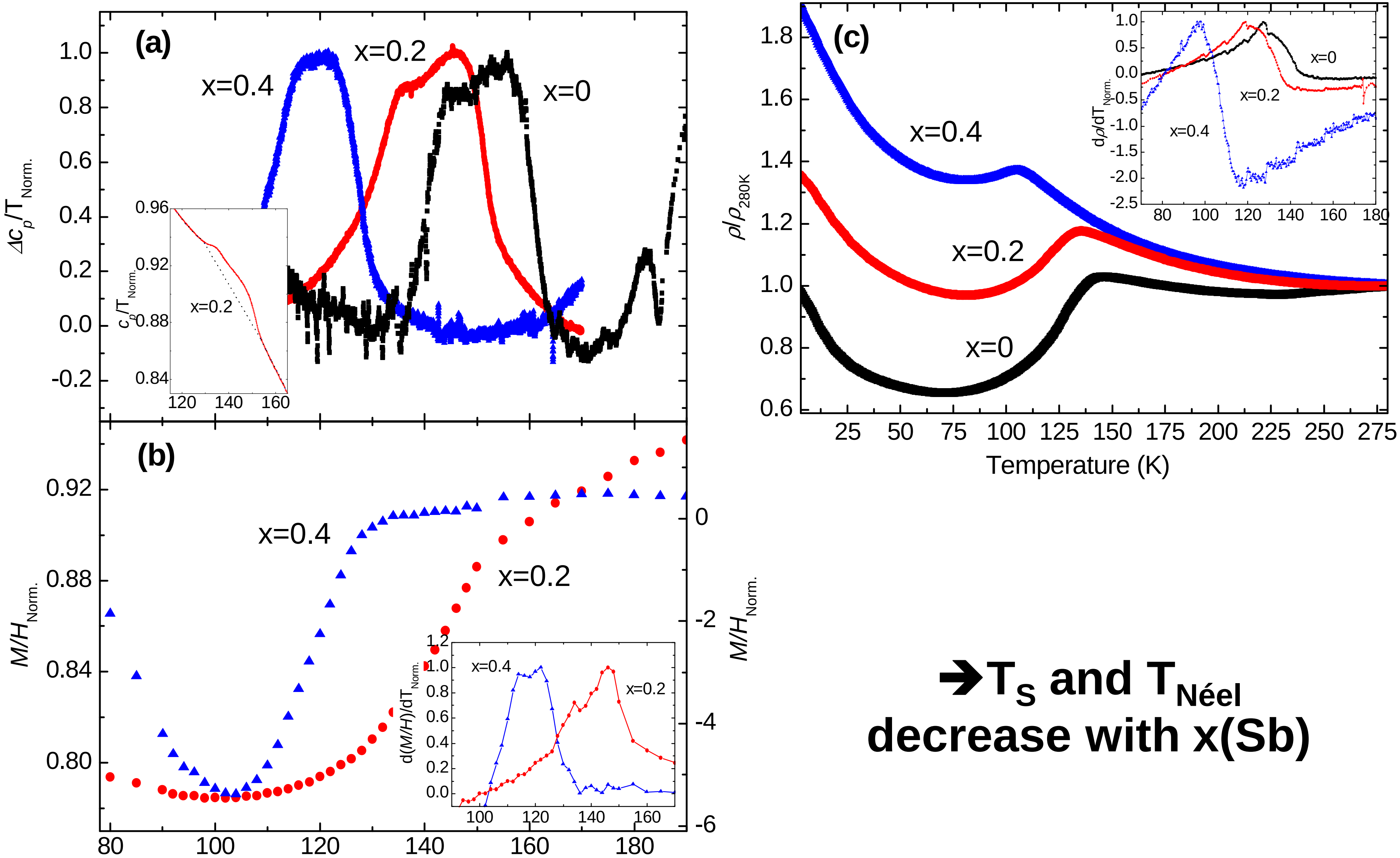
Klintberg et al. JPSJ 79 (2010)

Ba-122 system:

mechanical P ~ chemical pressure (isovalent subst. P/As)

Isovalent substitution of As by Sb in LaFeAsO

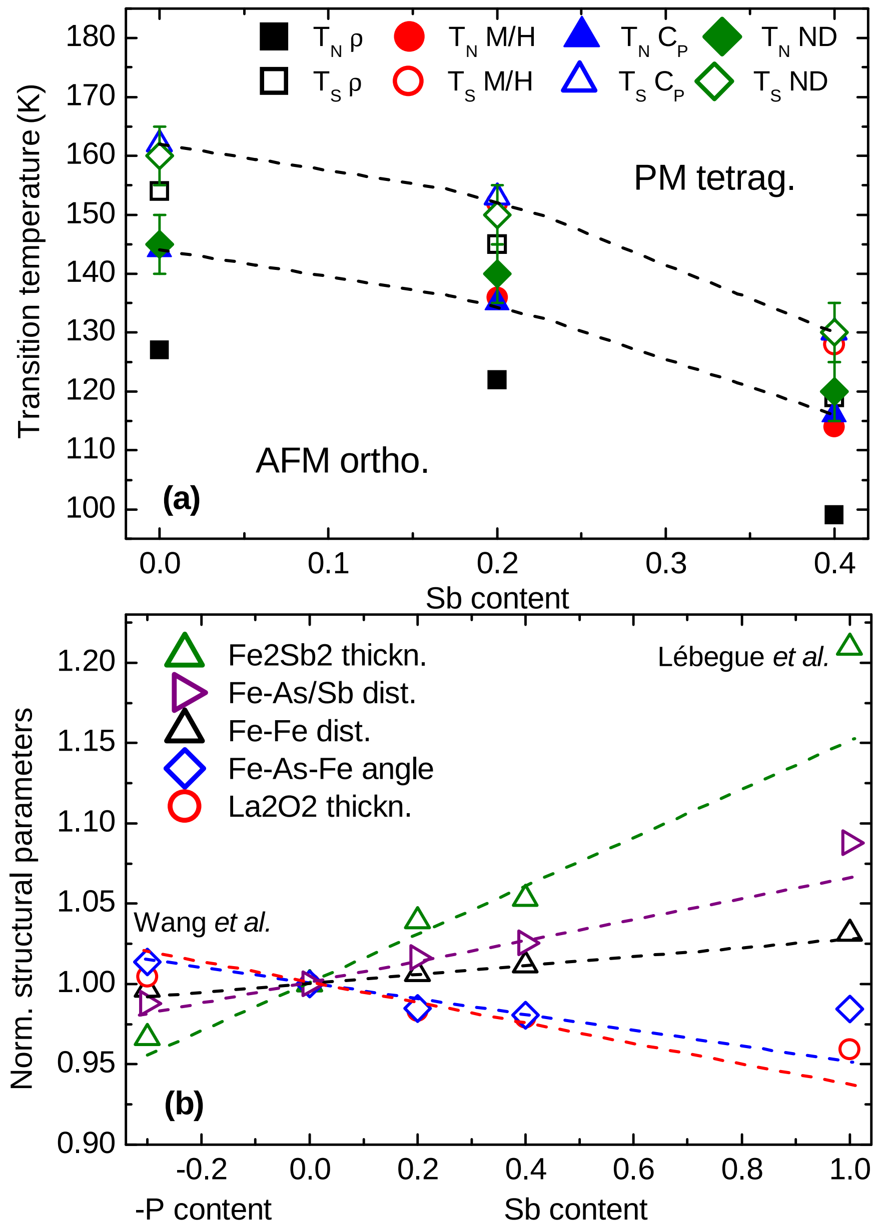
$LaFe(As_{1-x}Sb_x)O$: M(T), Cp(T) and R(T)



