RMC 8(+1)

THE INFLUENCE OF LATTICE ANISOTROPY ON THE LOCAL DYNAMICS IN HEXAGONAL TITANIUM AND ZIRCONIUM METALS

LATVIJAS UNIVERSITĀTES
CIETVIELU FIZIKAS INSTITŪTS
INSTITUTE OF SOLID STATE PHYSICS
UNIVERSITY OF LATVIA

Vitalijs Dimitrijevs, Alexei Kuzmin

dimitrijevs@cfi.lu.lv

OUTLINE

- Motivation
- Experiment and RMC analysis
- Radial Distribution Functions (RDFs) and Mean-Squared Relative Displacements (MSRDs) in hcp Ti and Zr metals
- Conclusions

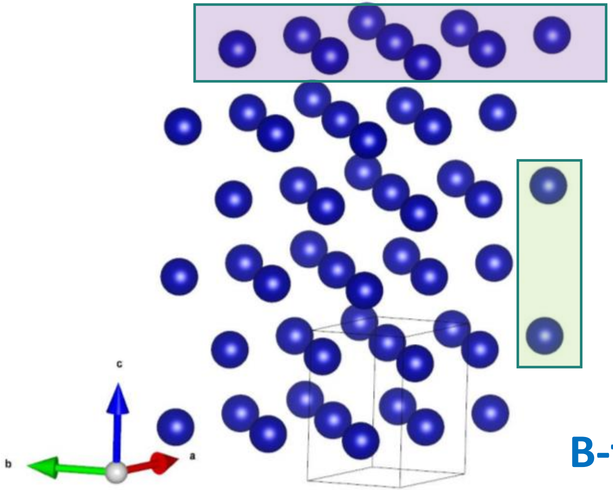
ANALYZED SAMPLES

- Titanium
- hcp
- c/a = 1.588
- IV B group
- Debye temperature = 250 (K)
- Thermal exp.= 8.5e-6 (1/K)
- Molar mass = 47.867 (g/mol)

- Zirconium
- hcp
- c/a = 1.593
- IV B group
- Debye temperature = 380 (K)
- Thermal exp.= 5.7e-6 (1/K)
- Molar mass = 91.224 (g/mol)

Analyzed samples have similar *hcp* structures, but different Debye temperatures and molar masses.

STRUCTURAL FEATURE OF HCP METALS



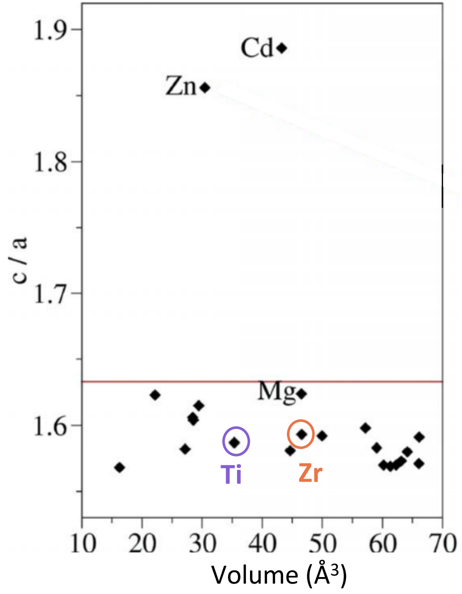
hcp structure

A-type – atoms in *ab* plane

C-type – atoms located along *c*-axis

B-type – all other atomic pairs

c/a ratio for hcp metals



Wedig, U.; Nuss, H.; Nuss, J.; Jansen, M.; Andrae, D.; Paulus, B.; Kirfel, A.; Weyrich, W. Erratum: Electronic Origin of the Structural Anomalies of Zinc and Cadmium. Z. Für Anorg. Allg. Chem. 1950 2013, 639 (12-13), 2112-2112

Because of structural anisotropy, we need to distinguish different types of atomic pairs!

