Positron annihilation study of high entropy alloys

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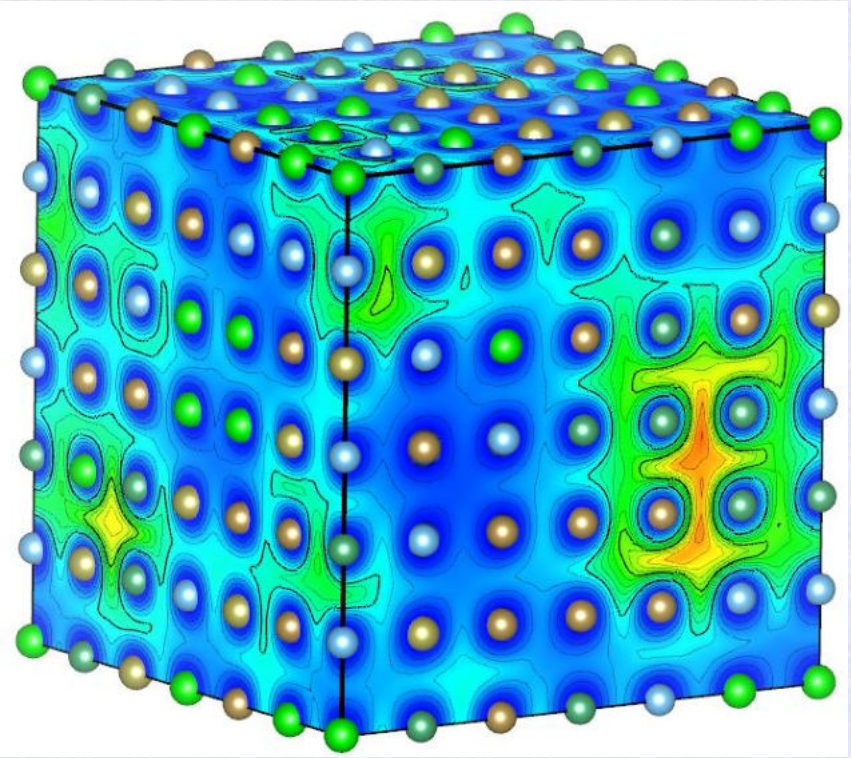
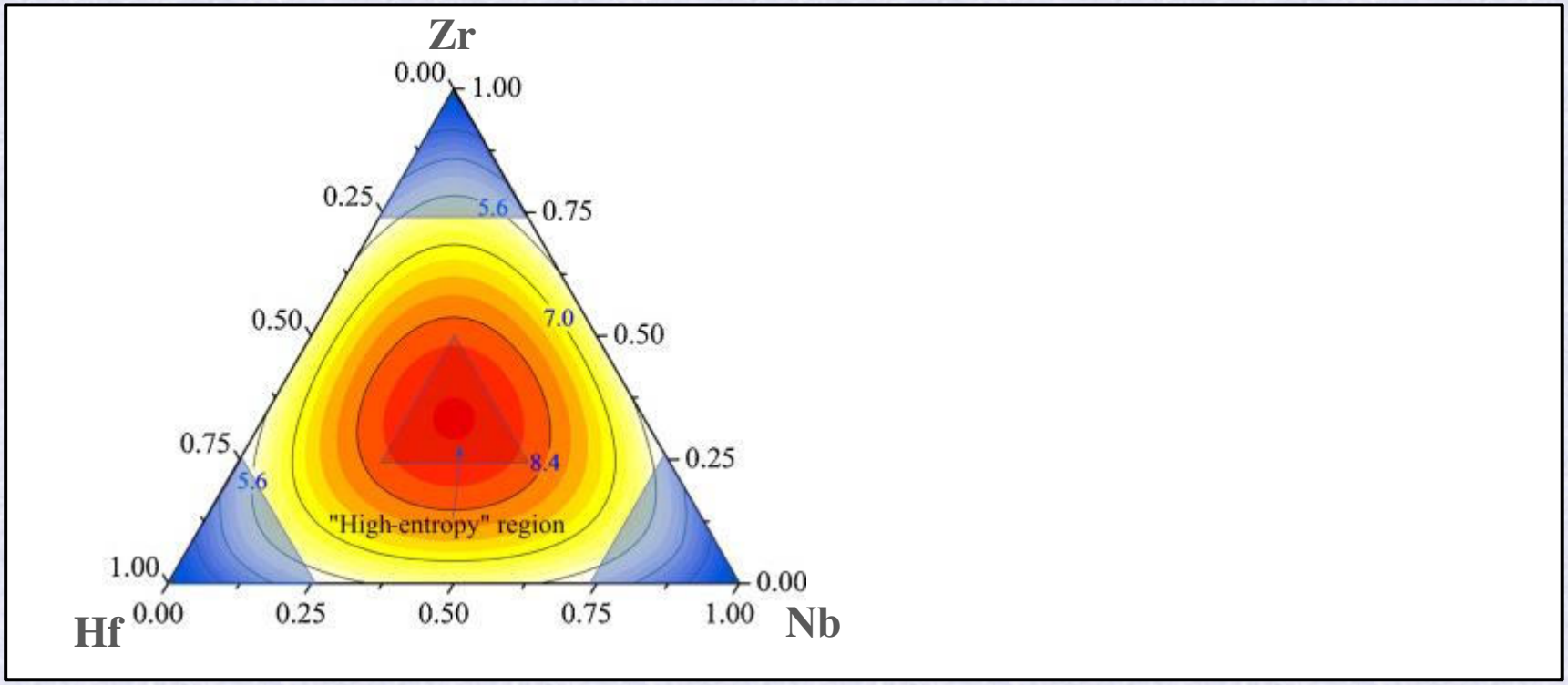


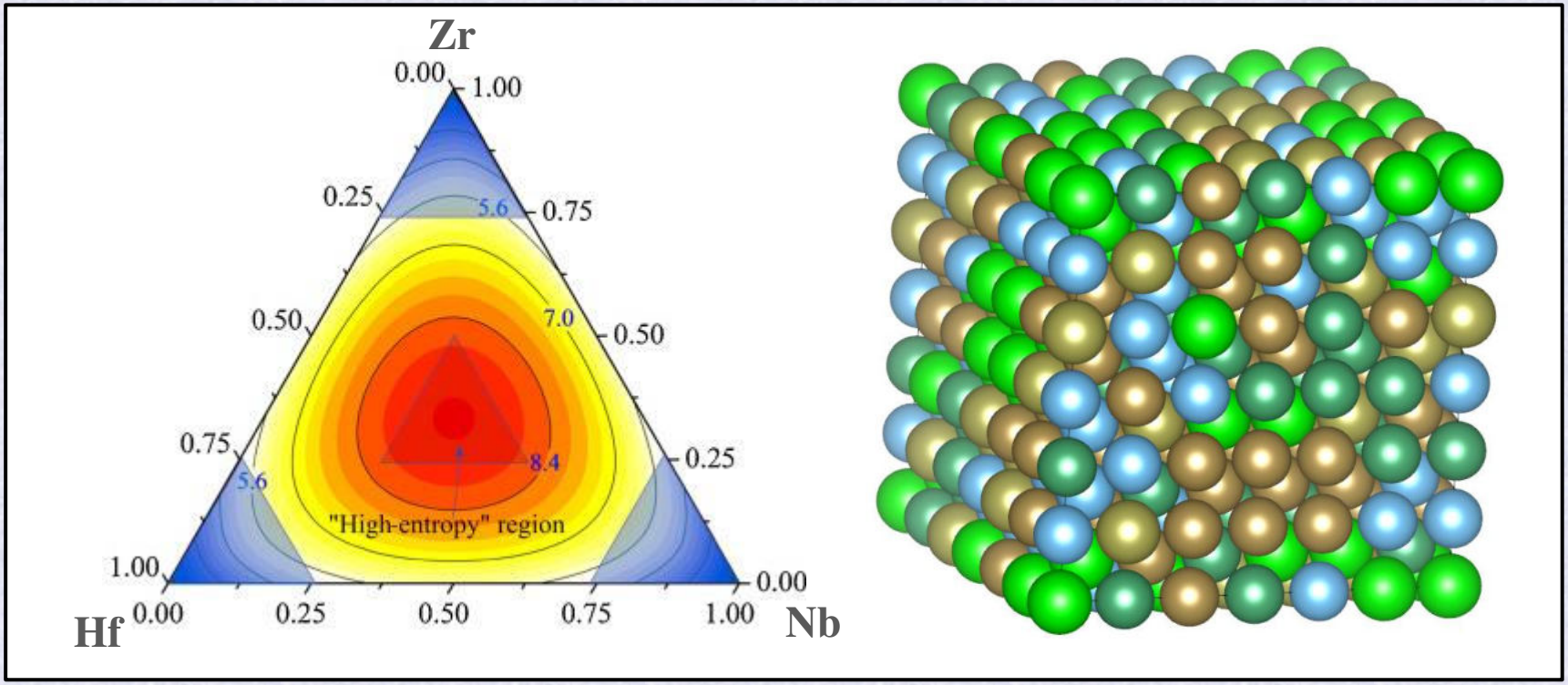
High entropy alloys (HEAs)

- Alloys consisting of at least 5 alloying elements with concentrations 5-35 at.%
- Complex concentrated alloys
- Exploring of central regions of multi-element equilibrium phase diagrams



High entropy alloys (HEAs)

- cubic structure (fcc or bcc)
- lattice sites randomly occupied by alloying elements
- favorable mechanical properties in a broad temperature range
- resistance against radiation damage
- high hydrogen storage capacity



Thermodynamics of HEAs

- Alloys consisting of at least 5 alloying elements with concentrations 5 -35 at.%
- Alloys with configurational entropy of mixing $S^{SS} \geq 1.6\,R$

random solid solution (SS)
configurational entropy of mixing: $S^{SS} = -R\sum_{i=1}^{N} c_i \ln c_i$

concentration of i-th element

equimolar concentration of N elements: $S^{SS} = R \ln N$

e.g. 5 element alloy, equimolar concentration: $S^{SS} \approx 1.61R$

universal gas constant
R = 8.314 $JK^{-1}mol^{-1}$

Thermodynamics of HEAs

- Alloys consisting of at least 5 alloying elements with concentrations 5 -35 at.%
- $-TS^{SS} < H^{IM} \Rightarrow$ random SS is thermodynamically stable state of HEA

random solid solution (SS)

configurational entropy of mixing: $S^{SS} = -R\sum_i c_i \ln c_i$

Gibbs energy: $G^{SS} = H^{SS} - TS^{SS} \approx -TS^{SS}$

excess enthalpy of mixing

temperature

configurational entropy of mixing

ideal random SS: $H^{SS} \approx 0$

$G^{SS} < G^{IM}$

ordered intermetallics phase (IM)

Gibbs energy: $G^{IM} = H^{IM} - TS^{IM} \approx H^{IM} < 0$

perfectly ordered IM: $S^{IM} \approx 0$

Four “core effects” of HEAs

1. high entropy ($S^{SS} \geq 1.6\,R$) ⟵ true

- random SS might be energetically more favorable than competing IM phases

  J.W. Yeh, et al. Adv. Eng. Mater. 6 (2004) 299

2. lattice distortions

- several lattice distortion due to different atom sizes

  L.R. Owen, N.G. Jones, Scripta Mater. 187 (2020) 428

3. sluggish diffusion ⟵ ???? doubtful

- diffusion in HEAs is slower than in conventional alloys

  J.W. Yeh, et al. Adv. Eng. Mater. 6 (2004) 299

4. ‘cocktail effect’ ⟵ obvious

- HEA properties may significantly differ from superposition of constituent properties

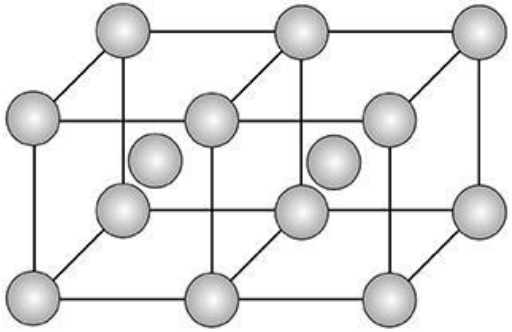
  S.Ranganathan , Curr. Sci. 85 (2003) 1404.

D.B. Miracle, O.N. Senkov, Acta Mater. 122 (2017) 448

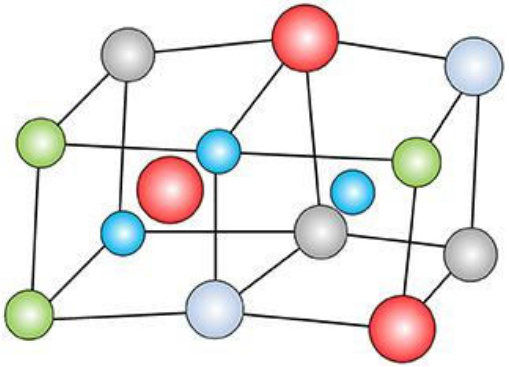
Empirical parameters describing HEAs

• various atom sizes of elements → lattice distortions

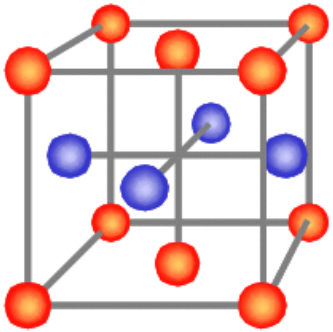
pure metal



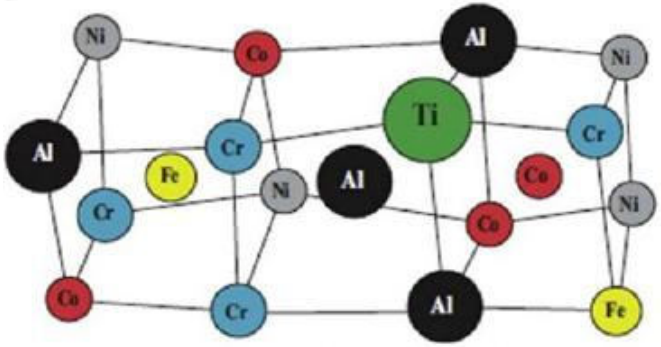
HEA



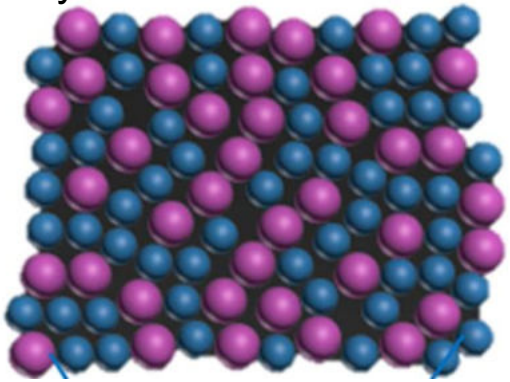
conventional alloy
- constant lattice parameter
- constant crystalline structure



high entropy alloy
- lattice parameter varies
- constant crystalline structure

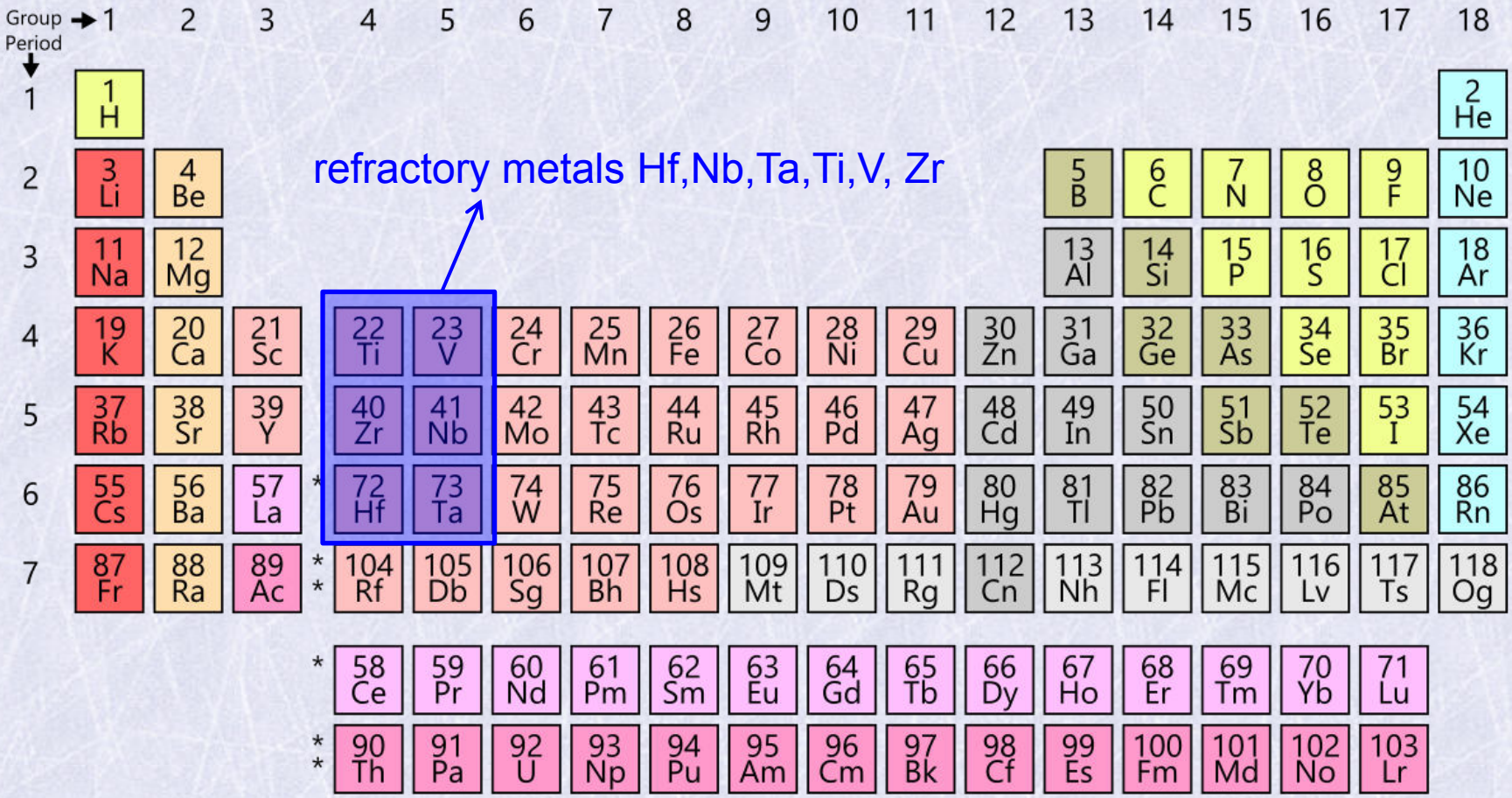


amorphous alloy
- lattice parameter varies
- crystalline structure varies



lattice distortions

Refractory metal HEAs



Empirical parameters describing HEAs

- various atom sizes of elements $\rightarrow$ lattice distortions
- measure of lattice distortions – misfit parameter δ

misfit parameter

$$\delta = \sqrt{\sum_i c_i (1 - r_i/\overline{r})^2}$$

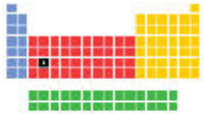
concentration of i-th element

atom radius of i-th element

composition weighted mean atom radius

Atomic radius

$$\delta = \sqrt{\sum_i c_i (1 - r_i/\overline{r})^2}$$



www.webelements.com

$_{72}$Hf

Available hafnium properties...