➔T_S and $T_{Néel}$ decrease with x(Sb)

S. Carlsson et al. Phys. Rev. B84, 104523, 2011.

$LaFe(As_{1-x}Sb_x)O$: phase diagram



→Successful replacement of As by Sb in LaFeAsO up to 40%

→Physical measurements show a decrease of $T_{Néel}$ but no superconductivity (in the contrary of P substitution)

→ NPD shows a slight increase of m(Fe) with Sb content in the low T AFM structure as expected by DFT calculations

→Our analysis suggest that the **crucial structural parameter** controlling the magnetic interaction and the occurrence of superconductivity in 1111 arsenides **is the Fe-As bond length**

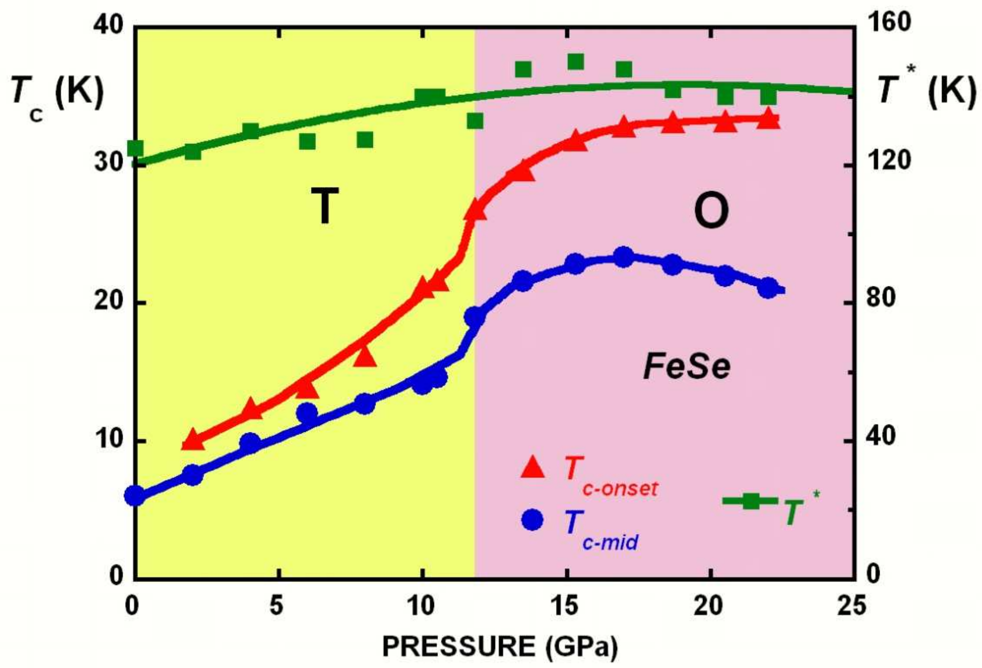
S. Carlsson et al. Phys. Rev. B84, 104523, 2011.

Part 1:

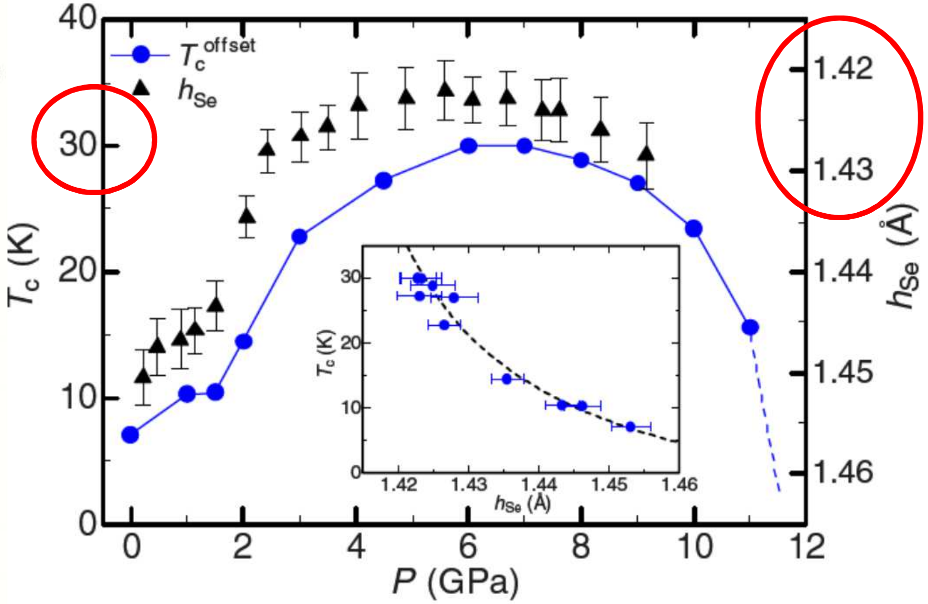
Isovalent substitution of Se by S in $TlFe_{2-z}Se_2$

Introduction: sensitivity of superconductivity to **pressure**

In the **$Fe_{1+\delta}Se$ chalcogenide** ?



G. Garbarino et al. EPL 86 (2009)



Okabe et al. Phys. Rev. B 81 (2010)

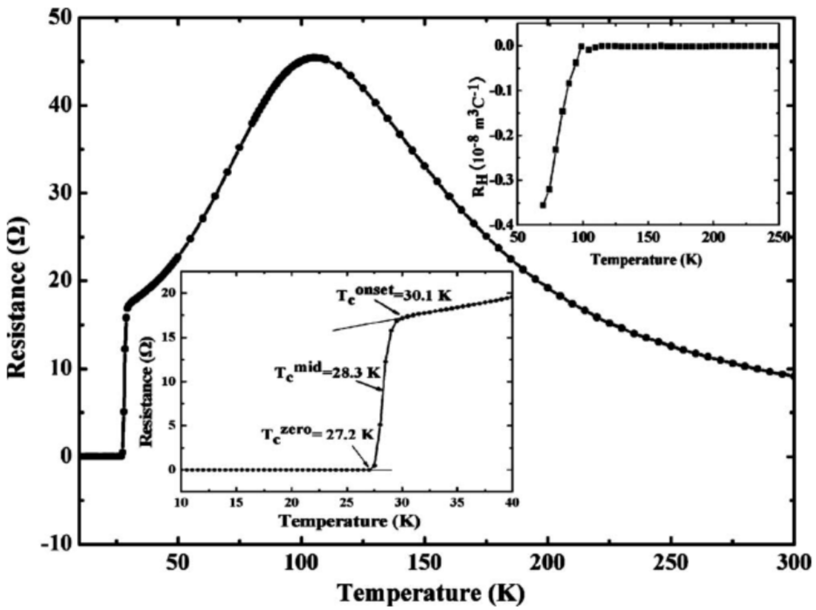
➔ Superconductivity is strongly enhanced by **mechanical pressure:**

From T_c= 8K to ~35K under 6-12GPa

Introduction: superconductivity in $AFe_{2-z}Se_2$!

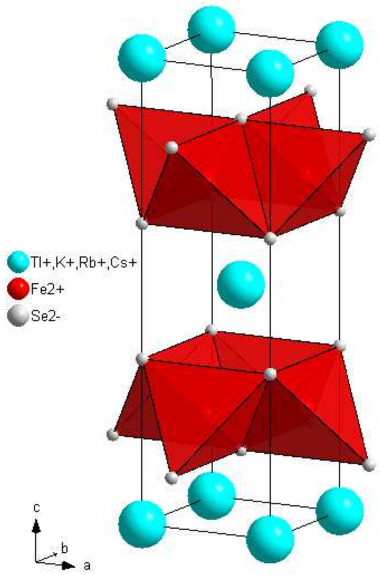
Superconductivity at T_c= 30K in $K_{1-y}Fe_{2-z}Se_2$!

i.e. at T_c similar to the one of FeSe/HP!