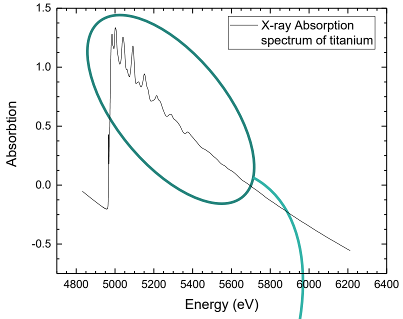
EXPERIMENT AND ANALYSIS OF DATA

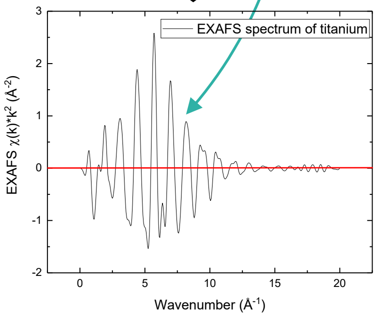
Samples – high purity metallic foils with thicknesses:

Zr – 0.020 mm (99.2%)

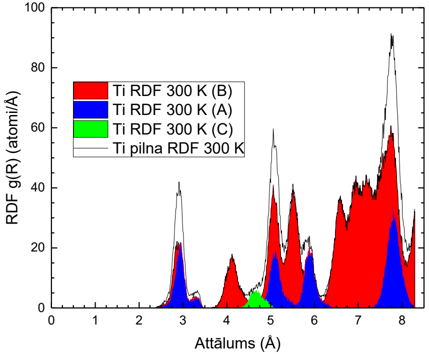
Ti – 0.004 mm (99.6%)