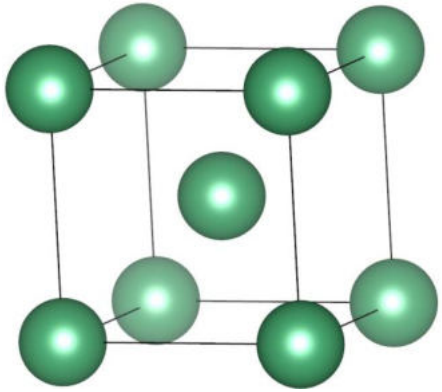
Essentials | More properties...

Radius type	Radius value / pm	Periodicity link
Atomic radius (empirical)	155	
Atomic radius (calculated)	208	
Covalent radius (2008 values)	175	
Molecular single bond covalent radius	152 (coordination number 4)	
Molecular double bond covalent radius	128	
Molecular triple bond covalent radius	122	
Covalent radius (empirical)	150	
van der Waals radius	253	

Atomic radius

- half of distance between elements in their equilibrium configuration

bcc structure



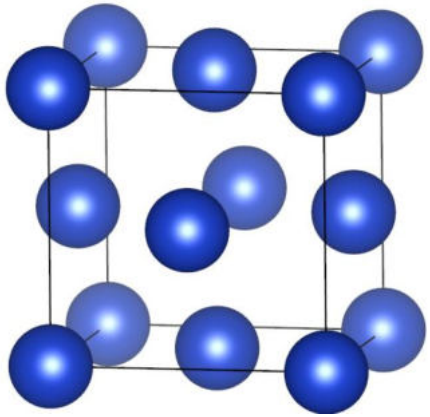
$$r = a\frac{\sqrt{3}}{4}$$

Nb, $r = 1.44$ Å

Ta, $r = 1.43$ Å

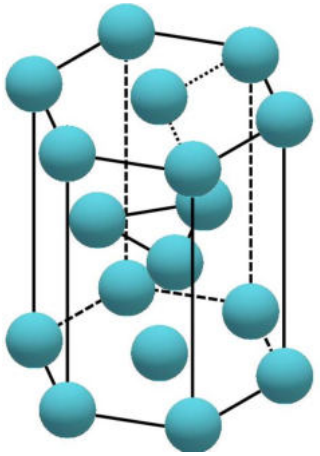
V, $r = 1.31$ Å

fcc structure



$$r = a\frac{\sqrt{2}}{4}$$

hcp structure



$$r = \frac{1}{2}\sqrt{\frac{a^2}{3} + \frac{c^2}{4}}$$

Hf, $r = 1.56$ Å

Ti, $r = 1.45$ Å

Zr, $r = 1.59$ Å

Empirical parameters describing HEAs

- various atom sizes of elements → lattice distortions
- measure of lattice distortions – misfit parameter δ
- heat of solution H^{IM} vs. entropy S^{SS}

$-TS^{SS}$ vs. H^{IM}

misfit parameter

$$\delta = \sqrt{\sum_i c_i(1 - r_i/\overline{r})^2}$$

concentration of i-th element

atom radius of i-th element

composition weighted mean atom radius

heat of solution of random SS

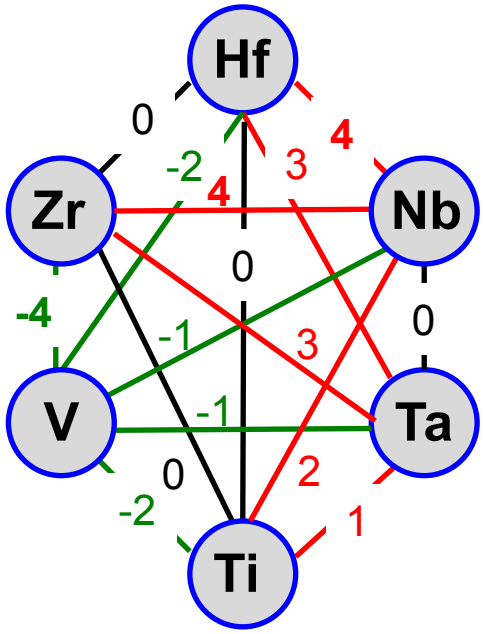
$$H^{SS} = \sum_{i<j} 4H_{i,j}c_ic_j$$

heat of solution for atomic pairs of elements *i*, *j* calculated using Miedena's model

A. Takeuchi, A. Inoue, Mater. Trans. 46 (2005) 2817

Empirical parameters describing HEAs

- various atom sizes of elements → lattice distortions
- measure of lattice distortions – misfit parameter δ
- heat of solution H^{IM} vs. entropy S^{SS}



binary heat of solutions $H_{i,j}$

- repulsive interaction between (Nb,Ta) and (Zr,Hf)

Empirical parameters describing HEAs

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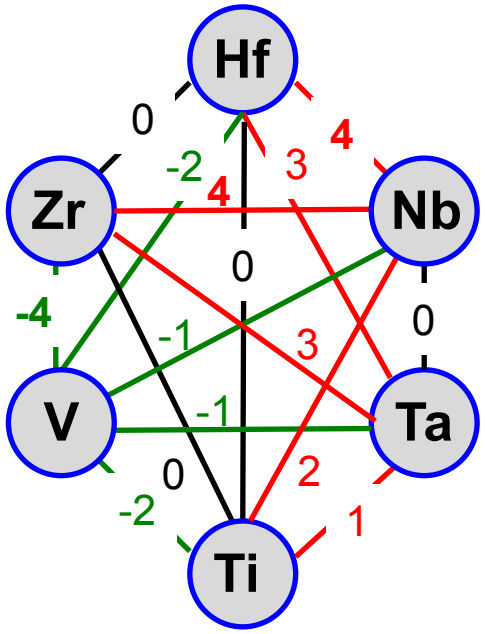
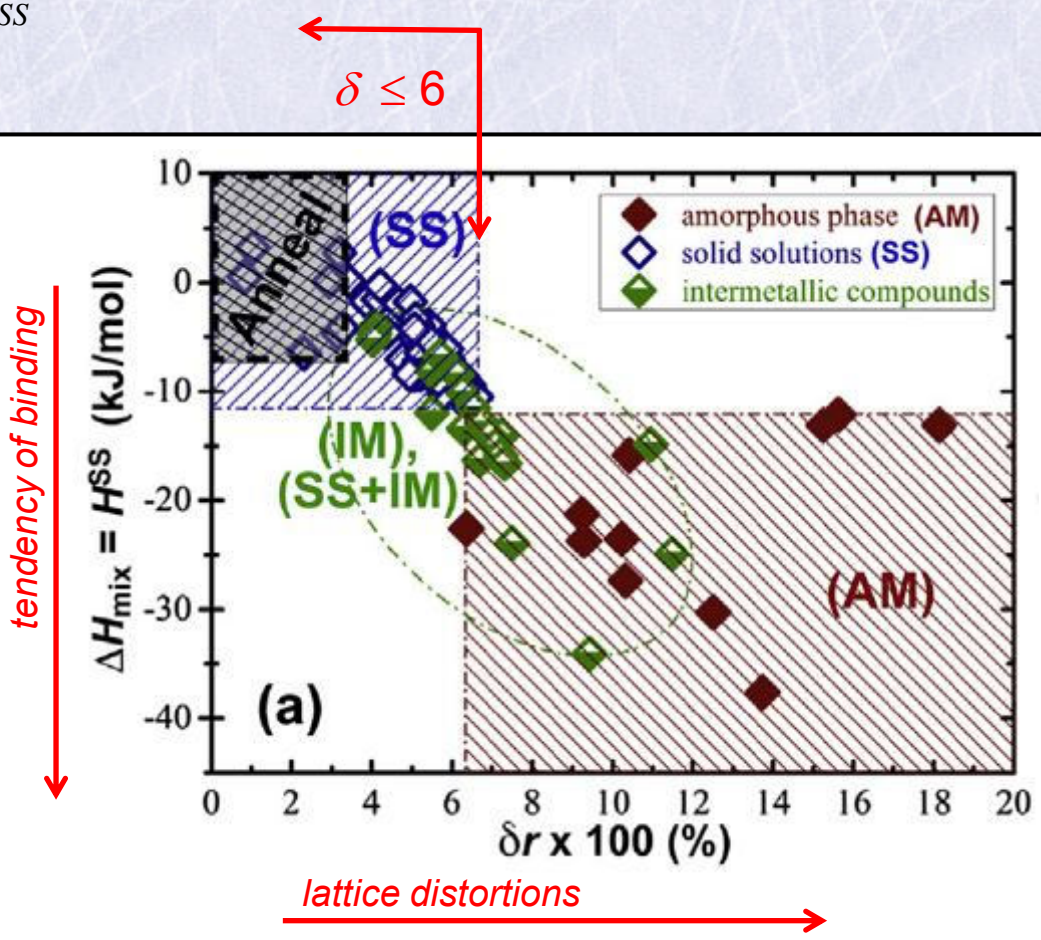
- measure of lattice distortions – misfit parameter δ
- heat of solution H^{IM} vs. entropy S^{SS}





S Guo et al. Intermetallics 41 (2013) 96

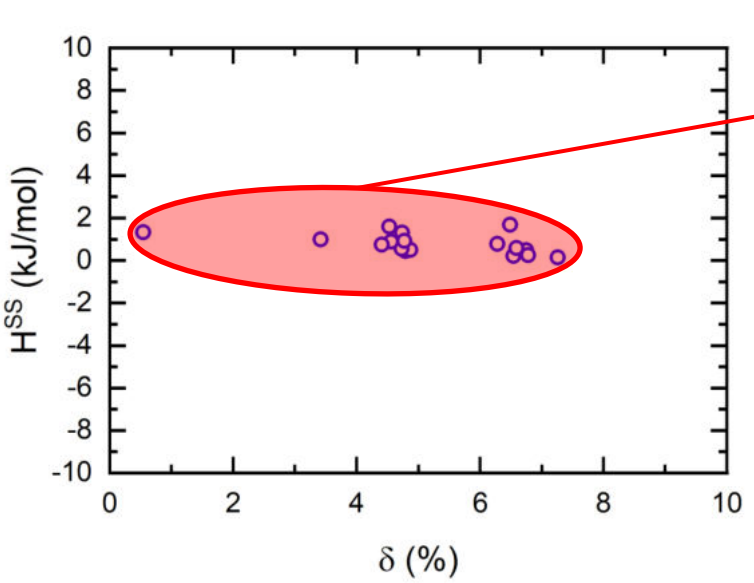
Alloys studied

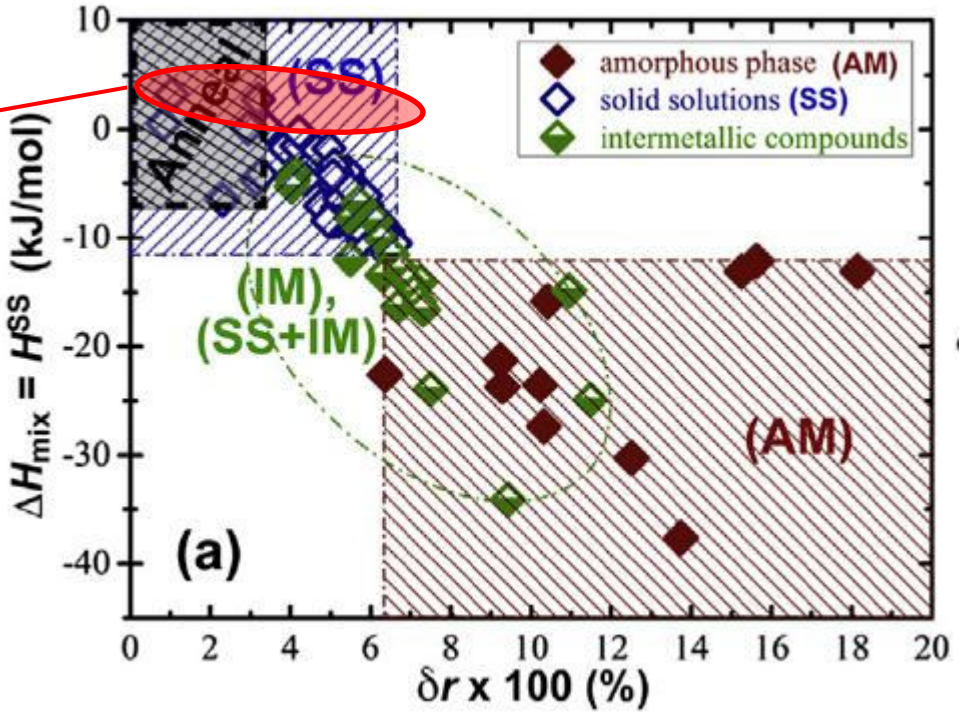
- 17 alloys
- concentrated solutions of refractory metals
  Hf, Nb, Ta, Ti, V, Zr
- all alloys have bcc structure

Alloy	$S^{SS}(R)$	δ (%)	H^{SS} (kJ/mol)
NbTaTi	1.10	1.05	1.33
NbTiZr	1.10	5.03	0.89
TaTiZr	1.10	5.01	0.44
NbTaTiZr	1.39	4.83	0.75
NbTiVZr	1.39	7.04	0.25
$Nb_{0.5}TaTiZr_{1.5}$	1.32	5.22	0.50
$Nb_{1.5}TaTiZr_{0.5}$	1.32	3.83	1.00
$Nb_2TaTiZr_2$	1.33	5.27	0.56
Nb_2TiVZr_2	1.33	6.91	0.22
$HfNb_4TaTiZr_4$	1.39	5.43	0.93
HfNbTaTiZr	1.61	4.98	1.60
HfNbTiVZr	1.61	7.06	0.48
$Hf_{0.5}Nb_{1.5}TiV_{1.5}Zr_{0.5}$	1.50	6.70	1.68
$Hf_{0.75}Nb_{0.75}TiV_{1.25}Zr_{1.25}$	1.58	7.53	0.15
$HfNbTiVZr_{0.5}$	1.58	6.88	0.59
$Hf_{0.5}NbTa_{0.5}TiZr$	1.56	5.00	1.31
HfNbTaTiVZr	1.79	6.58	0.78

Empirical parameters describing HEAs

- various atom sizes of elements → lattice distortions
- measure of lattice distortions – misfit parameter δ
- heat of solution H^{IM} vs. entropy S^{SS}

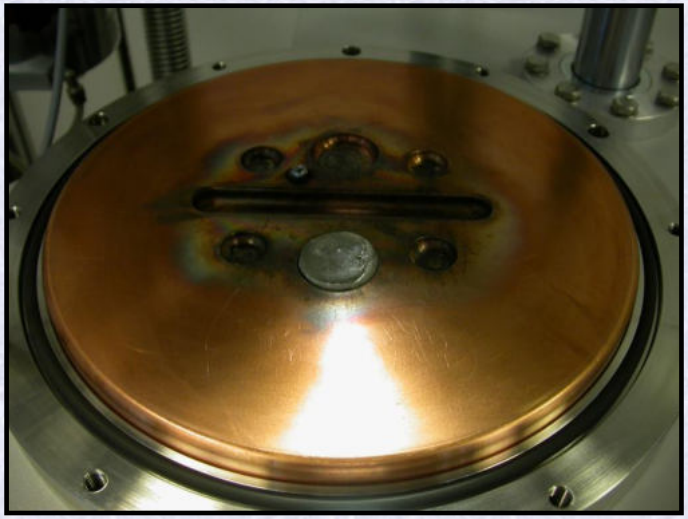




S Guo et al. Intermetallics 41 (2013) 96

Preparation of samples

- casting from 99.99% elements
- UHV arc melting (base pressure 5×10^{-6} mbar)
- Edmund Bühler AM200, max. temperature 3500°C
- water cooled Cu plate mould
- ingot diameter 30 mm