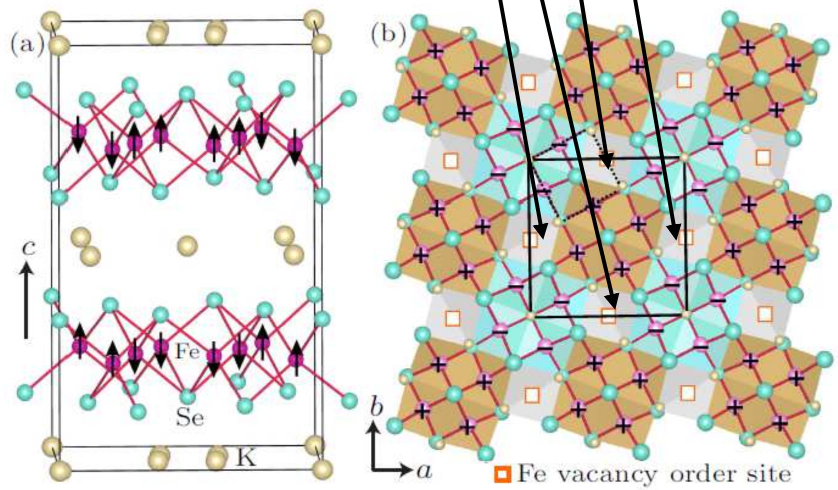
*Guo et al. Phys. Rev. B 82 (**nov. 2010**)*

A=K,Rb,Cs



Structure analogous to the one of 122 arsenides

But iron vacancies ! (ordered or not)



Could $Tl_{1-y}Fe_{2-z}Se_2$ be SC by adequate substitution or pressure?

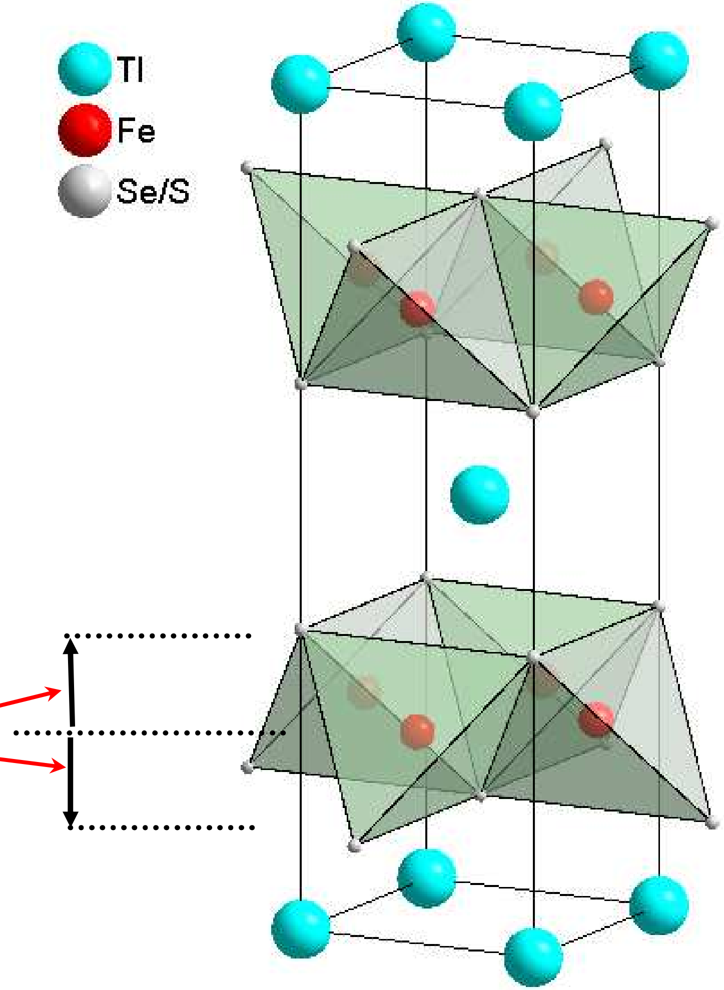
In this talk: **Se substitution by Sulfur**

Pressure effect on $TlFe_{1.6}Se_2$

$TlFe_{2-z}Se_2$: a parent phase to induce superconductivity?

Crystallographic structure of $Tl_yFe_{2-z}Se_2$ I4/mmm (N°139) space group				
Atomic site	Wyckoff position	x	y	z
Tl	2a	0	0	0
Fe	16i	0	1/2	3/4
Se	4e	0	0	0.3534(1)