DESY P65 synchrotron beamline



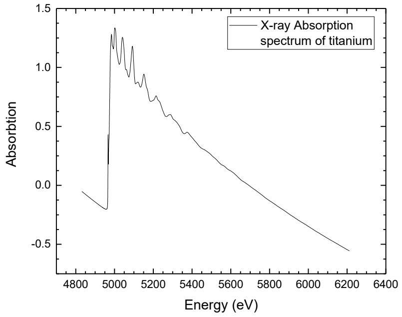


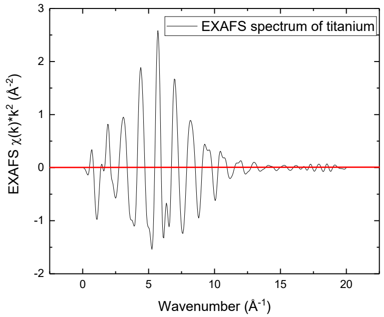
RMC

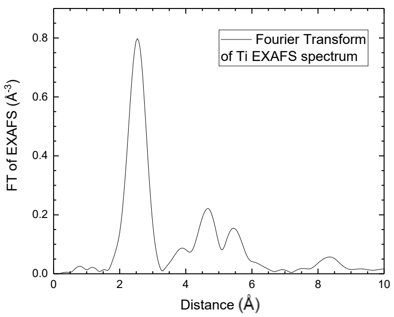


EXPERIMENTAL Ti AND Zr K-EDGE EXAFS SPECTRA

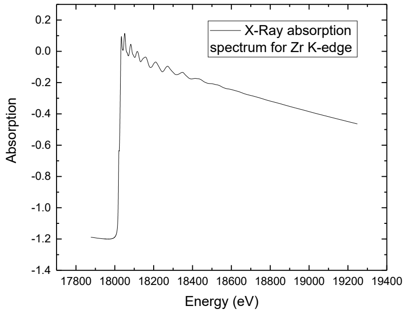
Ti

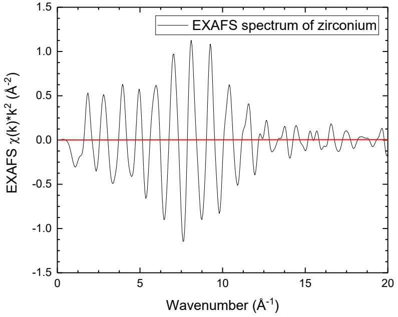


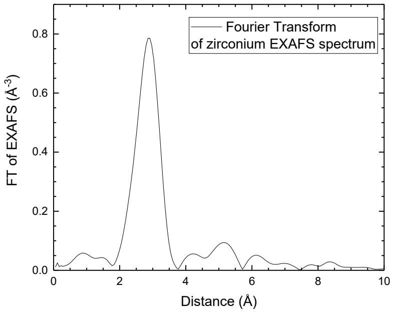




Zr

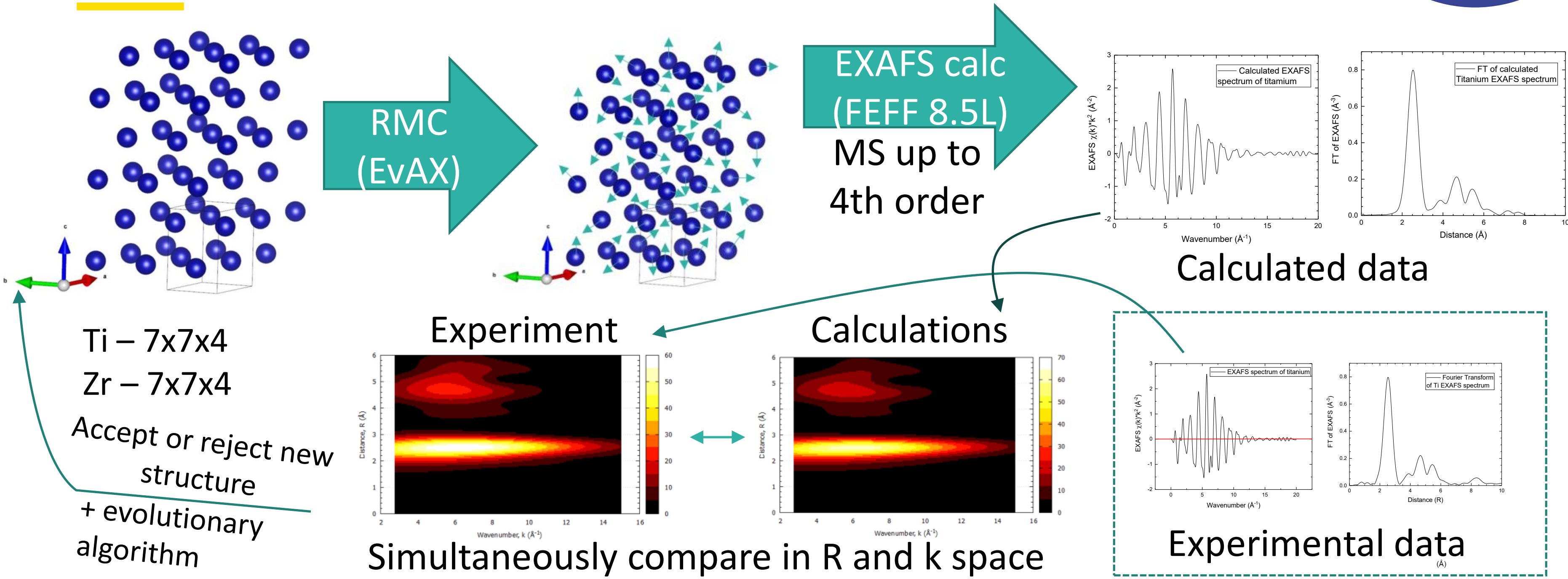






*7 temperatures (10 K…300 K)