Preparation of samples

- $10 \times 10 \times 1$ mm^3 samples for positron annihilation studies were cut from ingots using diamond saw

Preparation of samples

- $10 \times 10 \times 1$ mm^3 samples for positron annihilation studies were cut from ingots using diamond saw

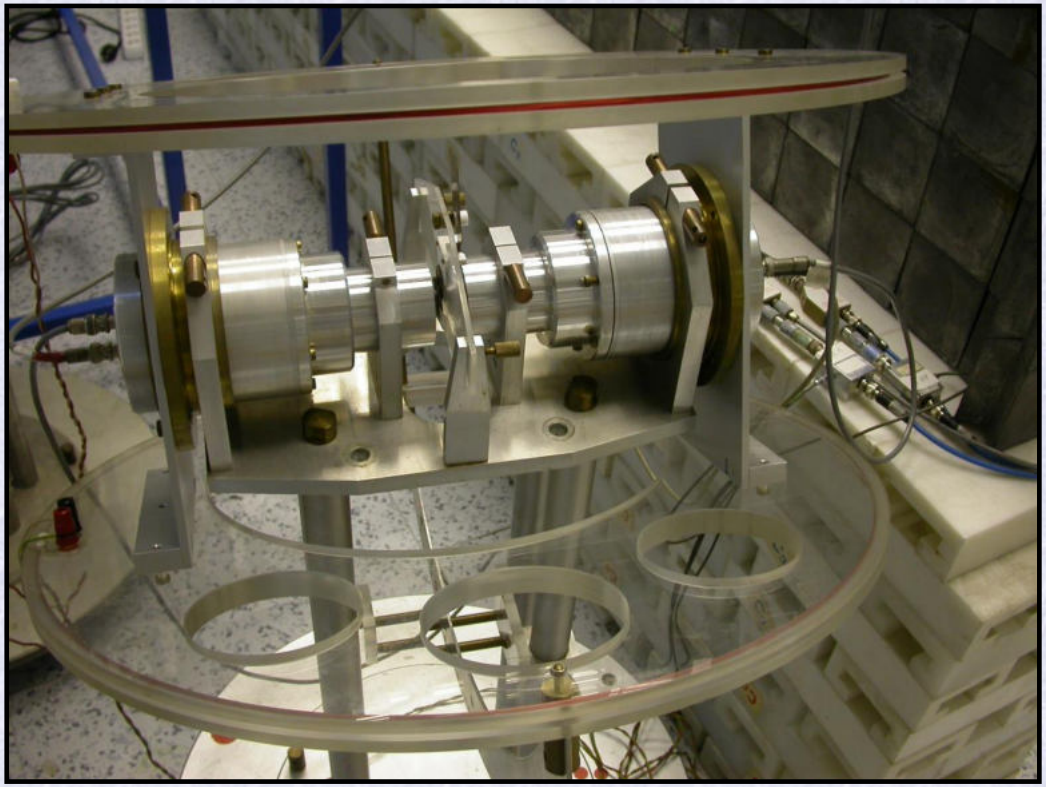
- samples were annealed in UHV (10^{-6} mbar) at 1200^{o}C for 2 h

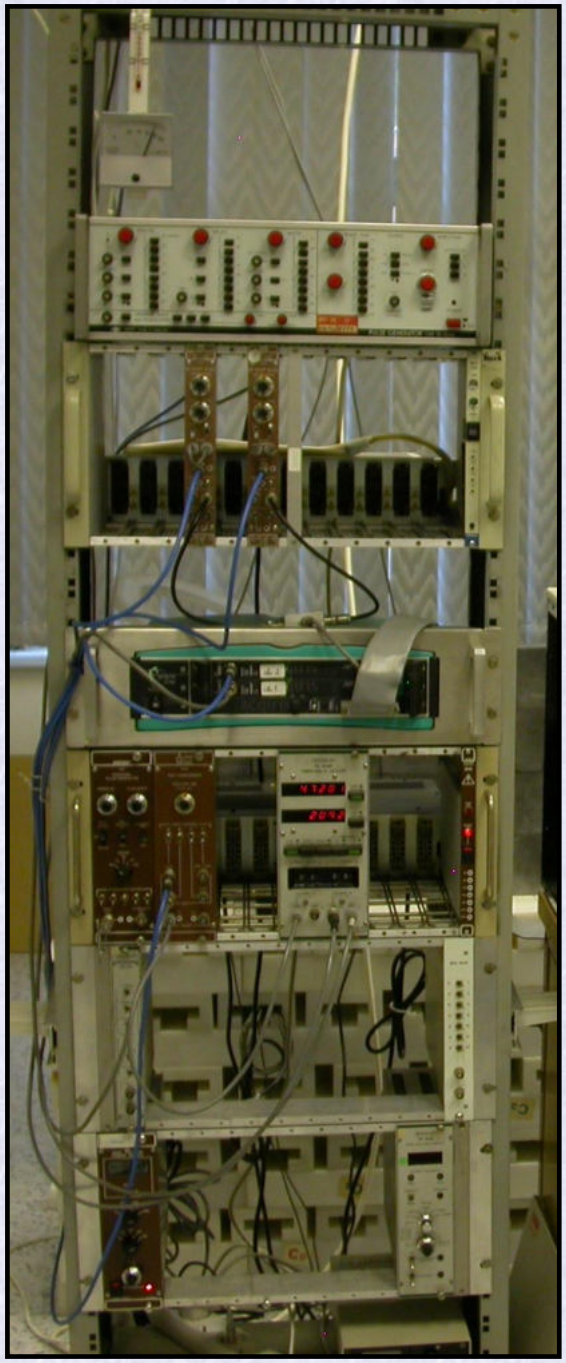
- annealing was finished by quenching

Positron lifetime investigations

- digital positron lifetime spectrometer
- photomultipliers Hamamatsu H3378
- BaF_2 scintillators
- time resolution 145 ps (FWHM ^{22}Na)
- effective coincidence count rate 100 s^{-1}
- >10^7 positron annihilation events in each spectrum

*F. Bečvář et al., Nucl. Instrum. Methods A **539**, 372 (2005)*

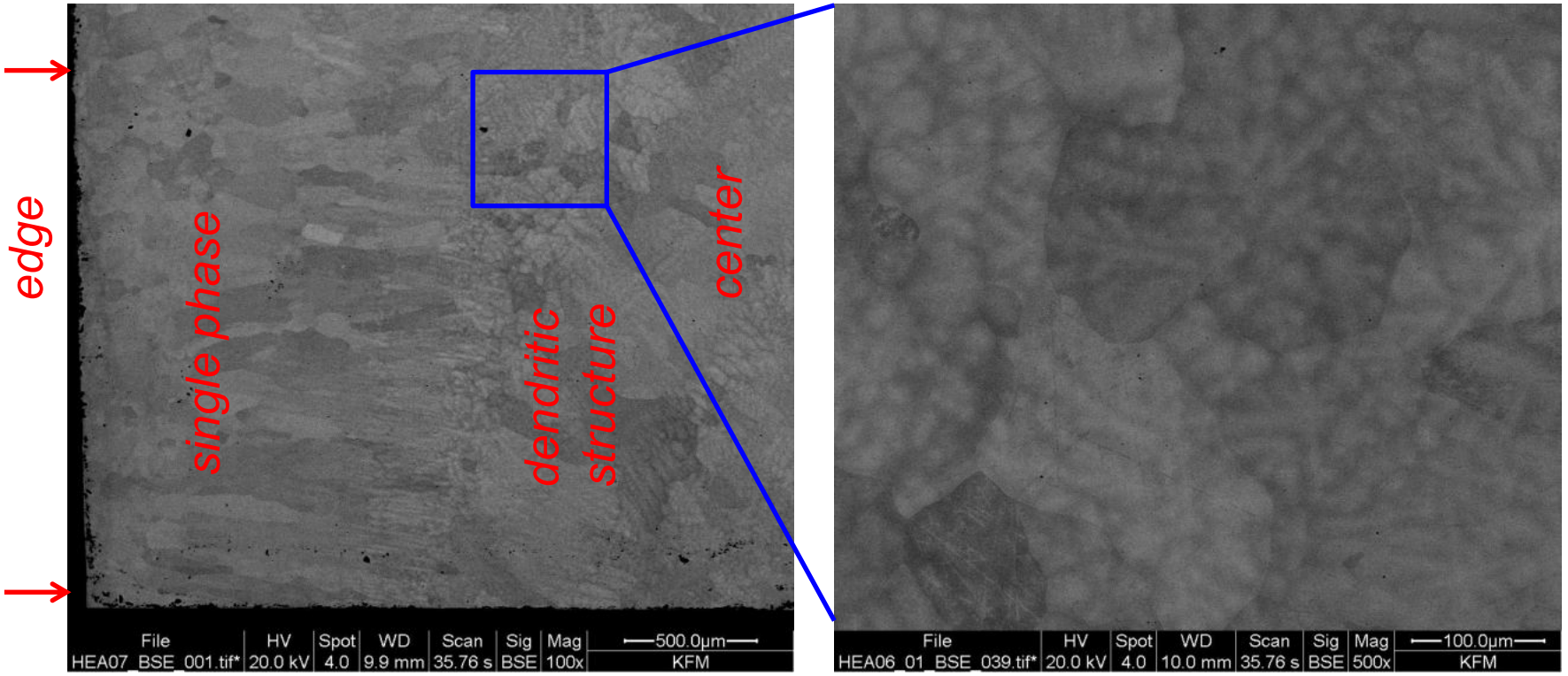




HfNbTaTiZr alloy - microstructure

- **as-cast state**

- scanning electron microscopy (back-scattered electrons)



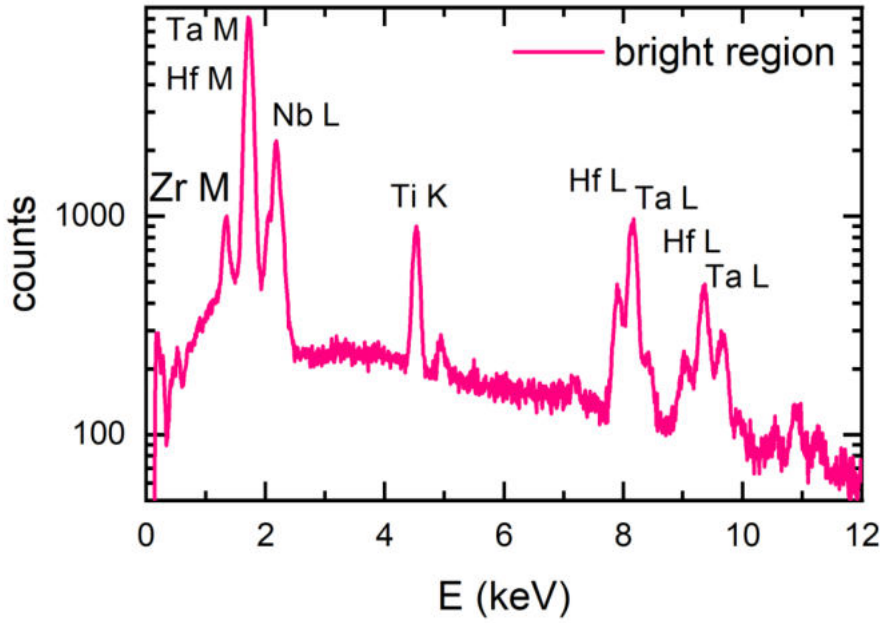
HfNbTaTiZr alloy - microstructure

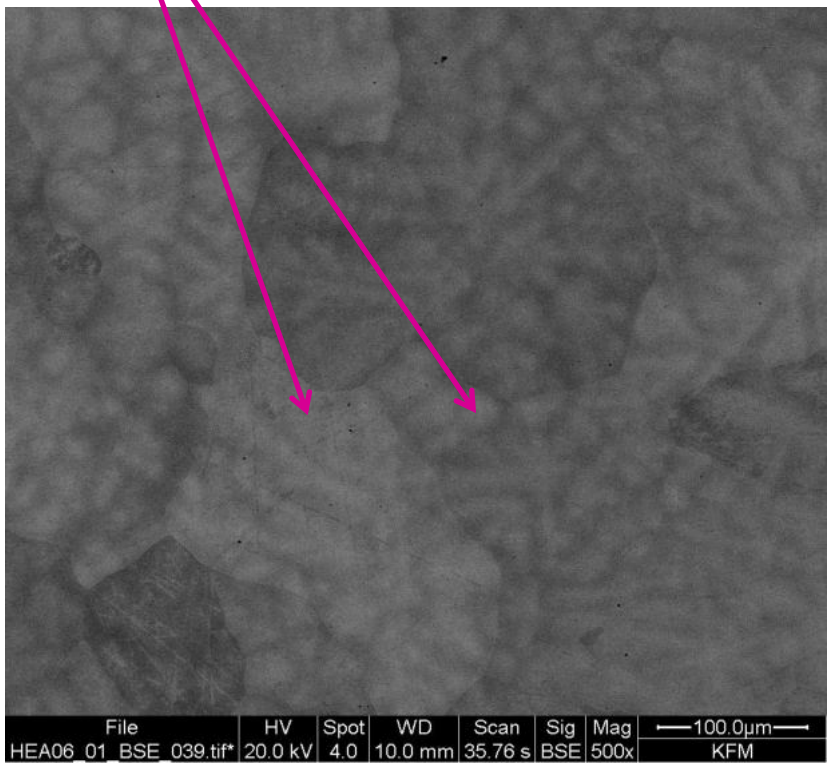
- **as-cast state**

scanning electron microscopy (back-scattered electrons)

bright regions
enriched in Nb,Ta

energy dispersive X-ray spectroscopy (EDS)





HfNbTaTiZr alloy - microstructure

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bright regions
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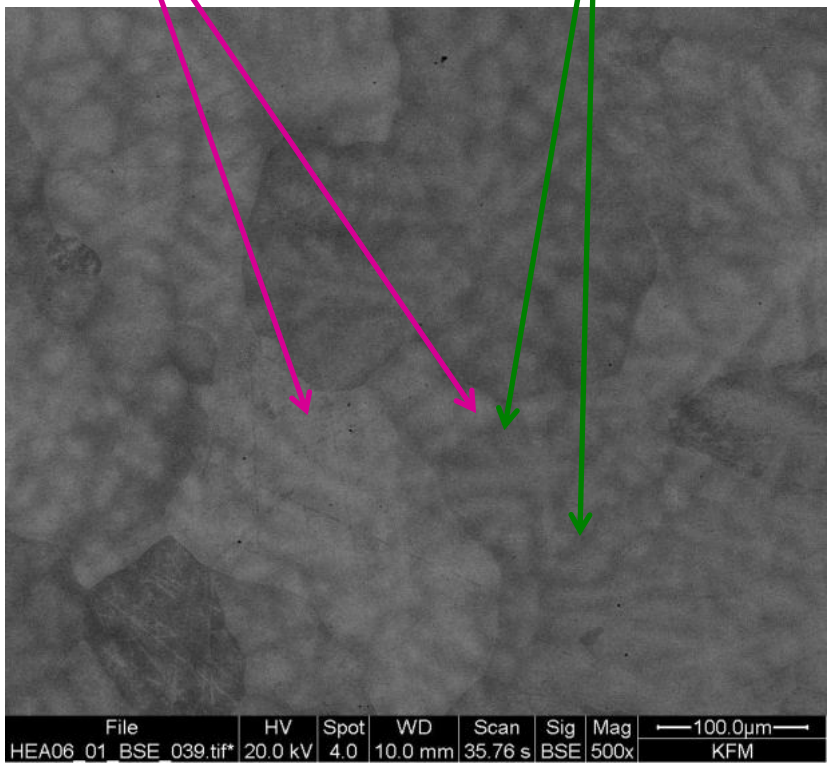
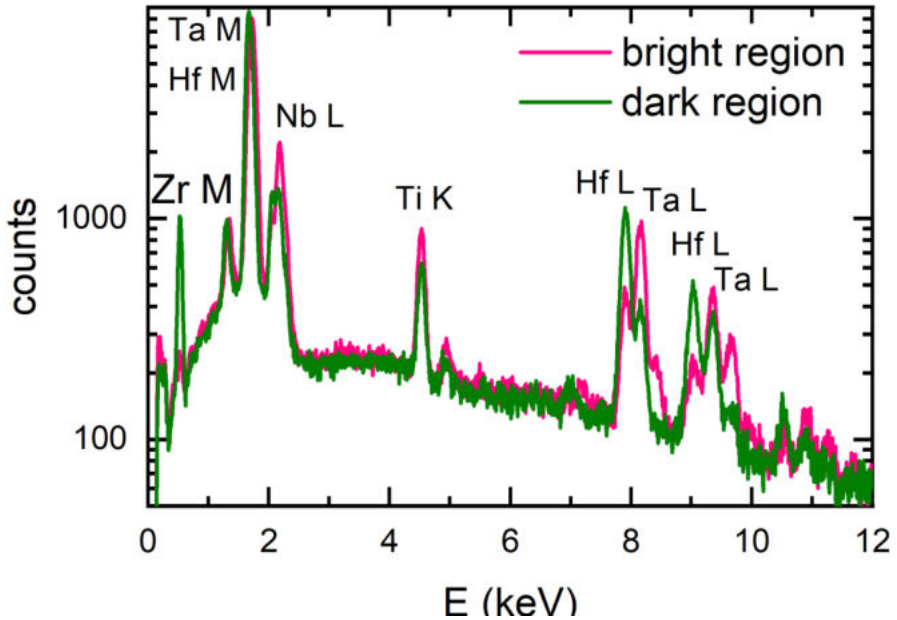
dark regions
enriched in Hf,Zr



energy dispersive X-ray spectroscopy (EDS)