Tunable Se/Te/S height

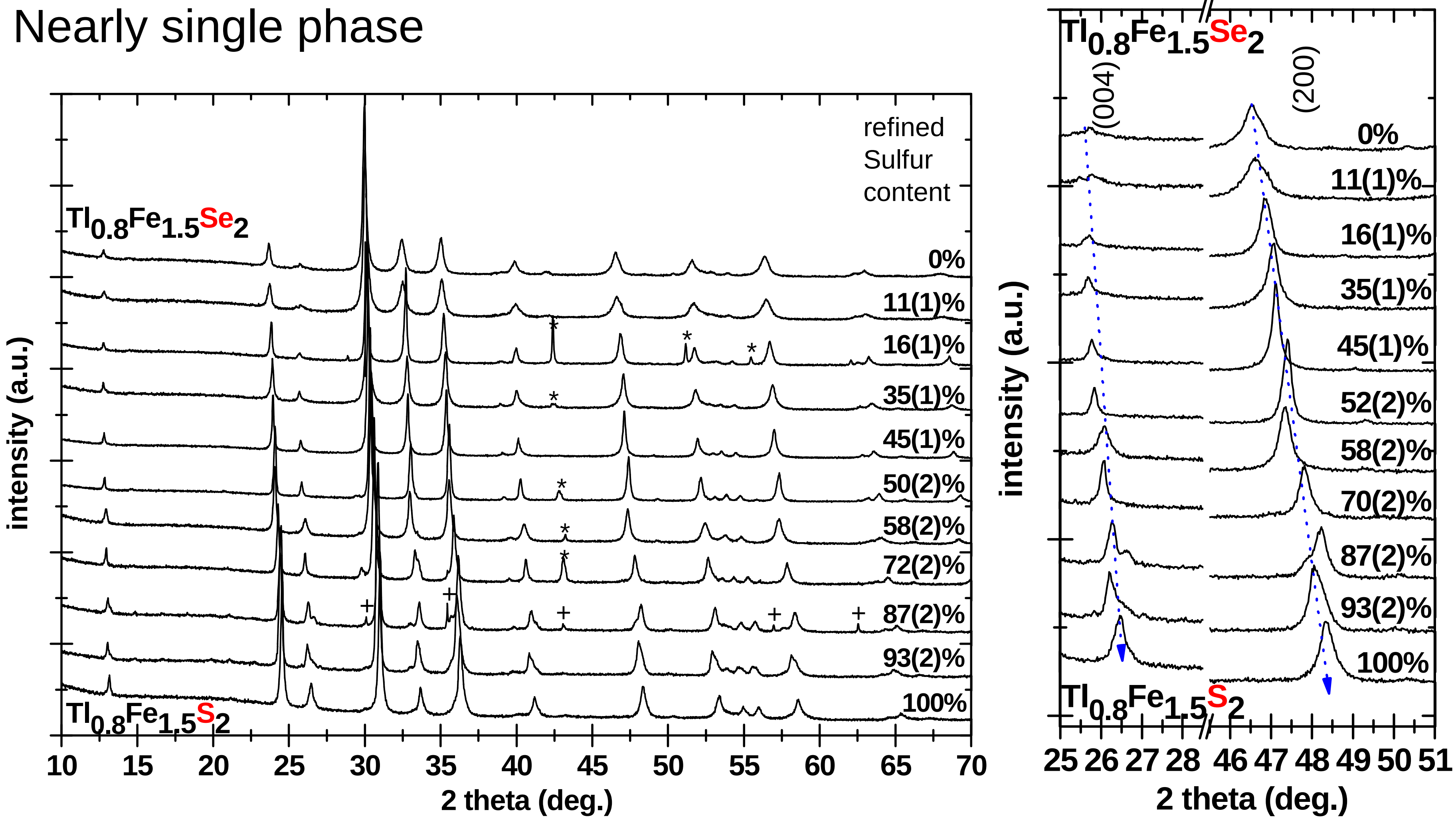


$TlFe_{2-z}(Se_{1-x}S_x)_2$: synthesis and x-ray diffraction

- **Synthesis**: Tl pieces + Fe + Se/S powders reacted at 700°C in sealed quartz tube and cooled down to 280°C at 5°C/h

→ Full solid solution 0<x(S)<100% in $Tl_{0.8}Fe_{1.5}(Se_{1-x}S_x)_2$

→ Nearly single phase

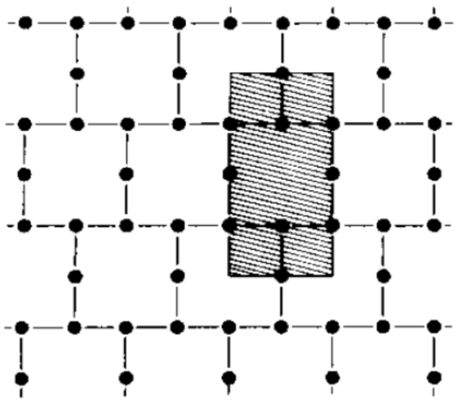


Toulemonde et al, accepted in JPCM (2013).

$TlFe_{2-z}(Se_{1-x}S_x)_2$: crystallographic study by XRD & ED/TEM

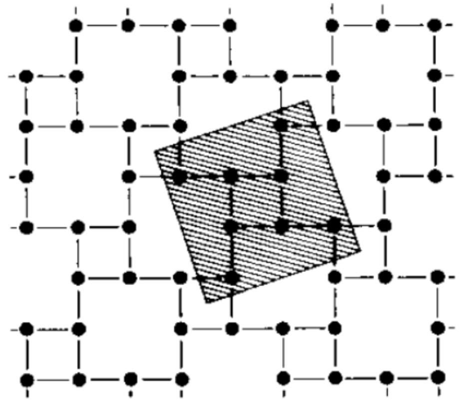
- Observation of **supercell peaks** in **XRD** patterns corresponding to ordered vacancies in iron plane:

z=0.5



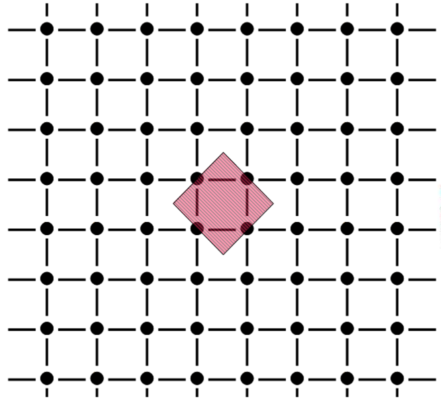
Ibam
orthorhombic supercell
$a\sqrt{2}\times 2a\sqrt{2}\times c$ type

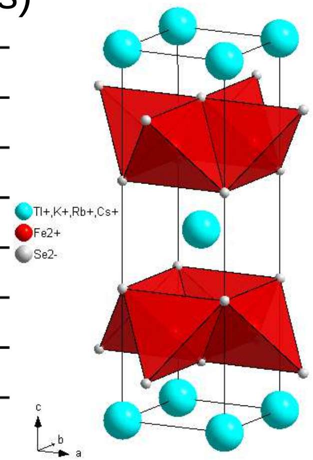
z=0.4



I4/m
tetragonal supercell
$a\sqrt{5}\times a\sqrt{5}\times c$ type

z=0 (no iron vacancies)





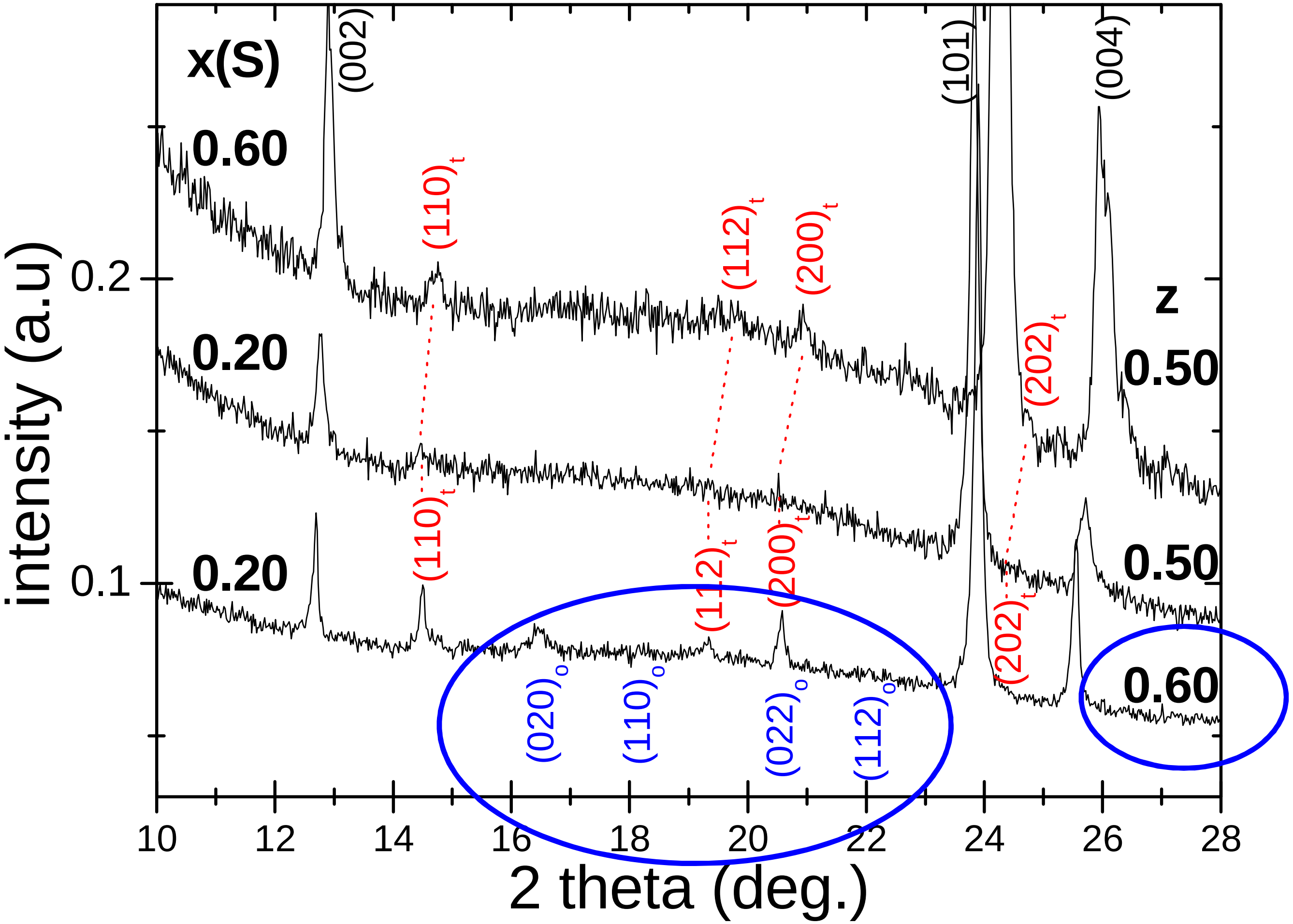
I4/mmm
tetragonal cell
$a\times a\times c$

Observed supercells by XRD and ED (by TEM)

Toulemonde et al, accepted in JPCM (2013).