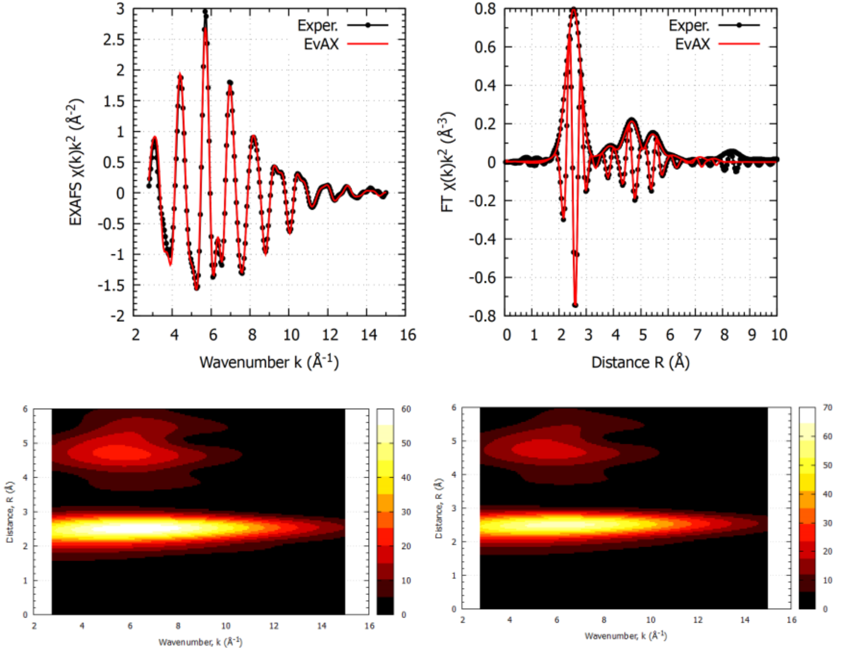
DETAILS OF RMC SIMULATIONS



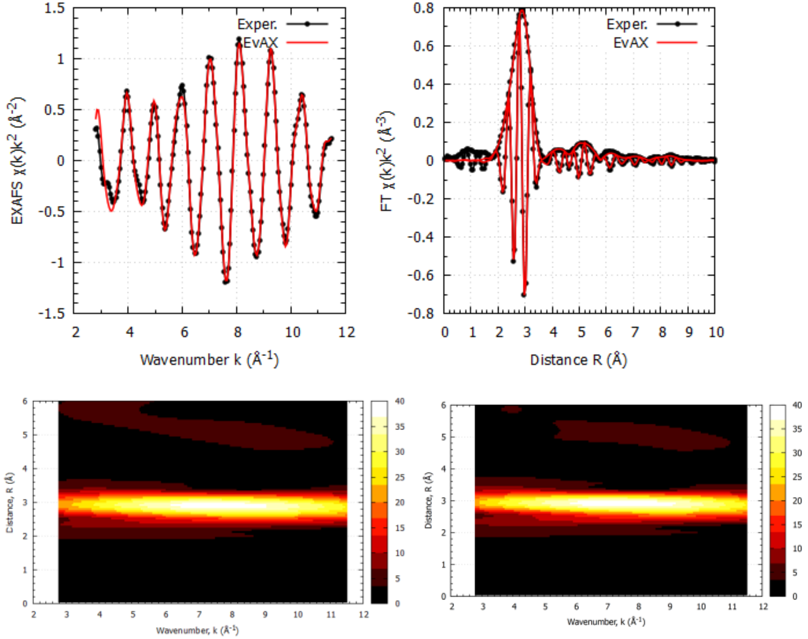
Timoshenko, Janis & Anspoks, Andris & Kalinko, Aleksandr & Kuzmin, Alexei. (2016). Local Structure of Cobalt Tungstate Revealed by EXAFS Spectroscopy and Reverse Monte Carlo/Evolutionary Algorithm Simulations. Zeitschrift für Physikalische Chemie. 230. 551-568. 10.1515/zpch-2015-0646.