HfNbTaTiZr alloy - microstructure

- **as-cast state**

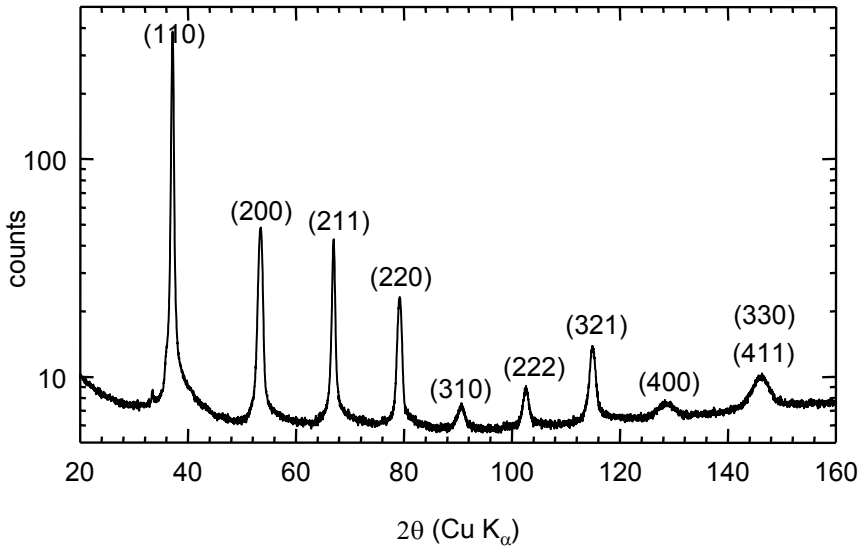
scanning electron microscopy (back-scattered electrons)

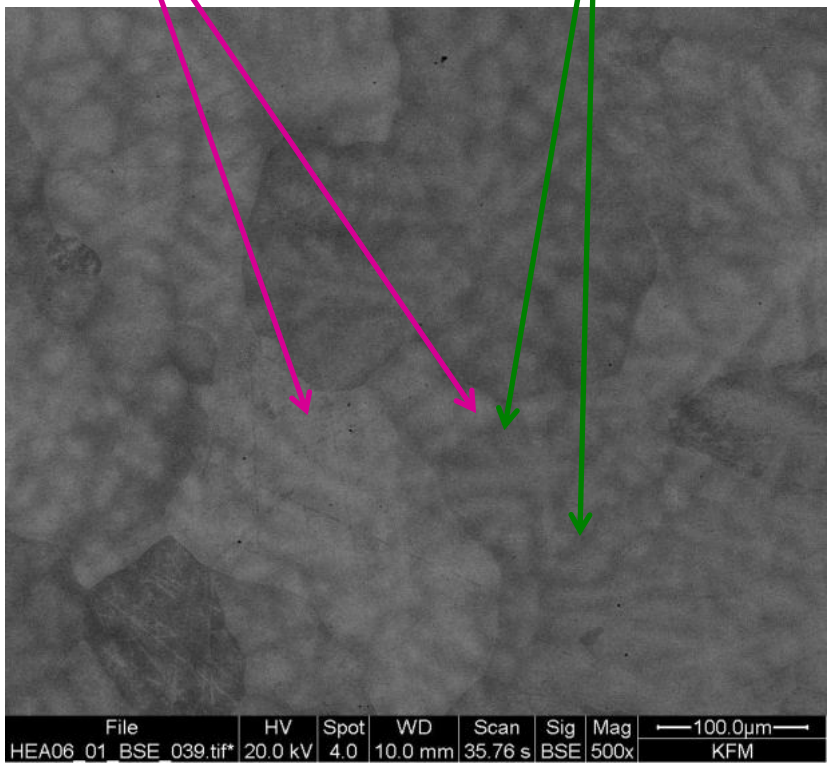
bright regions
enriched in Nb,Ta

dark regions
enriched in Hf,Zr

X-ray diffraction

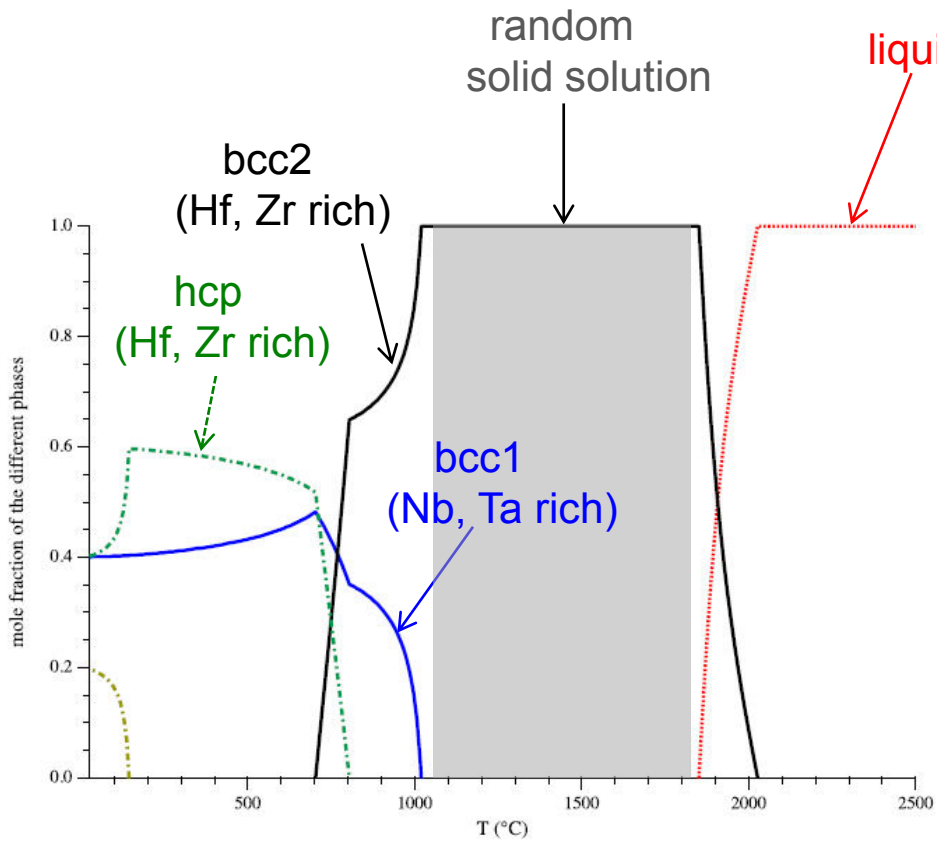
- bcc structure, *a* = 3.404 Å





HfNbTaTiZr alloy - microstructure

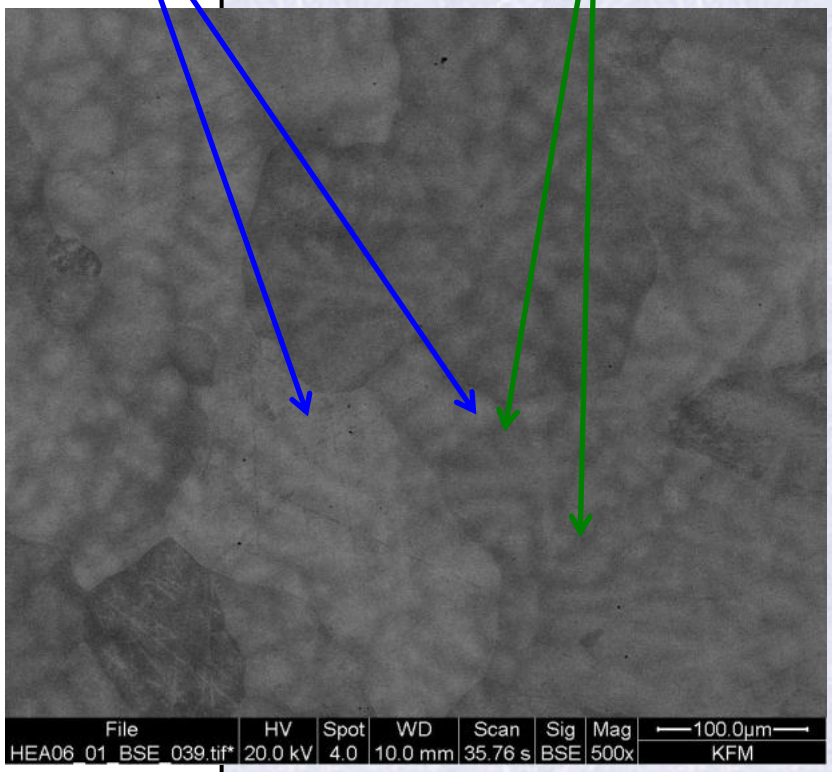
- Calphad modelling



B. Schuh et al. Acta Mater. ***142*** *(2018) 201-212*

bcc1
bright regions
enriched in Nb,Ta

bcc2
dark regions
enriched in Hf,Zr



HfNbTaTiZr alloy - microstructure

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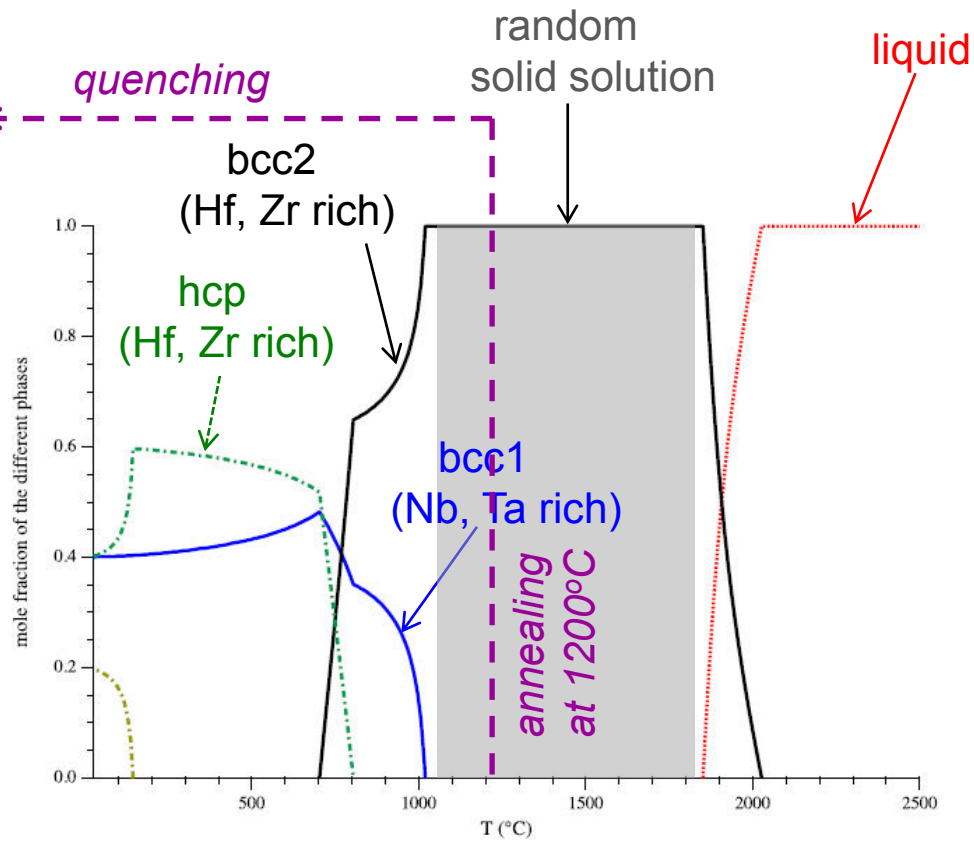


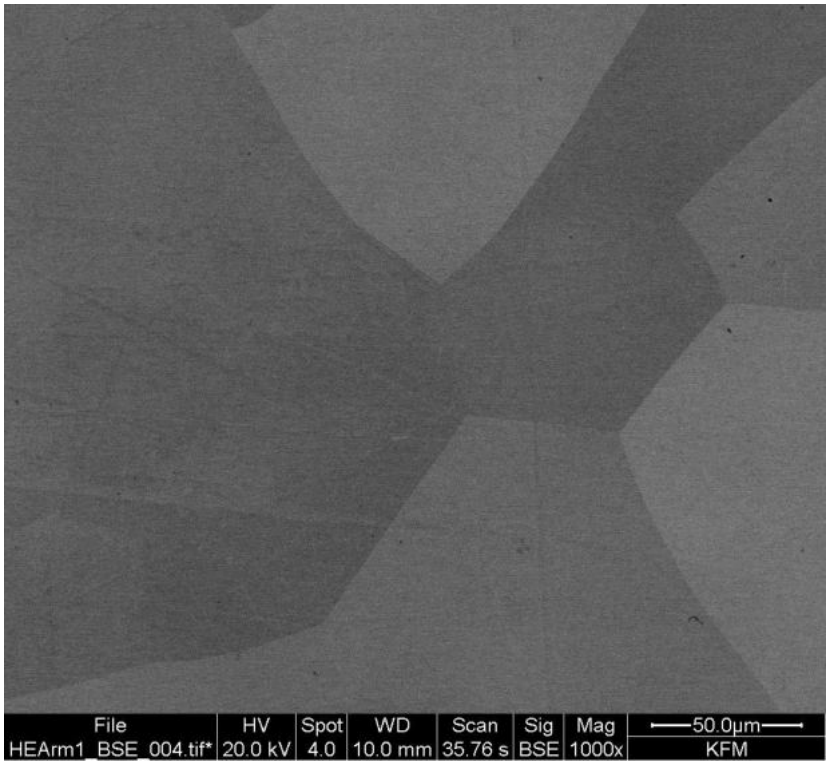
B. Schuh et al. Acta Mater. ***142*** *(2018) 201-212*

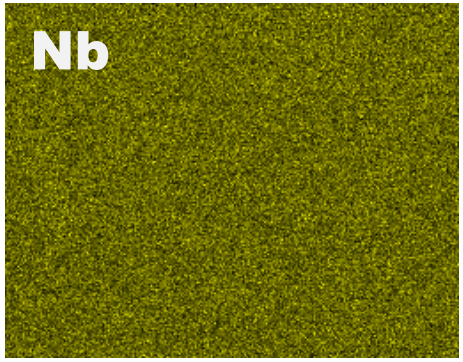
HfNbTaTiZr alloy - microstructure

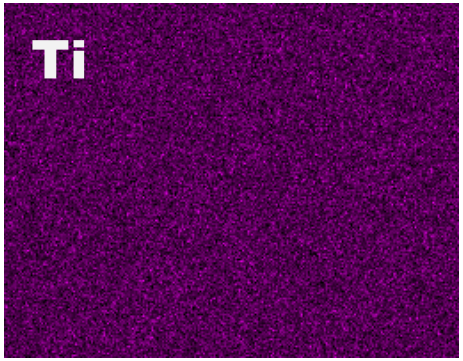
sample annealed in vacuum at 1200°C/2h

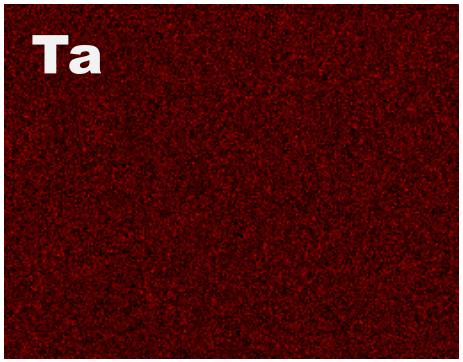
EDS elemental mapping

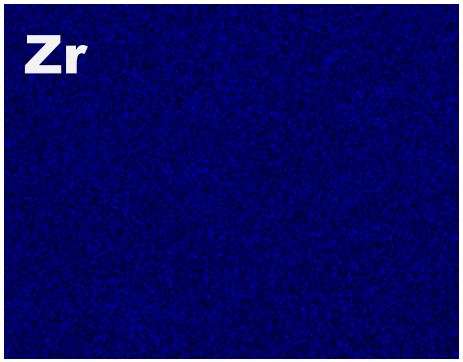
scanning electron microscopy
(back-scattered electrons)