$TlFe_{2-z}(Se_{1-x}S_x)_2$: crystallographic study by XRD & ED/TEM

- Observation of **supercell peaks** in **XRD** patterns corresponding to ordered vacancies in iron plane:

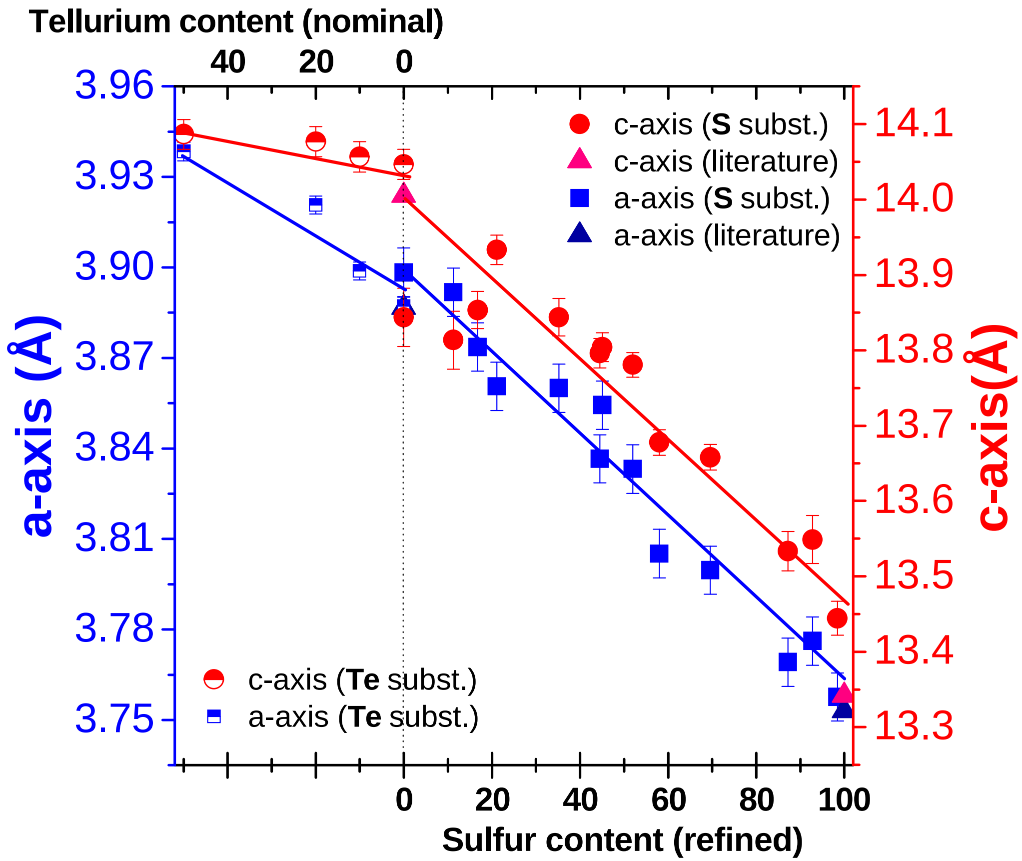


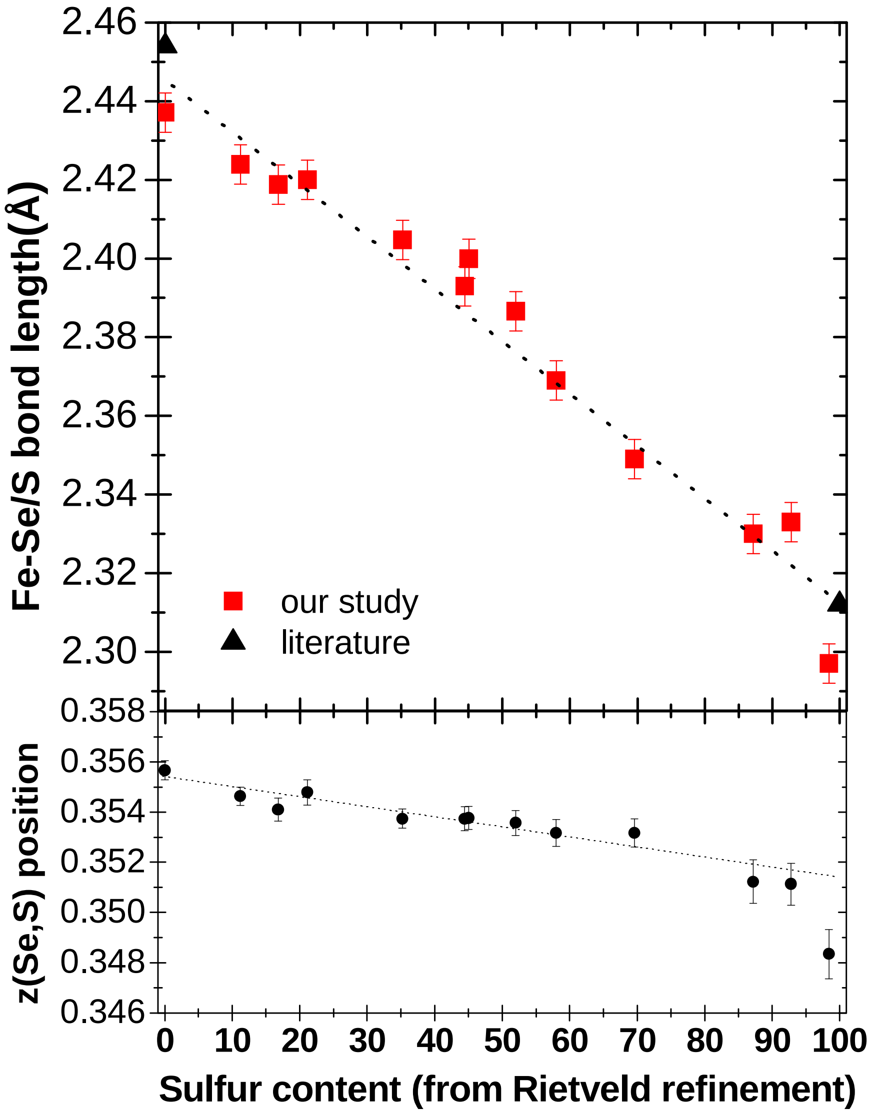
I4/m
tetragonal supercell
$a\sqrt{5} \times a\sqrt{5} \times c$ type

Ibam
orthorhombic supercell
$a\sqrt{2} \times 2a\sqrt{2} \times c$ type

Toulemonde et al, accepted in JPCM (2013).