RESULTS OF RMC SIMULATIONS

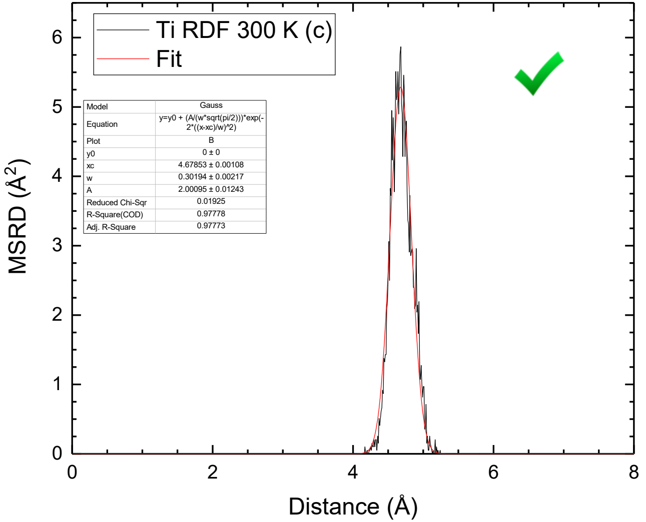
EvAX fit for Ti K edge

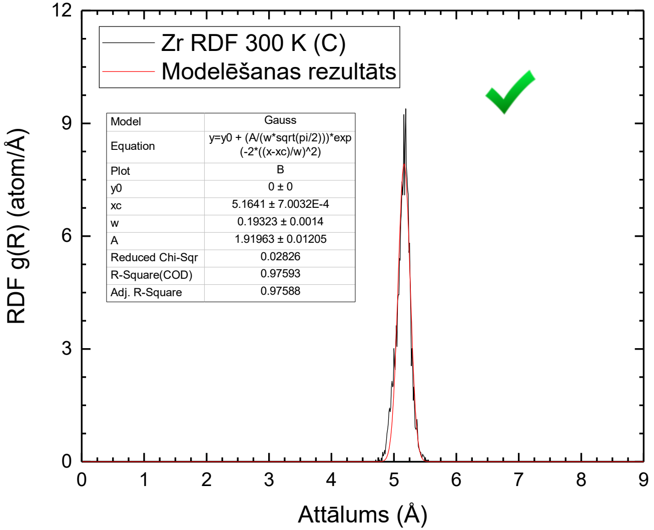


EvAX fit for Zr K edge



PARTIAL RADIAL DISTRIBUTION FUNCTION I



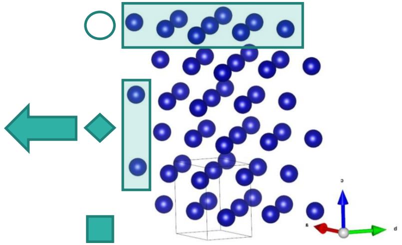


$$y = \frac{A}{w\sqrt{\frac{\pi}{2}}} e^{-2\frac{(x-x_c)^2}{w^2}}$$

A – coordination number

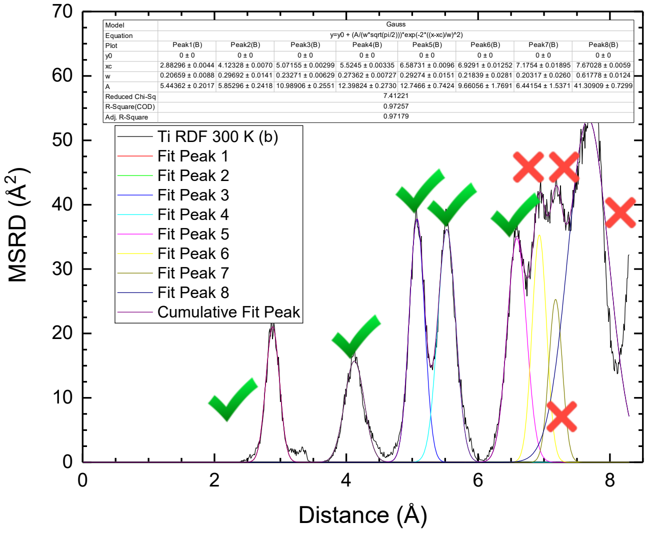
x_c – interatomic distance

w - $2\sqrt{MSRD}$

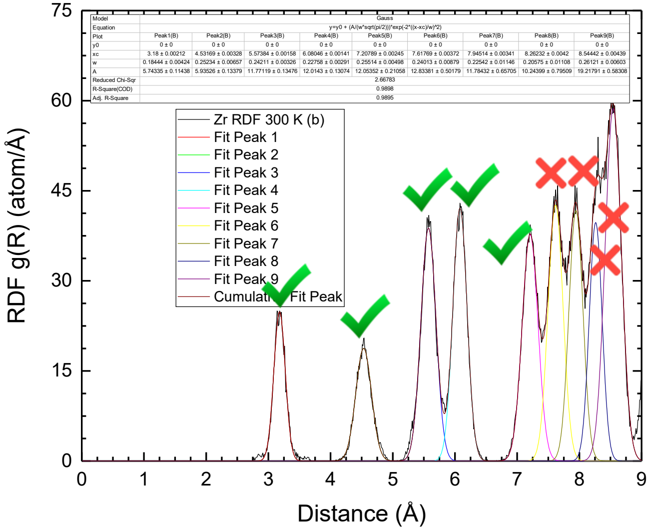


Radial Distribution function for C-type Ti-Ti and Zr-Zr atomic pairs at 300 K

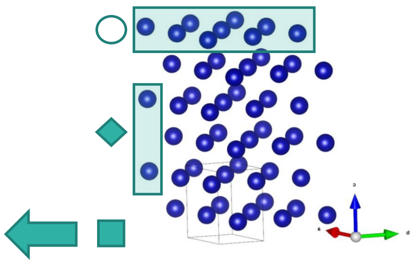
PARTIAL RADIAL DISTRIBUTION FUNCTION II



Model	Gauss							
Equation	y=y0 + (A/(w*sqrt(pi/2)))*exp(-2*((x-xc)/w)^2)							
Plot	Peak1(B)	Peak2(B)	Peak3(B)	Peak4(B)	Peak5(B)	Peak6(B)	Peak7(B)	Peak8(B)
y0	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0
xc	2.88296 ± 0.0044	4.12328 ± 0.0070	5.07155 ± 0.00299	5.5245 ± 0.00335	6.58731 ± 0.0096	6.9291 ± 0.01252	7.1754 ± 0.01895	7.67028 ± 0.0059
w	0.20659 ± 0.0088	0.29692 ± 0.0141	0.23271 ± 0.00629	0.27362 ± 0.00727	0.29274 ± 0.0151	0.21839 ± 0.0281	0.20317 ± 0.0260	0.61778 ± 0.0124
A	5.44362 ± 0.2017	5.85296 ± 0.2418	10.98906 ± 0.2551	12.39824 ± 0.2730	12.7466 ± 0.7424	9.66056 ± 1.7691	6.44154 ± 1.5371	41.30909 ± 0.7299
Reduced Chi-Sq	7.41221							
R-Square(COD)	0.97257							
Adj. R-Square	0.97179							