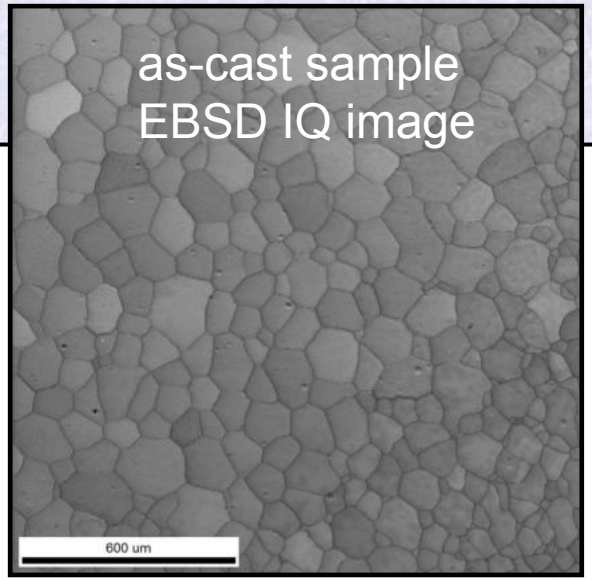






HfNbTaTiZr alloy – positron lifetime spectroscopy

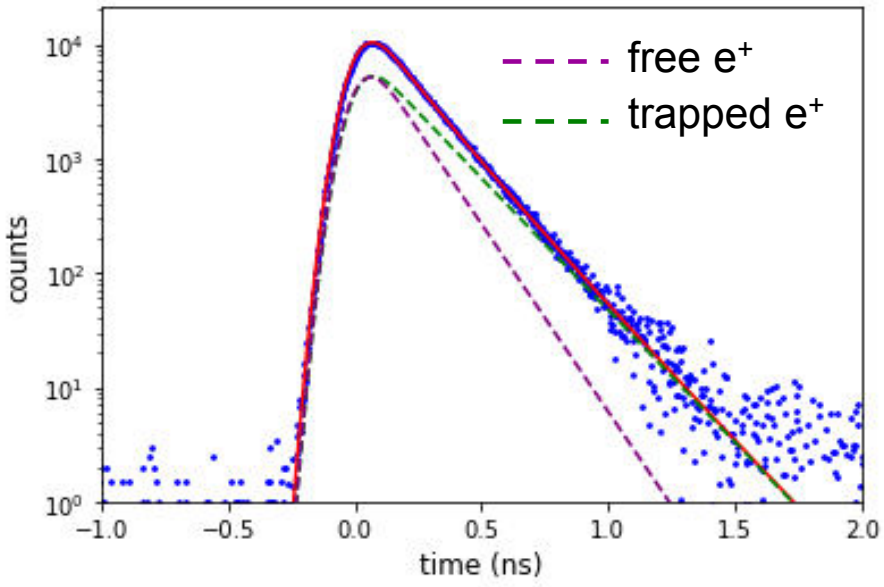
- **as-cast state**

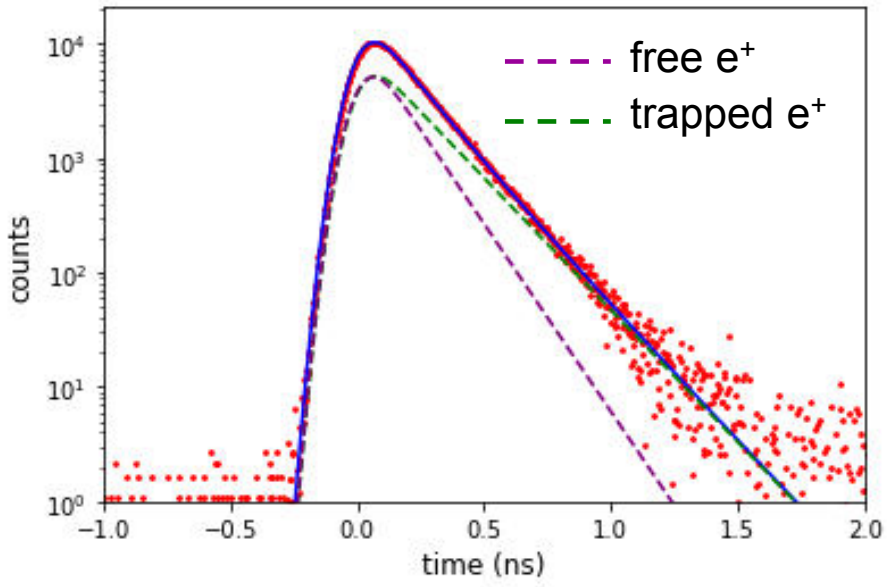


free positrons

positrons trapped at dislocations

state	τ_1 (ps)	I_1 (%)	τ_2 (ps)	I_2 (%)
as-cast	105(7)	31(3)	189(2)	69(3)

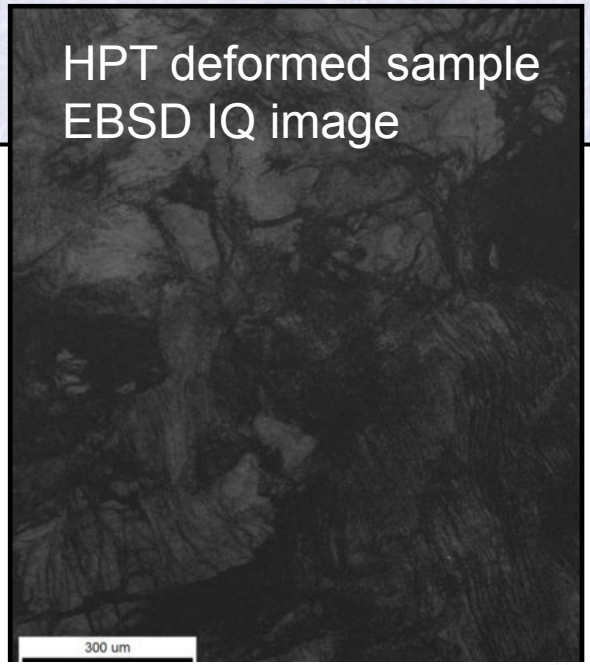




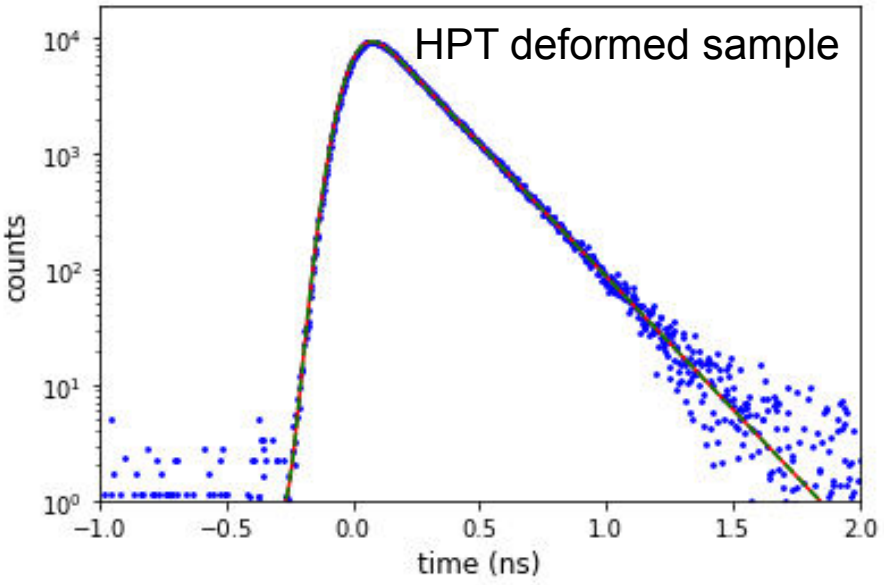
positron lifetime spectrum with subtracted source contribution

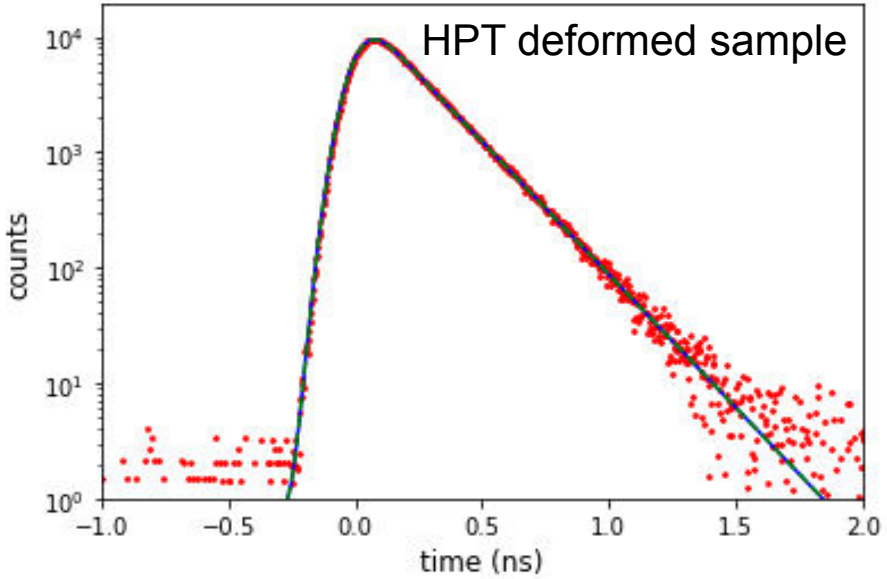
HfNbTaTiZr alloy – positron lifetime spectroscopy

- **deformed samples:**
  cold rolling, high pressure torsion (HPT)



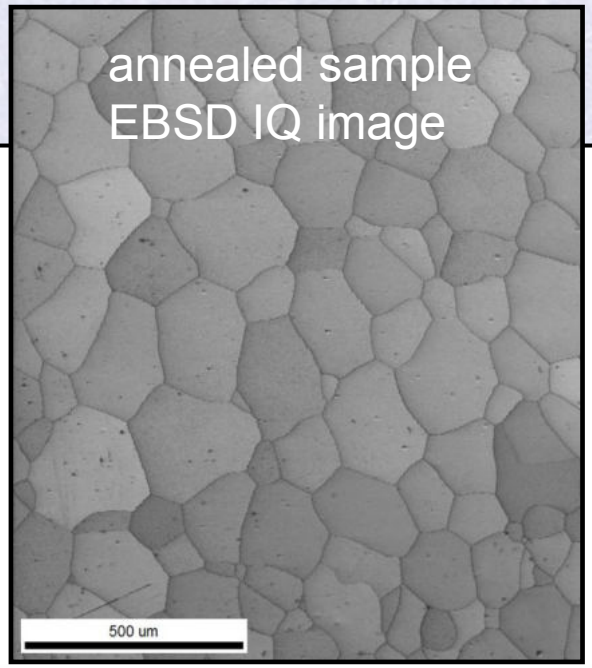
	free positrons		positrons trapped at dislocations	
state	**τ_1 (ps)**	**I_1 (%)**	**τ_2 (ps)**	**I_2 (%)**
as-cast	105(7)	31(3)	189(2)	69(3)
cold rolled	58(4)	12(2)	186(2)	88(2)
HPT deformed	-	-	188(1)	100





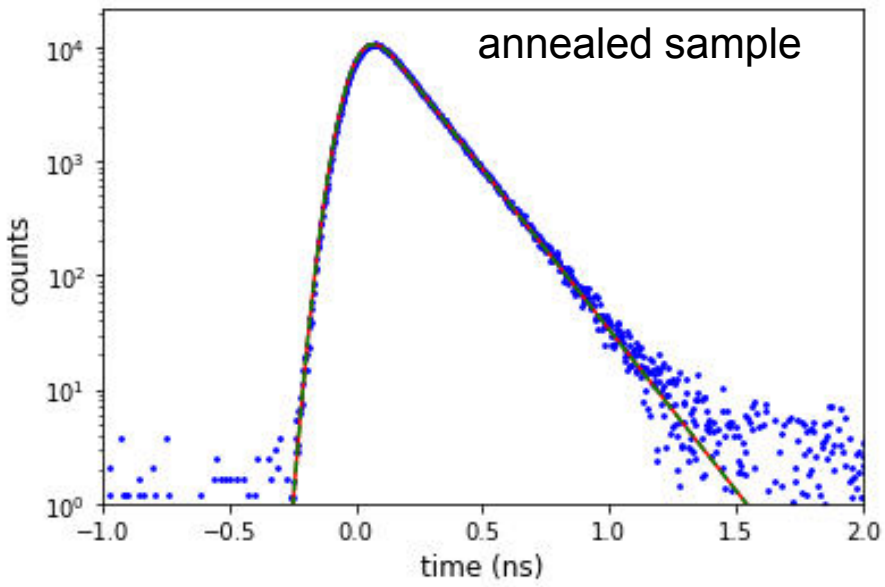
HfNbTaTiZr alloy – positron lifetime spectroscopy

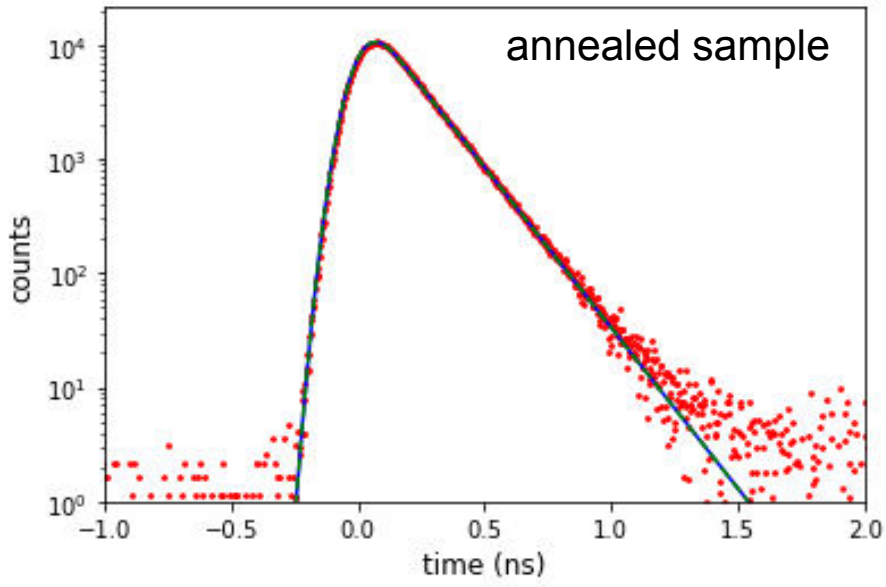
- **sample annealed in vacuum at 1200°C for 1h**