$TlFe_{2-z}(Se_{1-x}S_x)_2$: lattice parameters & bond length versus x(S)





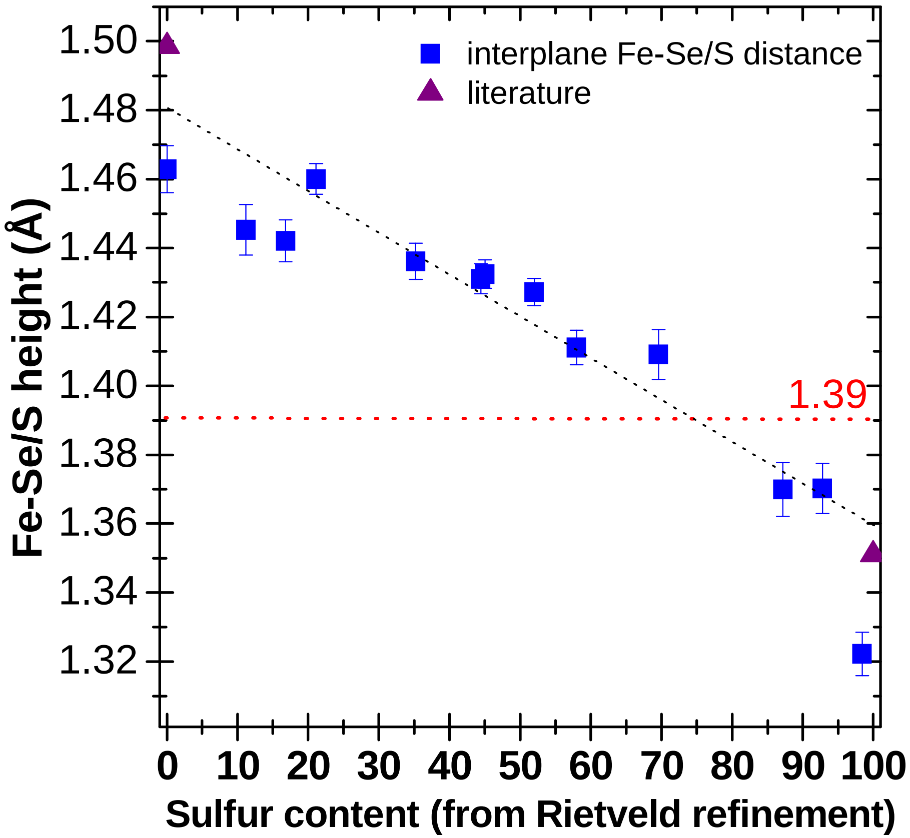
→nearly **isotropic decrease (~3.5%) of the lattice with S content**

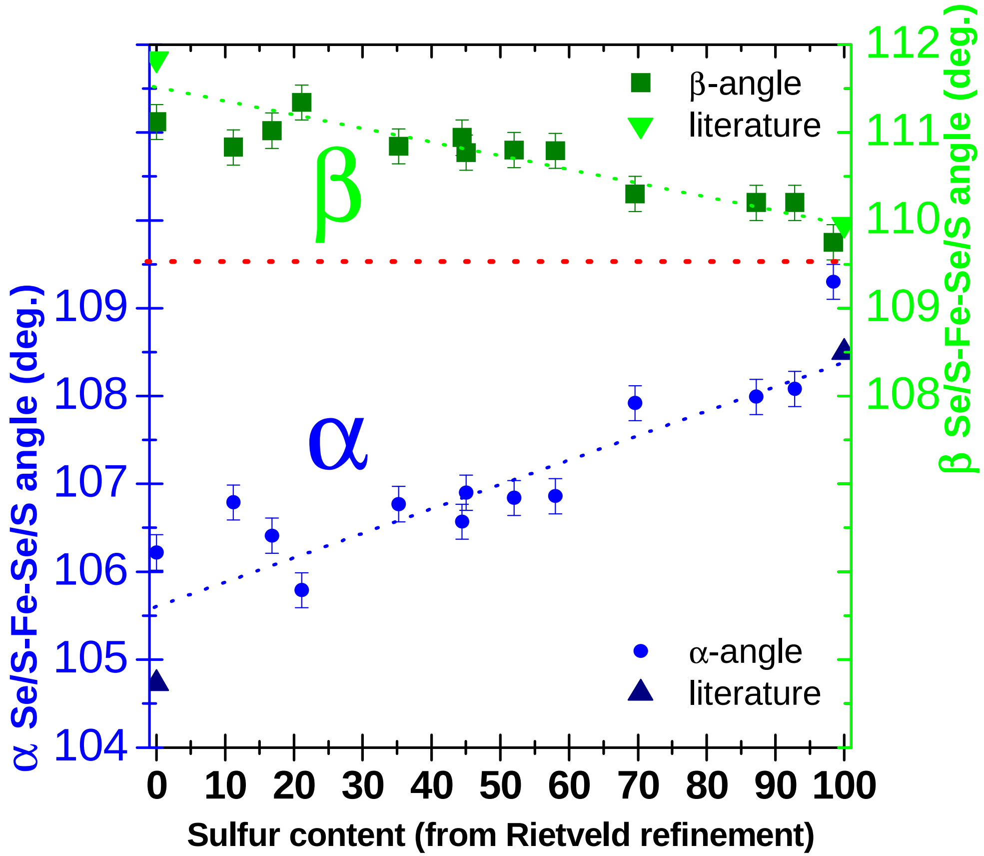
→c/a ratio quasi constant (~3.58)

→continuous decrease of Fe-Ch bond length & Fe-Ch height with S content

Toulemonde et al, accepted in JPCM (2013).

$TlFe_{2-z}(Se_{1-x}S_x)_2$: Fe-(Se/S) height & (Se/S)-Fe-(Se/S) angle versus x(S)





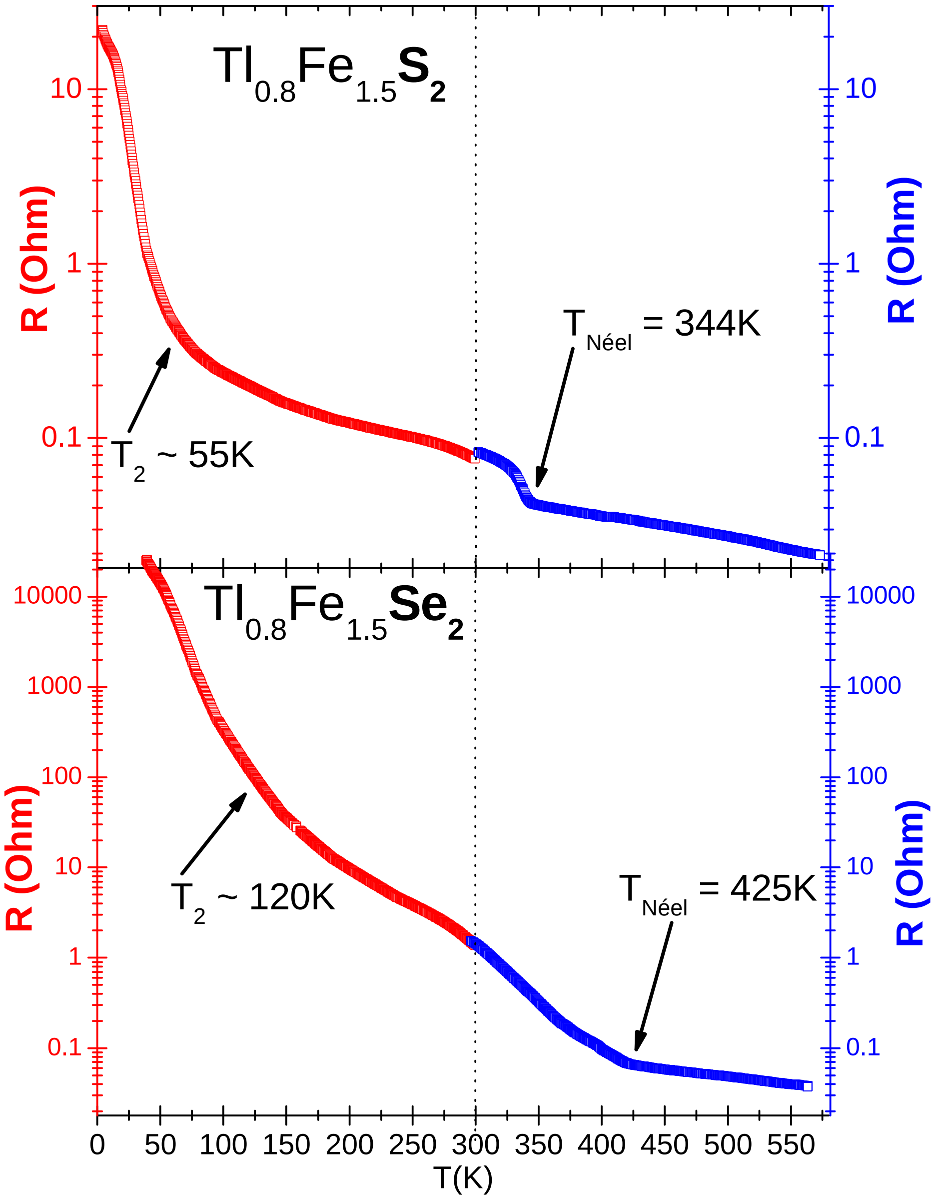
→optimized Fe-Ch height reached
(i.e. the one for T_c ~30K in FeSe/HP)