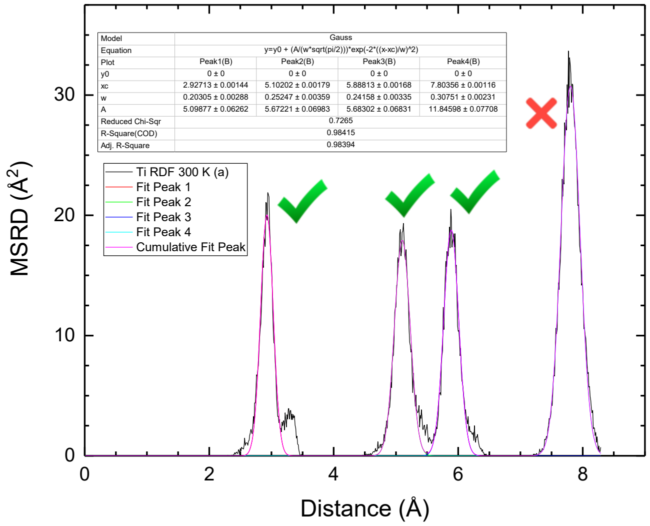


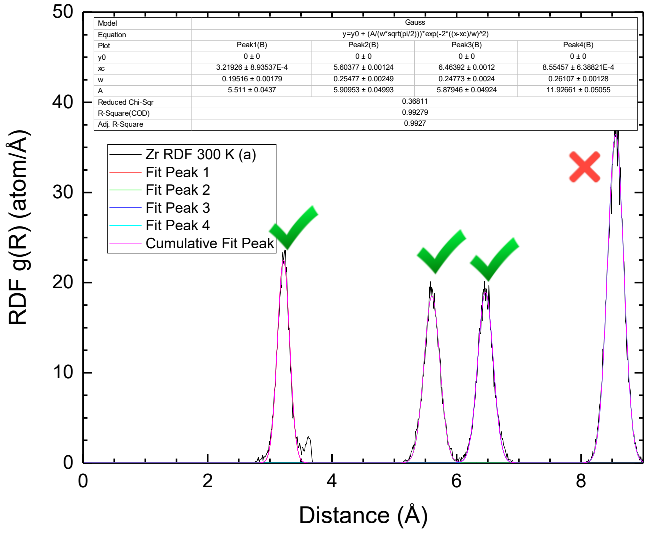
Model	Gauss								
Equation	y=y0 + (A/(w*sqrt(pi/2)))*exp(-2*((x-xc)/w)^2)								
Plot	Peak1(B)	Peak2(B)	Peak3(B)	Peak4(B)	Peak5(B)	Peak6(B)	Peak7(B)	Peak8(B)	Peak9(B)
y0	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0
xc	3.18 ± 0.00212	4.53169 ± 0.00328	5.57384 ± 0.00158	6.08046 ± 0.00141	7.20789 ± 0.00245	7.61769 ± 0.00372	7.94514 ± 0.00341	8.26232 ± 0.0042	8.54442 ± 0.00439
w	0.18444 ± 0.00424	0.25234 ± 0.00657	0.24211 ± 0.00326	0.22758 ± 0.00291	0.25514 ± 0.00498	0.24013 ± 0.00879	0.22542 ± 0.01146	0.20575 ± 0.01108	0.26121 ± 0.00603
A	5.74335 ± 0.11438	5.93526 ± 0.13379	11.77119 ± 0.13476	12.0143 ± 0.13074	12.05352 ± 0.21058	12.83381 ± 0.50179	11.78432 ± 0.65705	10.24399 ± 0.79509	19.21791 ± 0.58308
Reduced Chi-Sqr	2.66783								
R-Square(COD)	0.9898								
Adj. R-Square	0.9895								