free positrons

state	τ_1 (ps)	I_1 (%)	τ_2 (ps)	I_2 (%)
annealed	141(1)	100	-	-

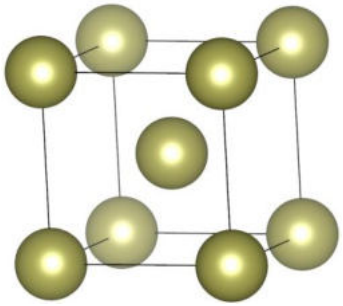




HfNbTaTiZr – positron lifetime calculations

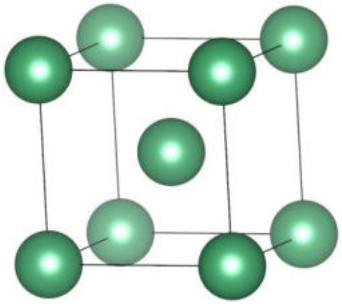
- bcc structure *a* = 3.4 Å

Hf



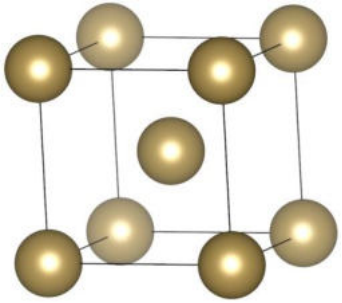
τ = 132 ps

Nb



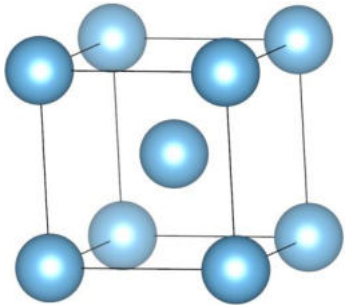
τ = 138 ps

Ta



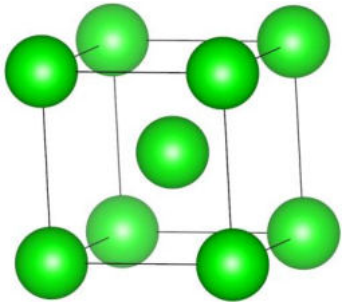
τ = 130 ps

Ti



τ = 161 ps

Zr

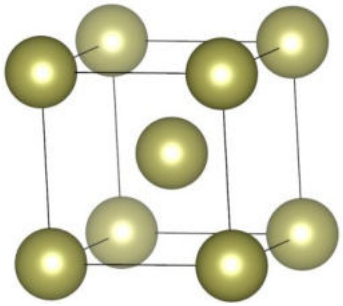


τ = 136 ps

HfNbTaTiZr – positron lifetime calculations

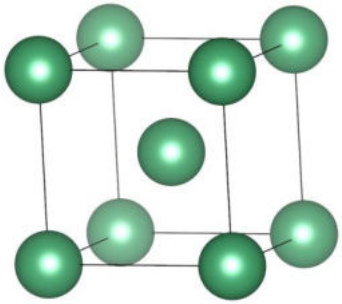
- bcc structure *a* = 3.4 Å

Hf



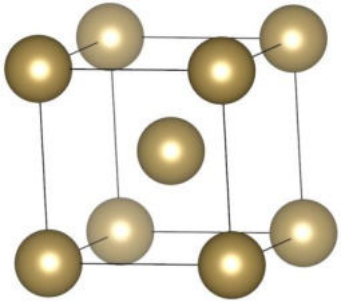
τ = 132 ps

Nb



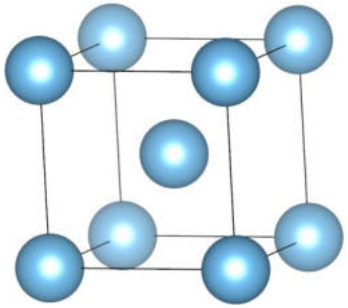
τ = 138 ps

Ta



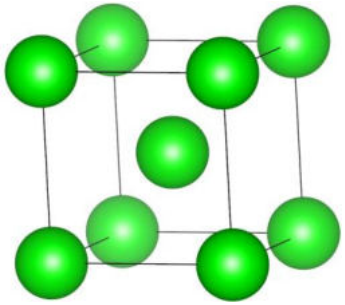
τ = 130 ps

Ti

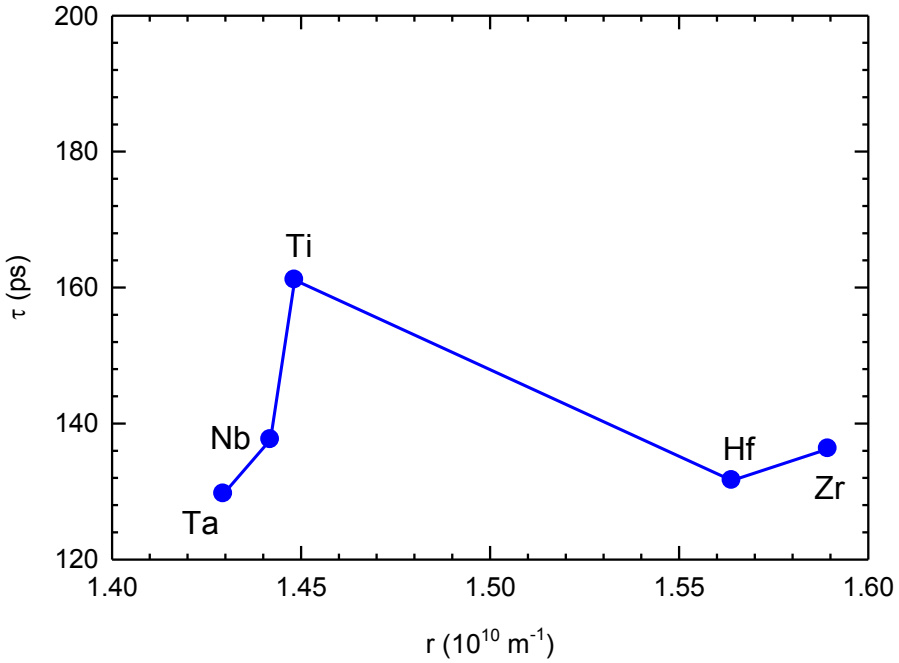


τ = 161 ps

Zr

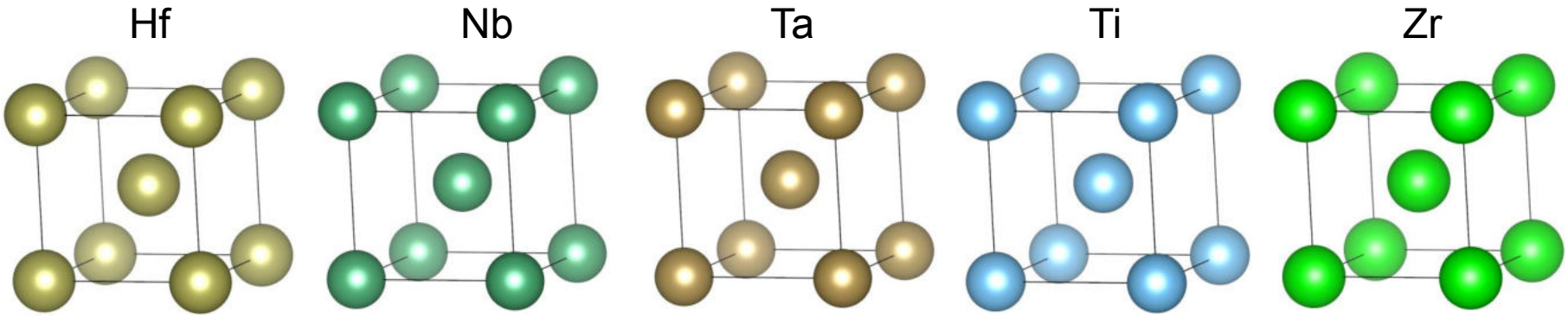


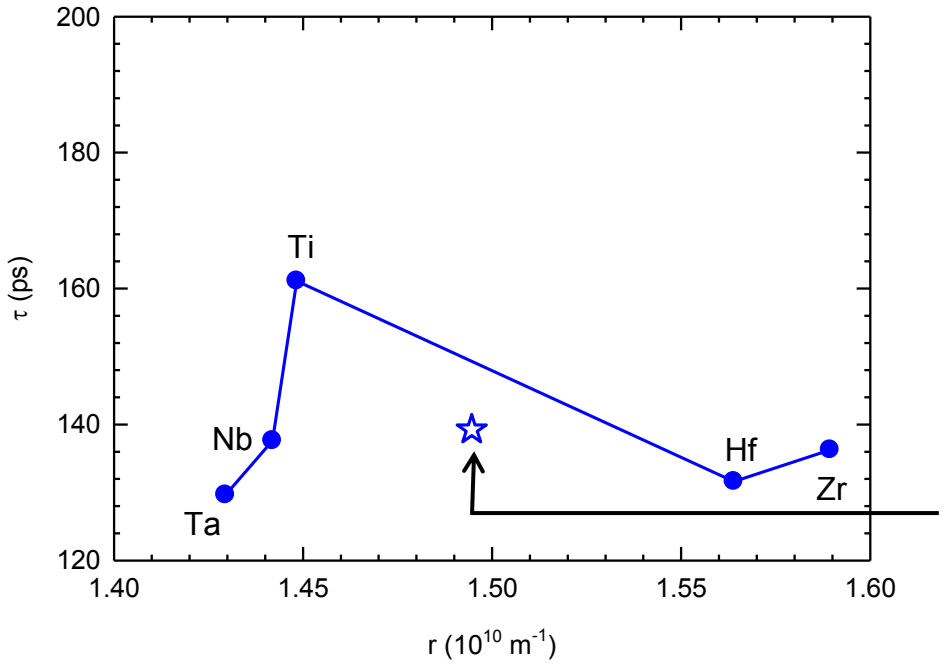
τ = 136 ps



HfNbTaTiZr – positron lifetime calculations

- bcc structure *a* = 3.4 Å



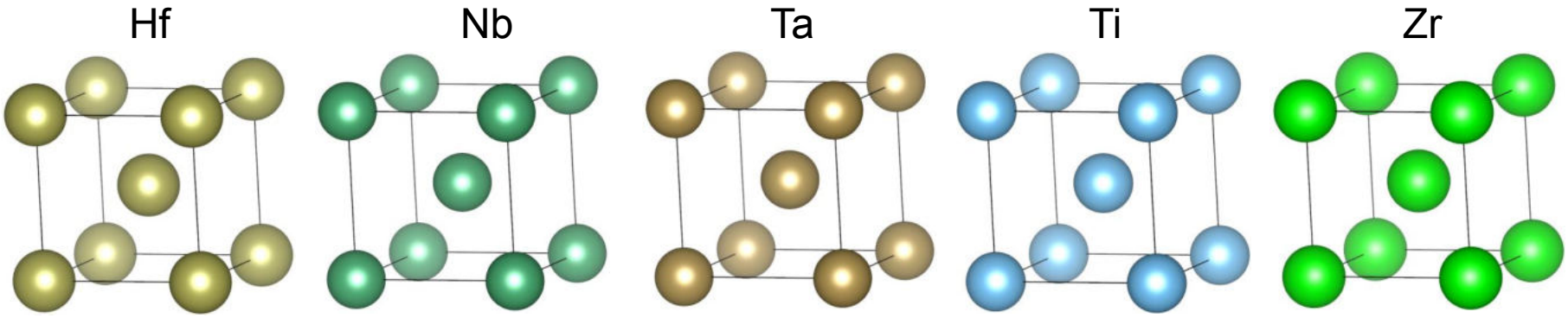


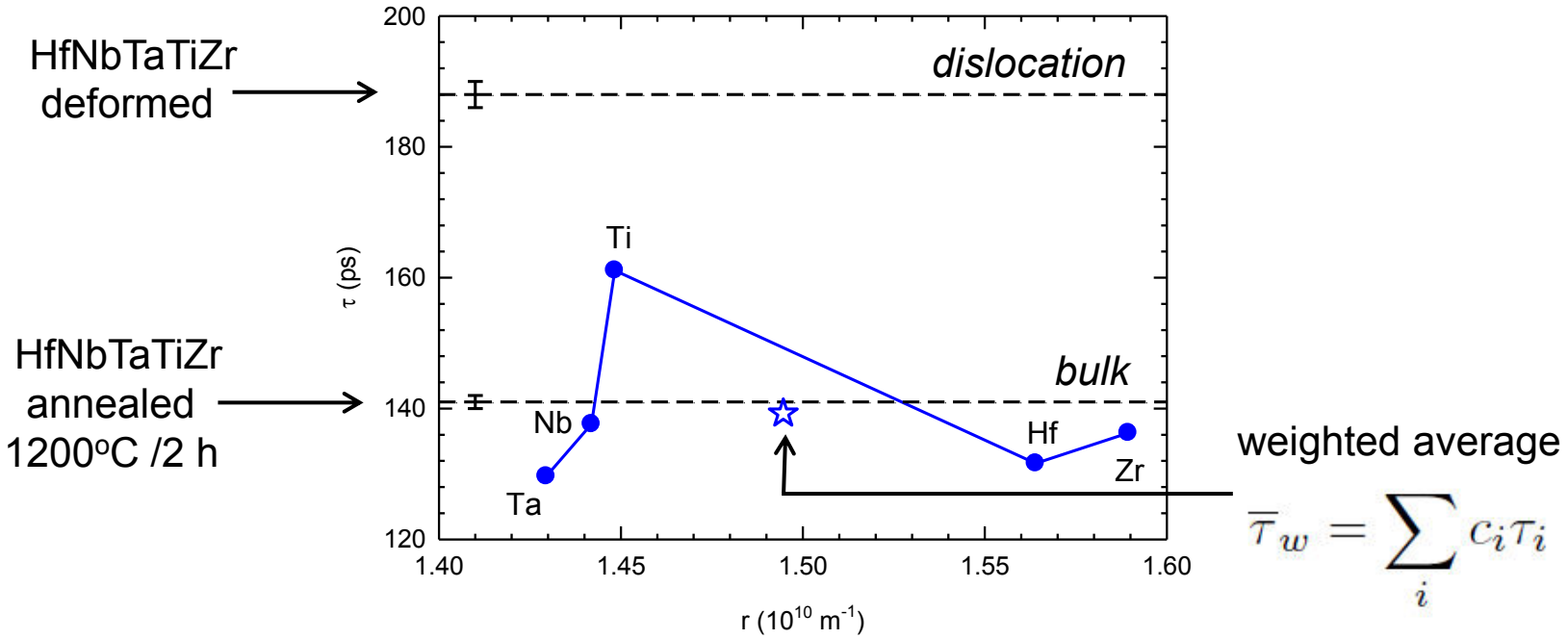
weighted average

$$\overline{\tau}_w = \sum_i c_i \tau_i$$

HfNbTaTiZr – positron lifetime calculations

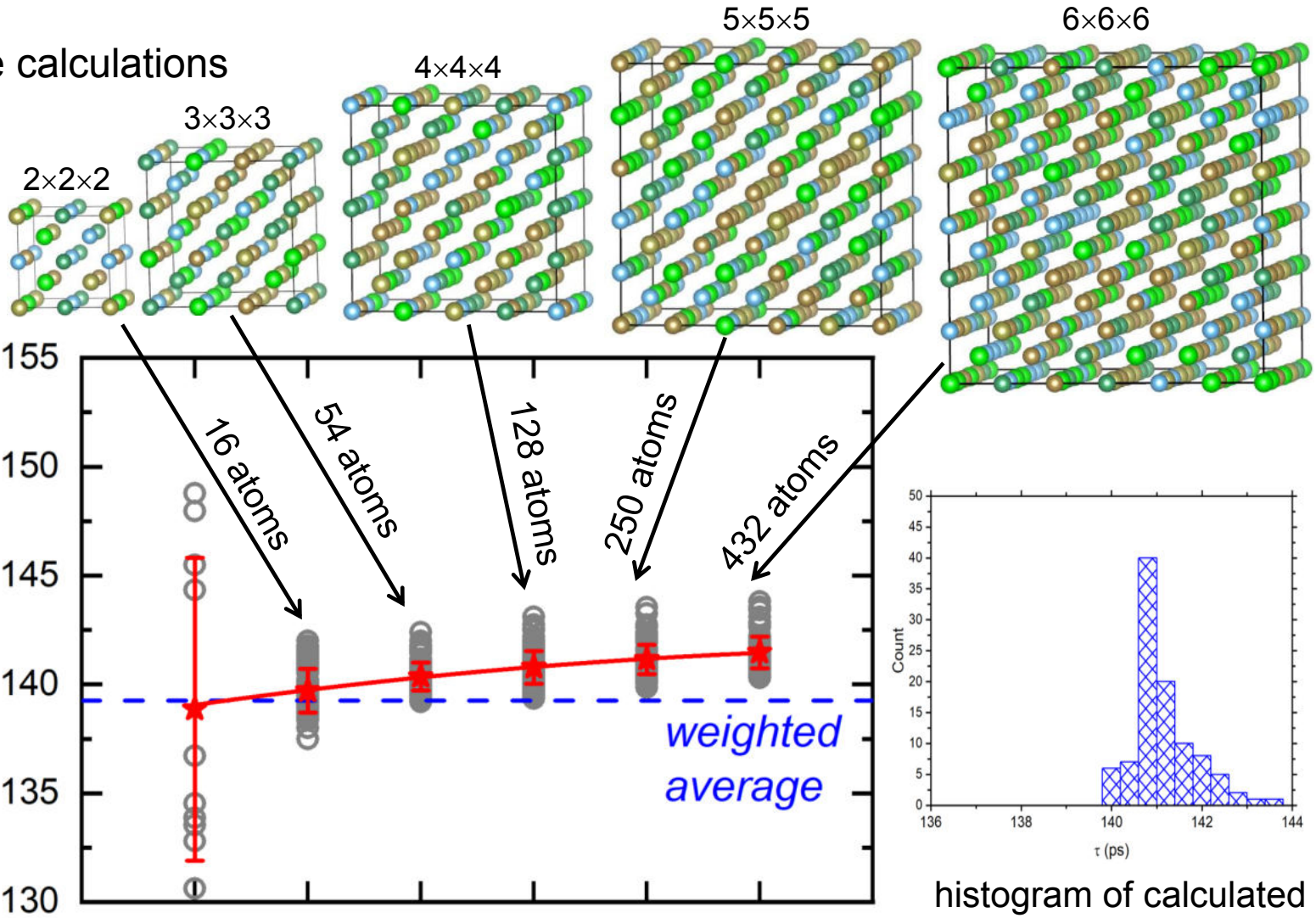
- bcc structure *a* = 3.4 Å





HfNbTaTiZr – positron lifetime calculations

- bulk lifetime calculations