→distorted $FeSe_4$ tetrahedron becomes nearly regular in $Tl_{0.8}Fe_{1.5}S_2$

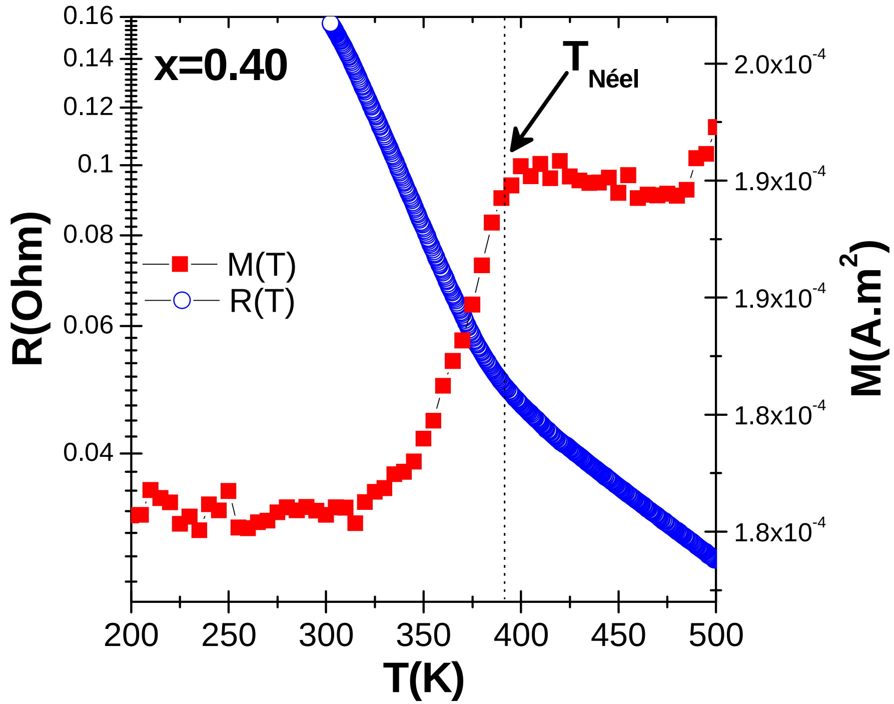
But No superconductivity!…

Toulemonde et al, accepted in JPCM (2013).

$TlFe_{2-z}(Se_{1-x}S_x)_2$: low T and high T M(T) and R(T)



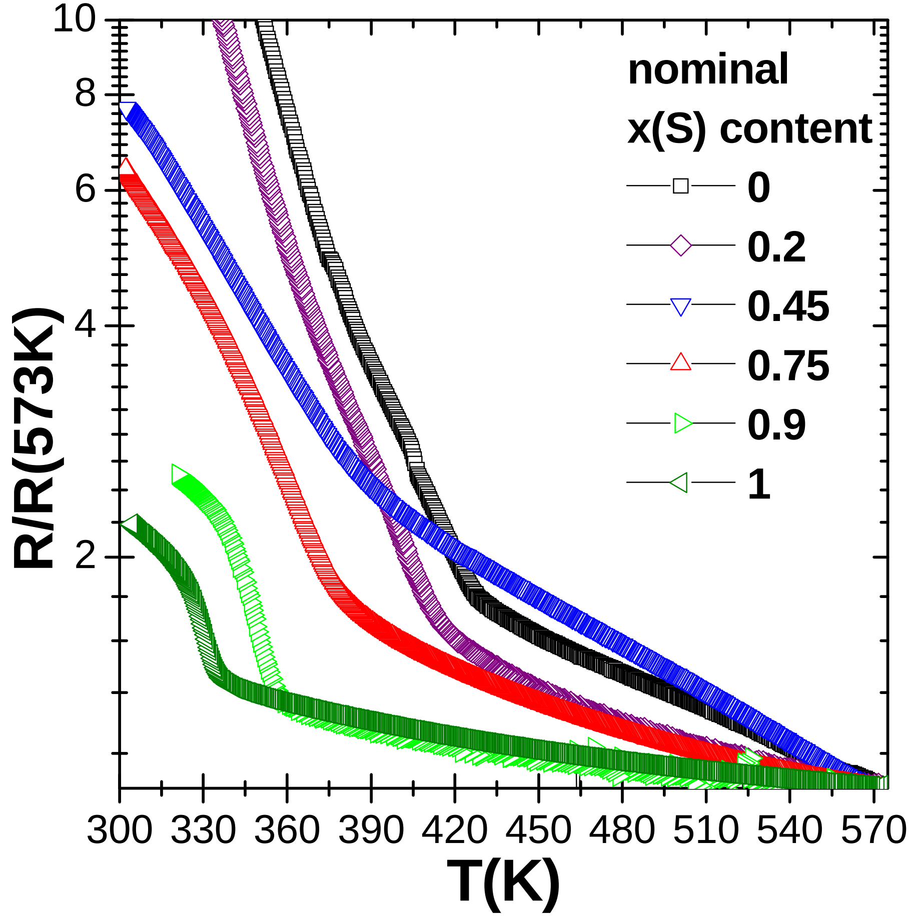
➔ **AFM with high $T_{Néel}$**
➔ **insulating @ low T**