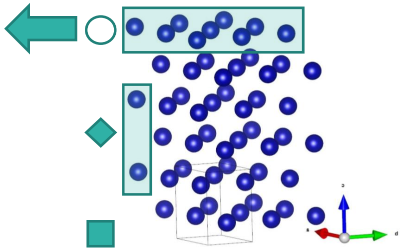


Radial Distribution function for B-type Ti-Ti and Zr-Zr atomic pairs at 300 K

PARTIAL RADIAL DISTRIBUTION FUNCTION III



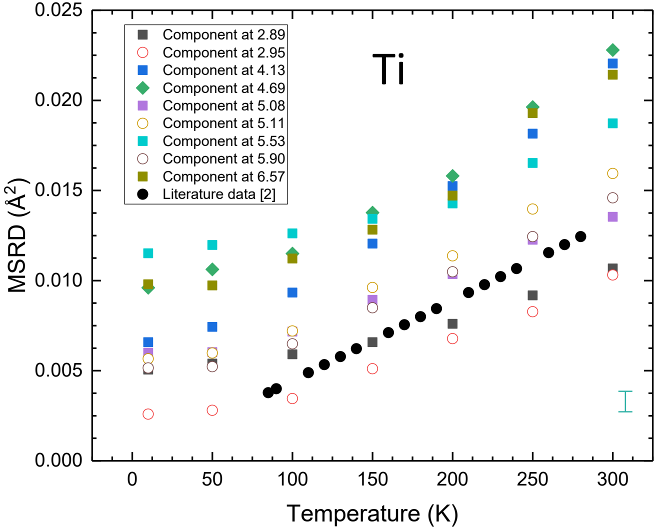


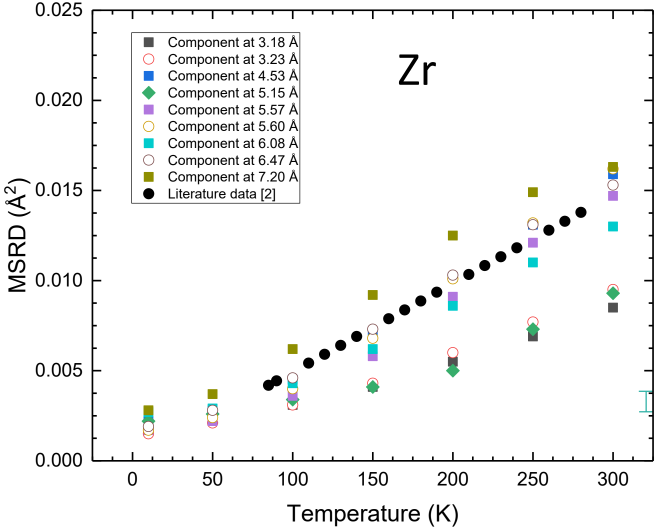


Radial Distribution function for A-type Ti-Ti and Zr-Zr atomic pairs at 300 K

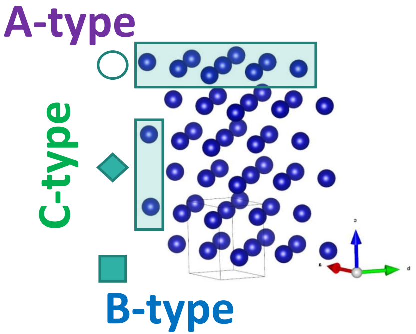
MSRD DEPENDENCE ON TEMPERATURE FOR Zr-Zr AND Ti-Ti ATOMIC PAIRS

$$MSRD(X_1\text{-}X_2) = MSD(X_1) + MSD(X_2) - DCF$$





Component – group of atoms fitted with one Gaussian function

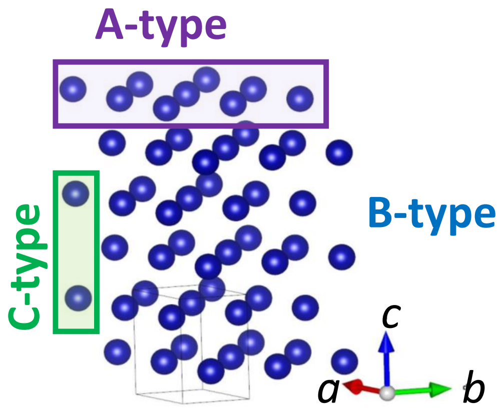


● Peng, L.-M.; Ren, G.; Dudarev, S. L.; Whelan, M. J. Debye-Waller Factors and Absorptive Scattering Factors of Elemental Crystals. *Acta Crystallogr. A* **1996**, *52* (3), 456–470.

$$\mathrm{MSRD}_{\parallel}^{\mathrm{ein}} = \hbar/(2\mu\omega_{\mathrm{E}})\coth(\beta\hbar\omega_{\mathrm{E}}/2).$$

SUMMARY

- Temperature dependent Ti and Zr K-edge EXAFS spectra of metal foils were analysed using the RMC method taking into account multiple-scattering contributions.
- Partial RDFs were successfully determined from the results of RMC simulations for three groups of non-equivalent atoms located in the ***ab*-plane**, along ***c*-axis**, and **all other** atoms.
- MSRD values for Ti-Ti and Zr-Zr atomic pairs were obtained from partial RDFs up to 6.5 Å.
- MSRD values for Ti-Ti and Zr-Zr atomic pairs differ significantly because of the differences in their molar masses and Debye temperatures.
- MSRD values for atomic pairs of **A-type** are in agreement with available literature data.



hcp structure

THANK YOU FOR YOUR ATTENTION!

LATVIJAS UNIVERSITĀTES
CIETVIELU FIZIKAS INSTITŪTS
INSTITUTE OF SOLID STATE PHYSICS
UNIVERSITY OF LATVIA

FLPP
FUNDAMENTAL AND APPLIED RESEARCH PROJECTS

The financial support from the Latvian Council of Science project No. lzp-2022/1-0608 is greatly acknowledged.