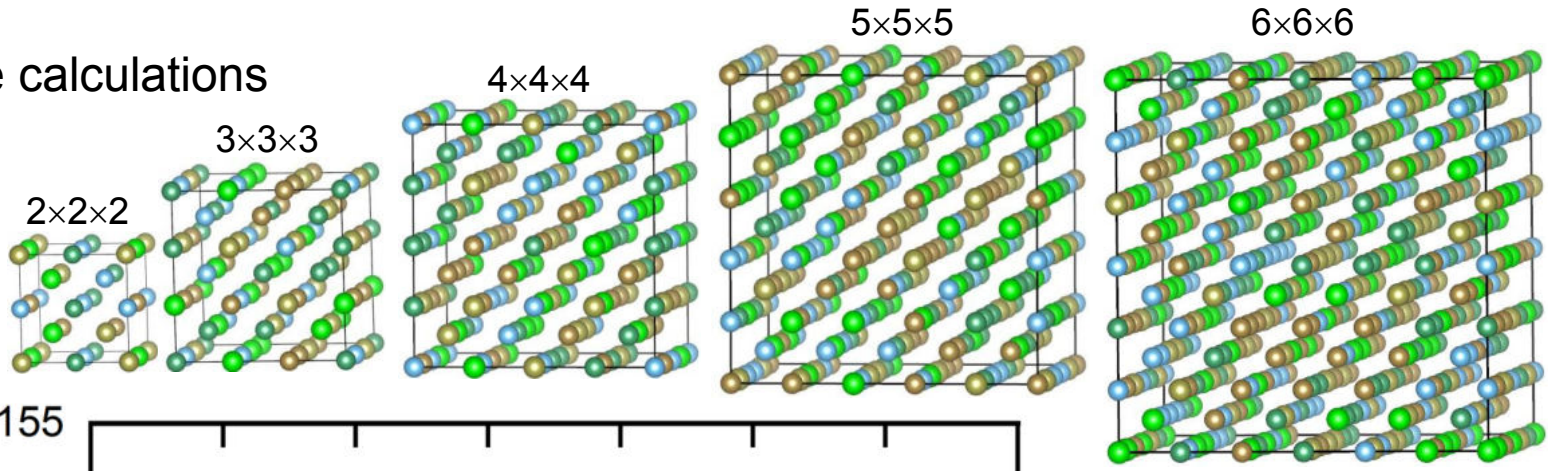


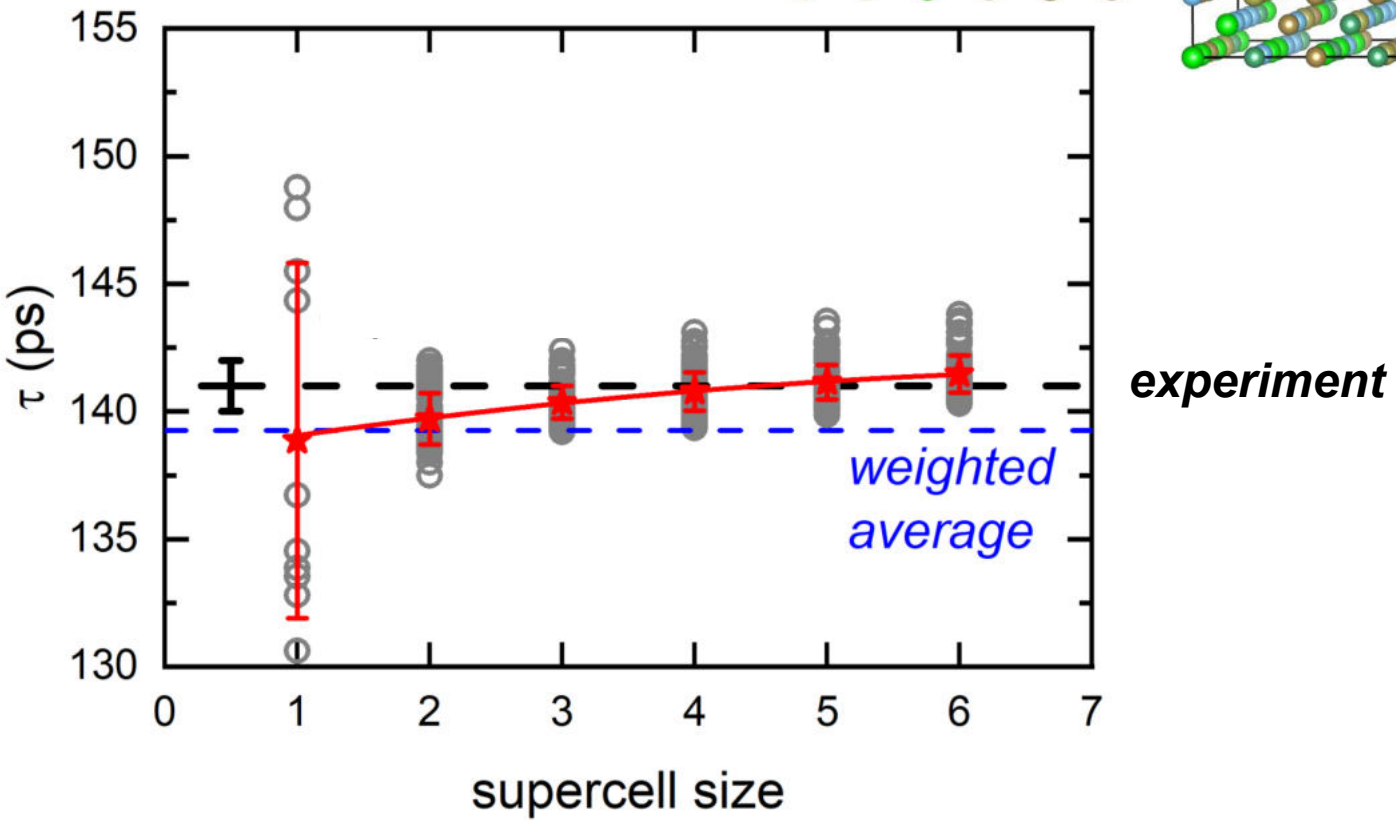
histogram of calculated bulk lifetimes for 432 atom supercell

- calculations repeated 100 times for each supercell

HfNbTaTiZr – positron lifetime calculations

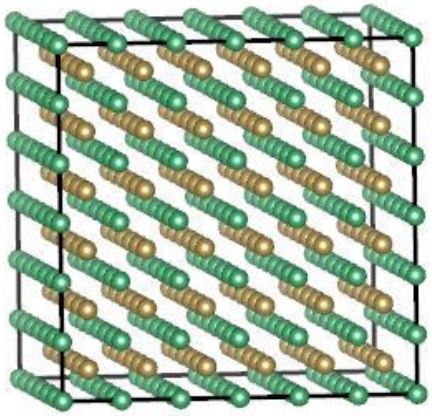
- bulk lifetime calculations





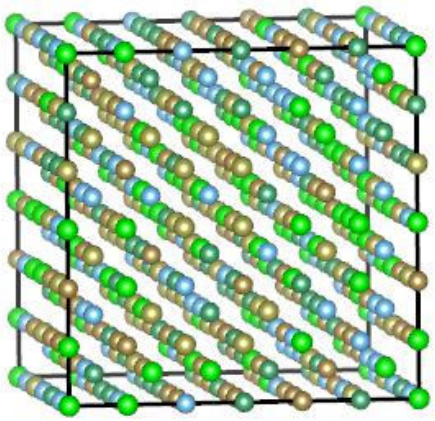
HfNbTaTiZr – positron lifetime calculations

ordered alloy (NbTa)

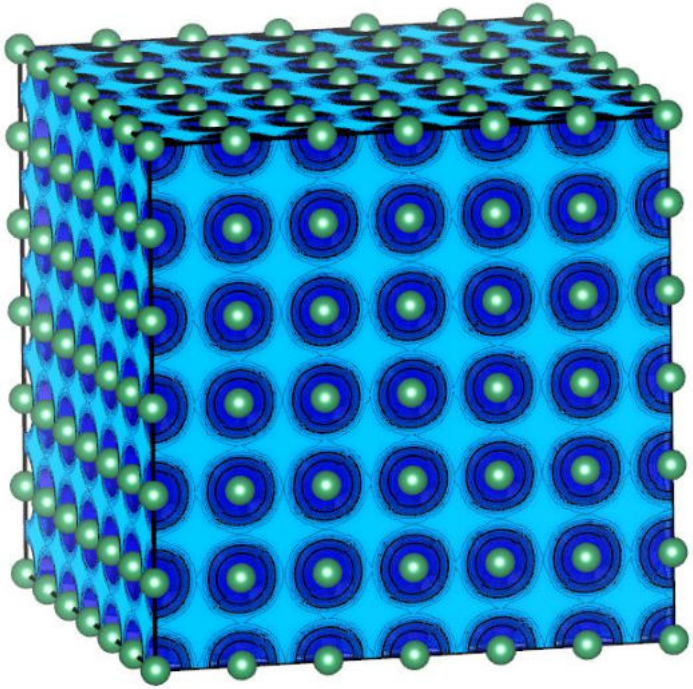


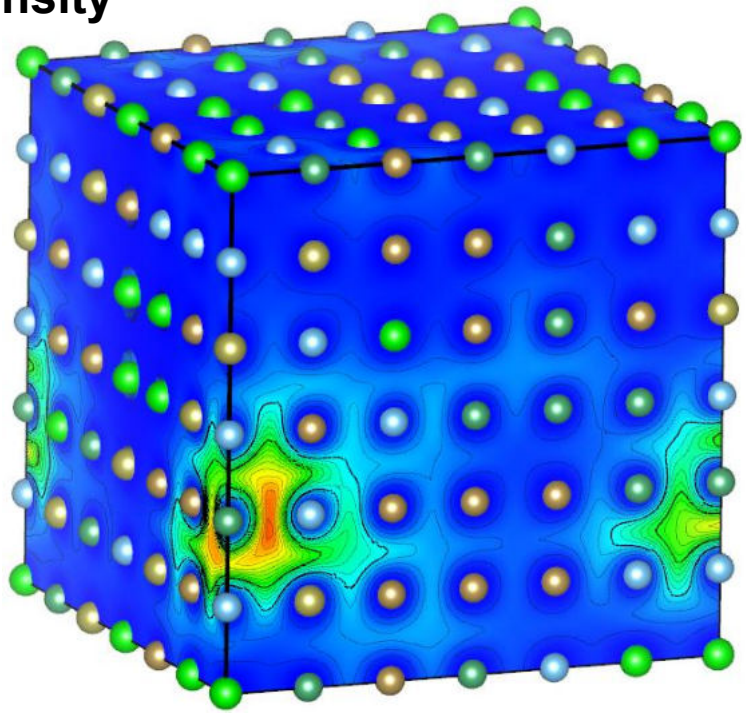
- e^+ searches for interstitial regions with enhanced open volume
- e^+ can be used as a probe of lattice distortions
- one can expect positive correlation between bulk e^+ lifetime and magnitude of lattice distortions

HEA (HfNbTaTiZr)



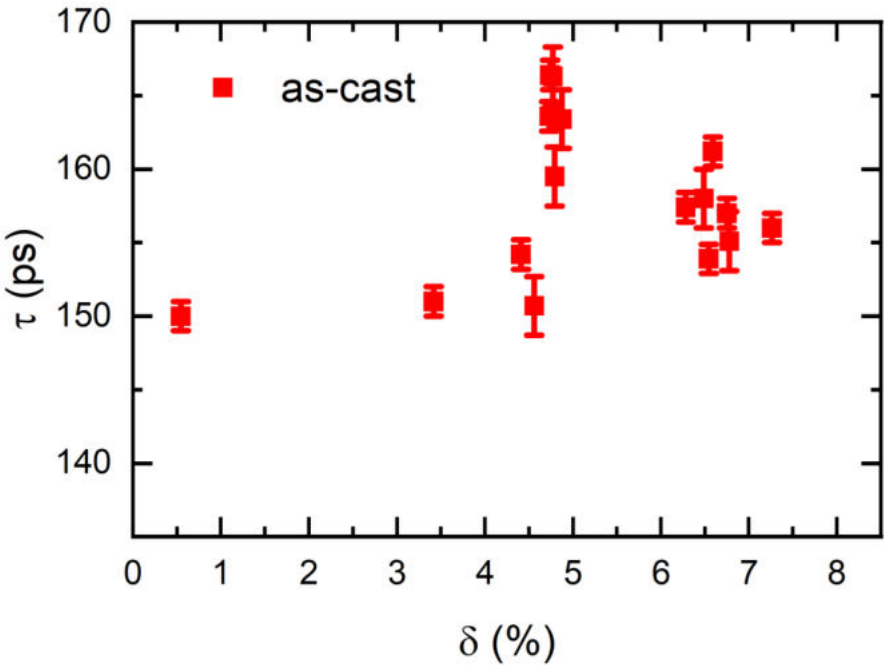
calculated positron density





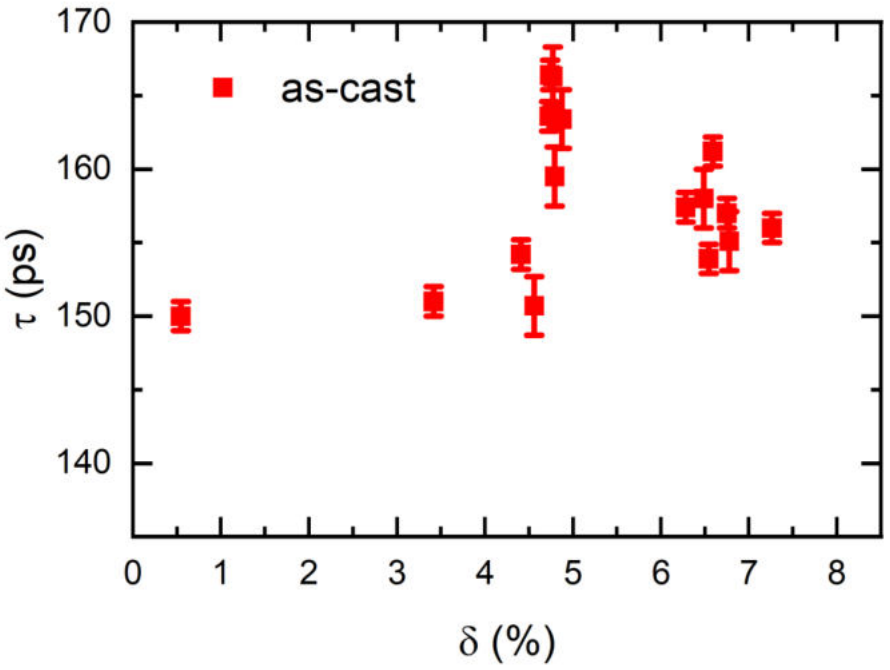
Positron lifetime investigations of HEAs

- mean positron lifetime → single component fit of positron lifetime spectra
- as-cast alloys



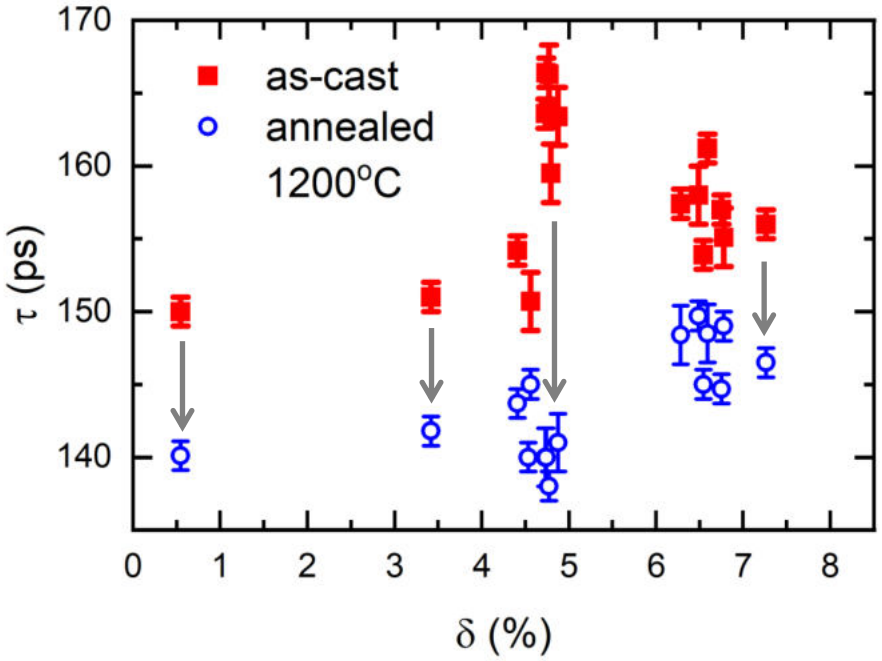
Positron lifetime investigations of HEAs

- mean positron lifetime → single component fit of positron lifetime spectra
- as-cast alloys → significant contribution of positrons trapped at dislocations



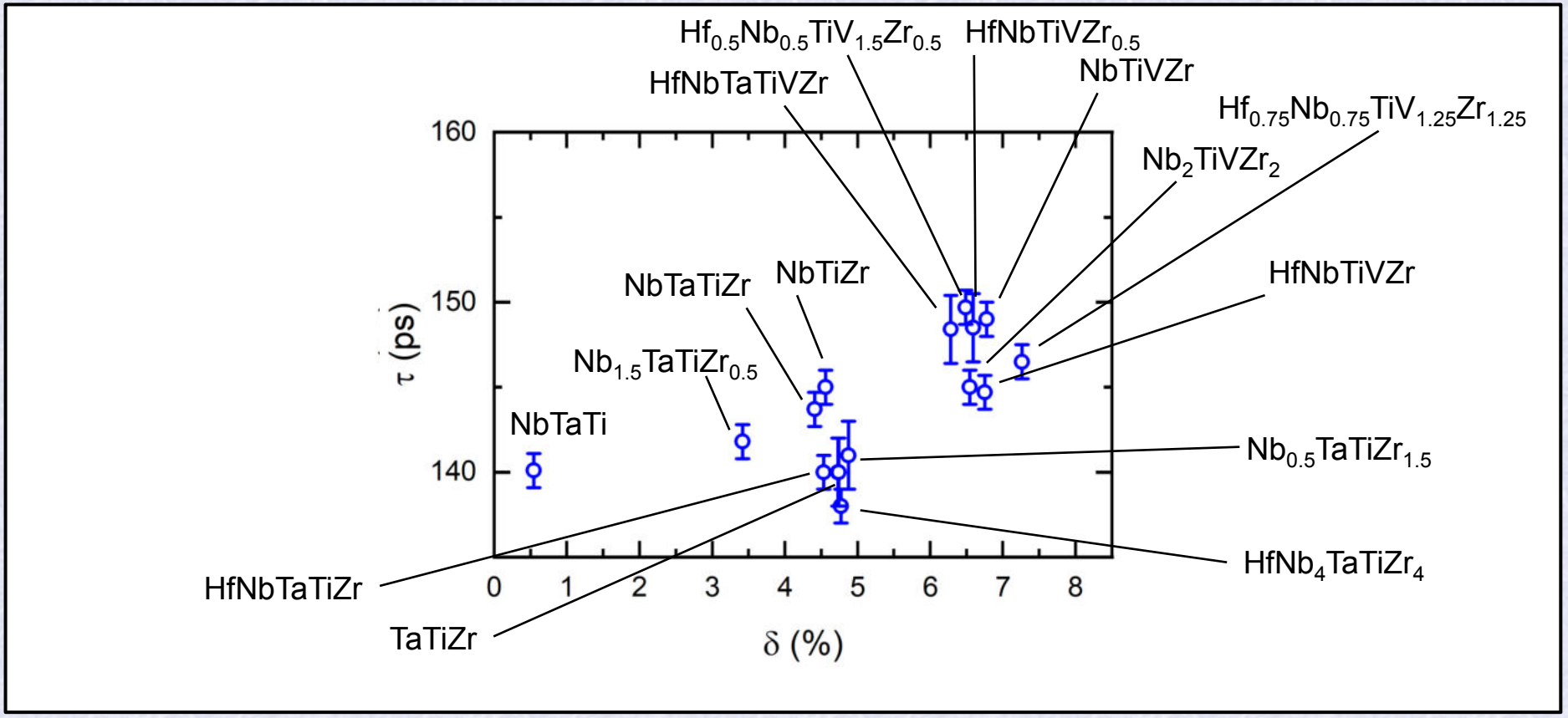
Positron lifetime investigations of HEAs