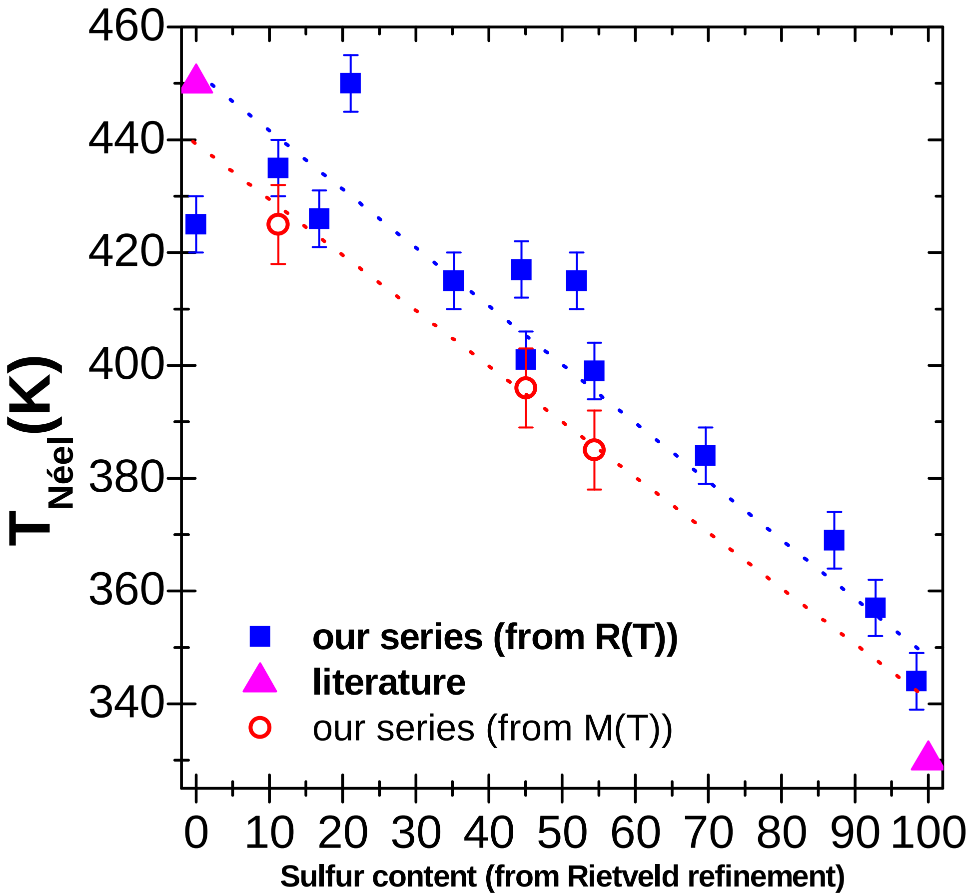


Toulemonde et al, accepted in JPCM (2013).

$TlFe_{2-z}(Se_{1-x}S_x)_2$: low T and high T M(T) and R(T)

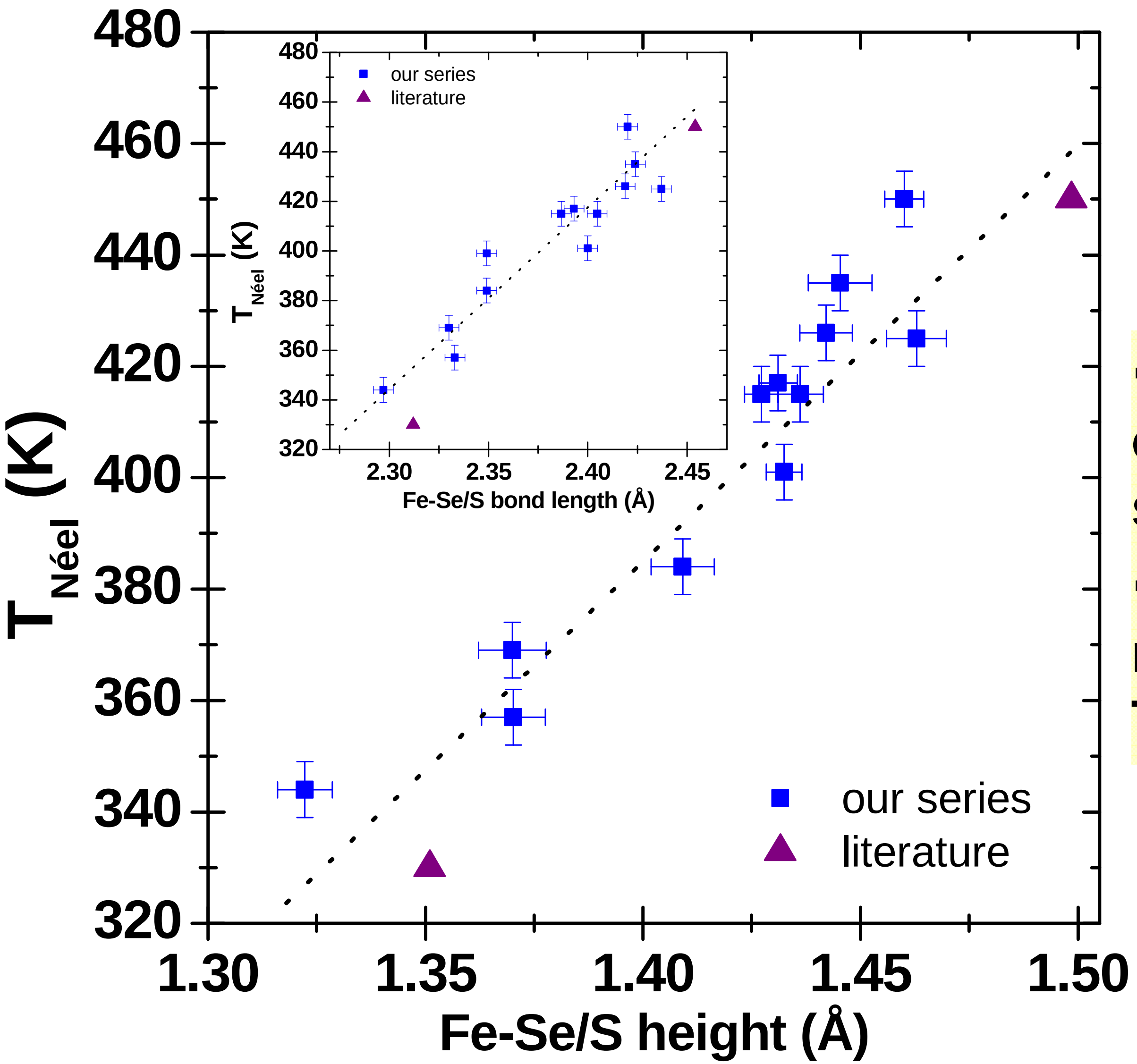
➔ $T_{néel}$ decreases with S content
➔ but No superconductivity induced by S substitution





Toulemonde et al, accepted in JPCM (2013).

$TlFe_{2-z}(Se_{1-x}S_x)_2$: conclusion



➔ No superconductivity observed in S- (or Te) substituted samples

➔ direct linear relationship between $T_{Néel}$ & Fe-Se/S height

Toulemonde et al, accepted in JPCM (2013).

Conclusion

• $TlFe_{2-y}(Se_{1-x}S_x)_2$

- **direct linear relationship between $T_{Néel}$ & Fe-Se/S height** (or Fe-Se/S bond length)
- **no superconductivity** observed over the full substitution range!
- *which ingredient is missing? Higher $N(E_F)$? No phase separation (Tl content fixed)?*

• $SmFeAs(O_{0.81}F_{0.19})$ under HP

- **1st study** showing the direct correlation between the regularity of the tetrahedron $FeAs_4$ & T_c

• $SmFe(As_{1-x}P_x)O$

- **ISO**electronic substitution but **Superconductivity** (!) like in $BaFe_2(As_{1-x}P_x)_2$
- Chemical pressure (As/P) effect **≠** mechanical pressure in 1111 system
- Evolution of the electronic structure with P substitution? *Need theoretical investigation…*

• $SmFe(As_{1-x}Sb_x)O$

- Sb substitution = "negative" chemical pressure
- phase diagram: **T(SDW) ➘ with Sb content**
- **superconductivity** in HP-HT synthesized samples (*probably because of oxygen vacancies*)!