- mean positron lifetime → single component fit of positron lifetime spectra
- as-cast alloys → significant contribution of positrons trapped at dislocations
- alloys annealed in vacuum at 1200°C for 2 h → positrons annihilated in the free state



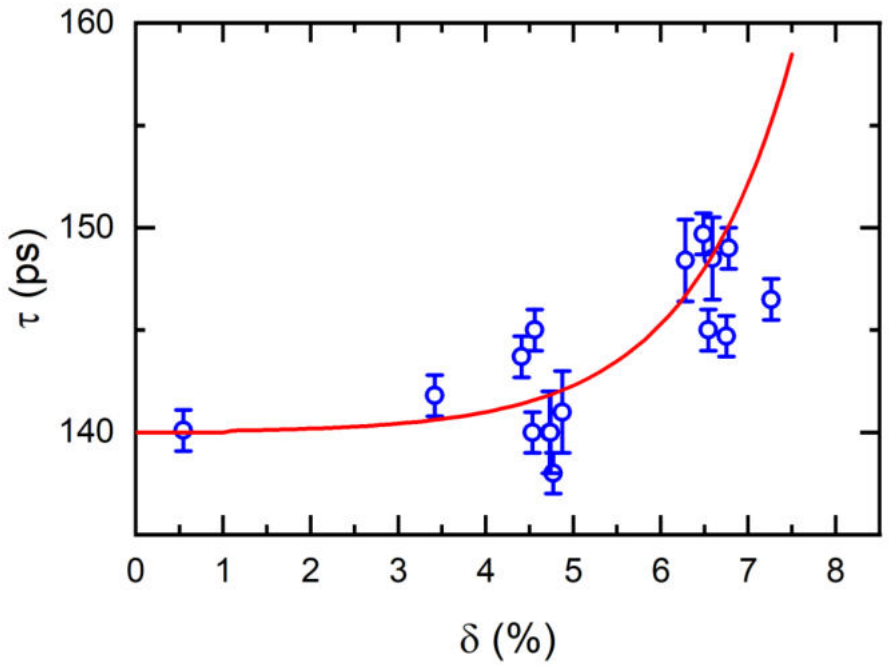
Positron lifetime investigations of HEAs

- positron lifetimes of samples annealed in vacuum at 1200°C for 2 h



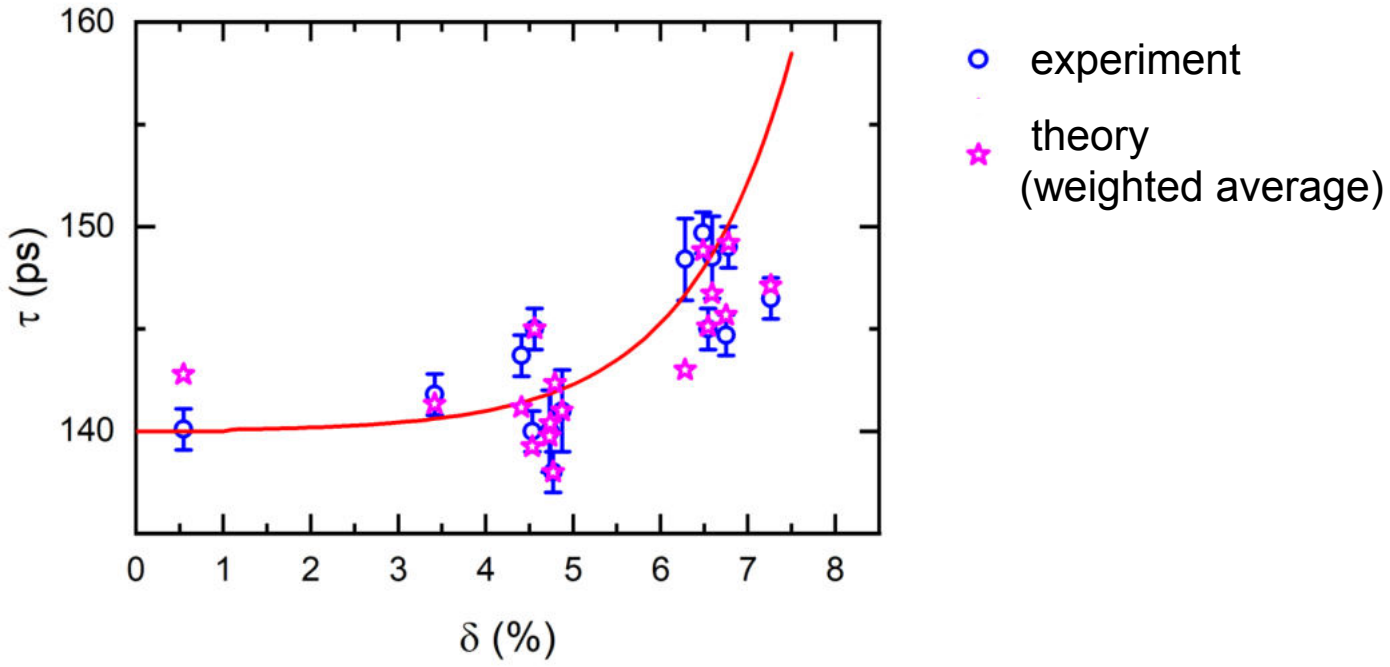
Positron lifetime investigations of HEAs

- positron lifetimes of samples annealed in vacuum at 1200°C for 2 h
- **bulk positron lifetime increases with increasing magnitude of lattice distortions**



Positron lifetime investigations of HEAs

- positron lifetimes of samples annealed in vacuum at 1200°C for 2 h
- **bulk positron lifetime increases with increasing magnitude of lattice distortions**



Positron lifetime investigations of HEAs

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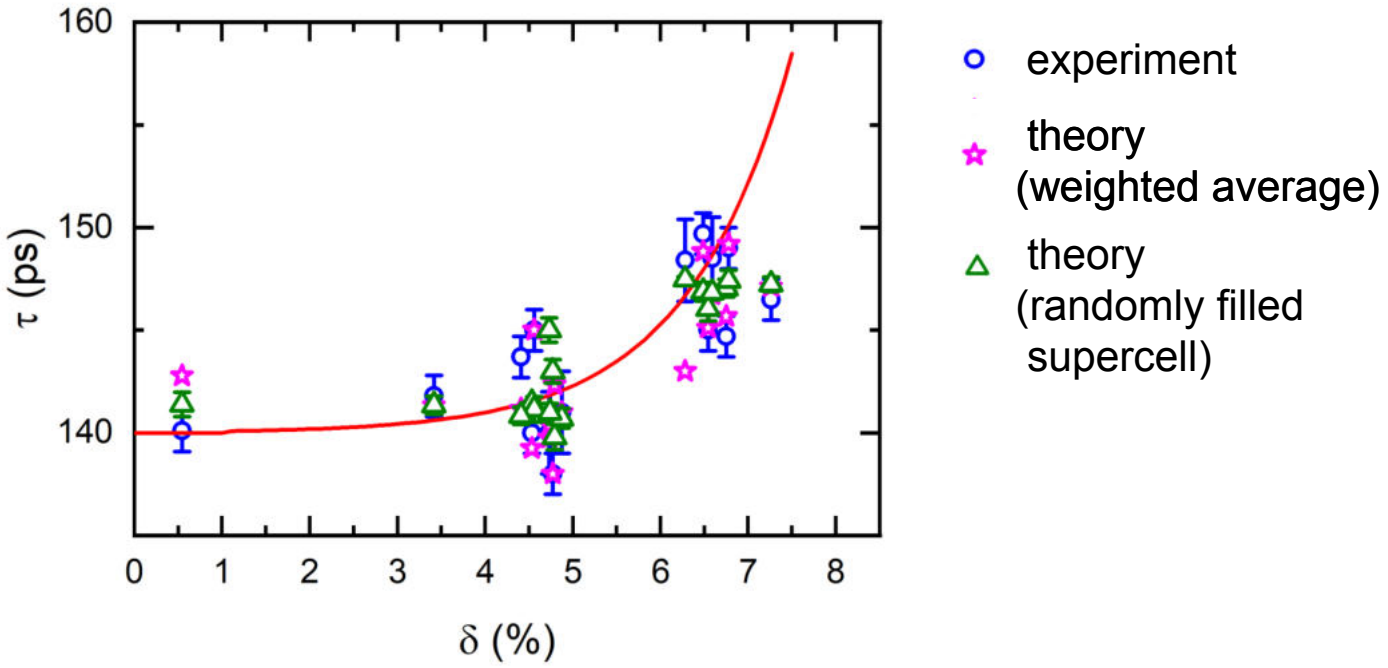
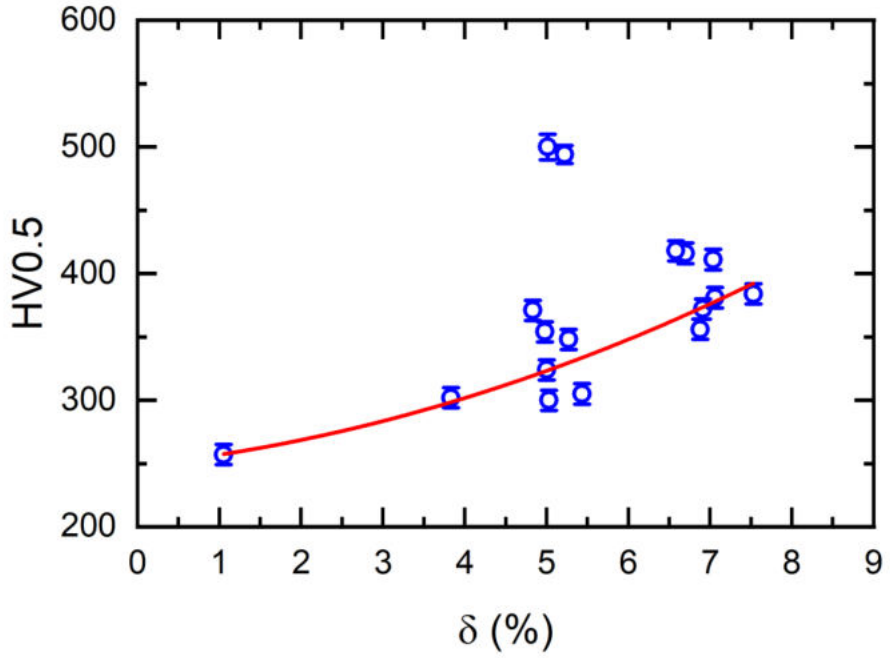


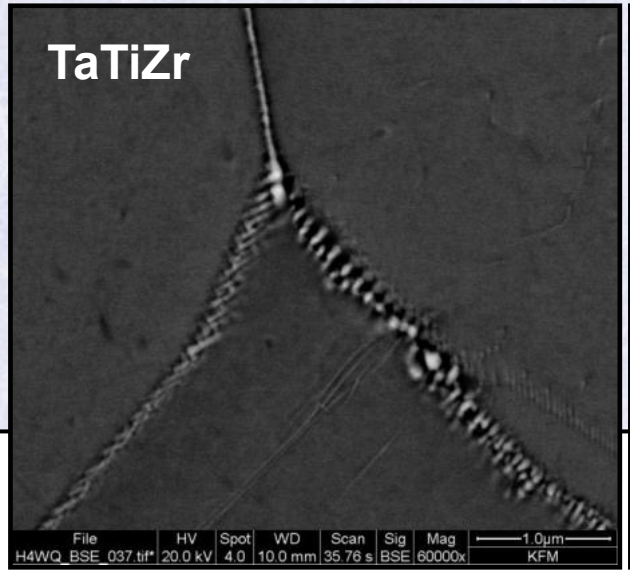
Hardness of HEAs

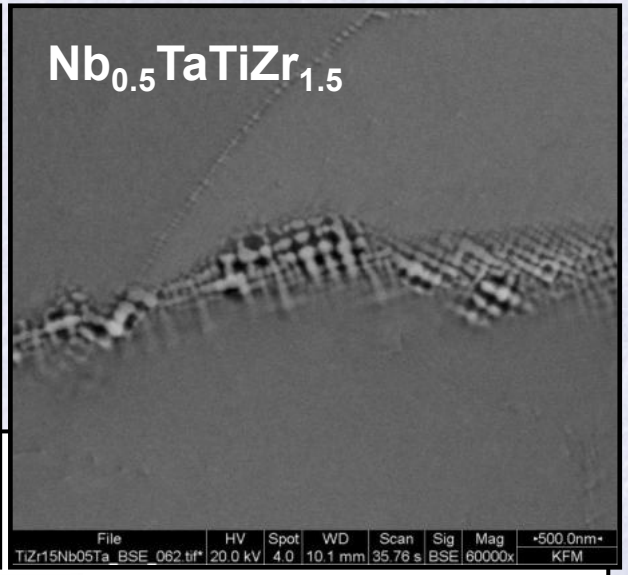
- Vickers hardness (HV), load 0.5 kg applied for 10 s
- **hardness increases with increasing magnitude of lattice distortions**

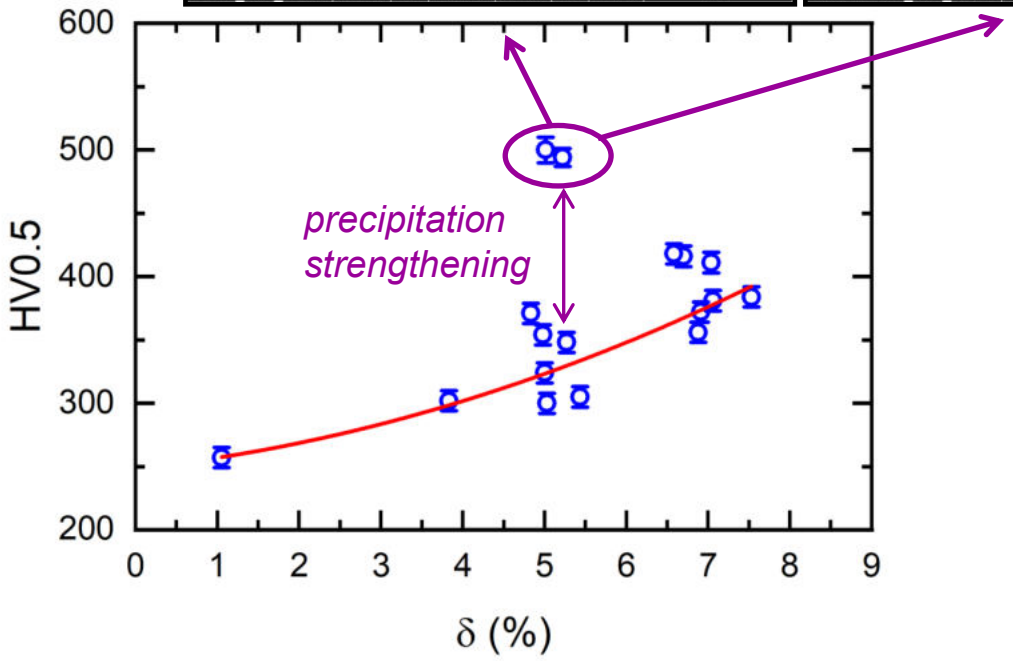


Hardness of HEAs

- additional precipitation strengthening
- Zr rich precipitates







Conclusions

- The lattice distortion effect was examined in set of complex concentrated alloys of refractory metals Hf, Nb, Ta, Ti, V, Zr

- Positrons actively search for interstitial regions with extended open volume

- Bulk positron lifetime increases with increasing magnitude of lattice distortions

- Positron lifetime spectroscopy enables direct measurement of lattice distortions

- Lattice distortions cause strengthening of alloys

- Positive correlation between hardness and atomic misfit parameter δ was observed

Acknowledgements

- This work was supported by the Czech Science Agency (project 21-16218S)
- Computational resources were supplied by the project "e-Infrastruktura CZ“ (e-INFRA LM2018140) provided within the program Projects of Large Research, Development and Innovations Infrastructures