13.06.2024.

EXPLORING SUBSTRATE-INDUCED PHASE TRANSITION IN METALLIC CHROMIUM FOIL USING X-RAY ABSORPTION SPECTROSCOPY

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International Workshop on Recent Advances and Future Trends in EXAFS Spectroscopy

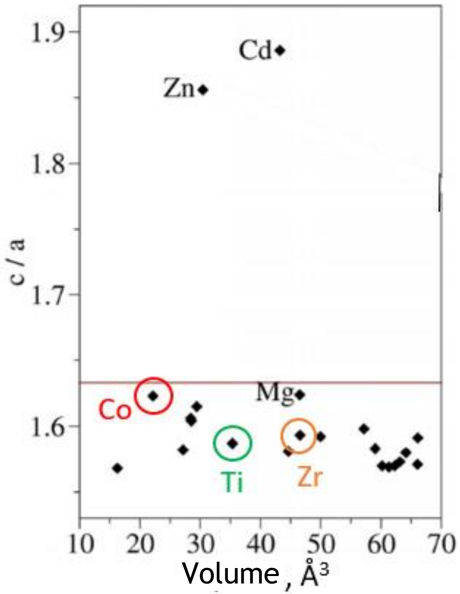
June 13-14, 2024, Riga, Latvia

OUTLINE

1. Anisotropy in metals
   - Samples
   - Experiment
   - Reverse Monte Carlo Simulations
   - Data analysis
   - Results
2. Thin chromium layer on a substrate

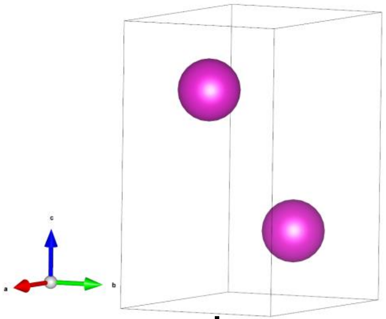
ANALYZED SAMPLES

Metallic foils were analyzed: purity 99.2%-99.99%; thickness 4-25 μm



Ti
Co
Zr

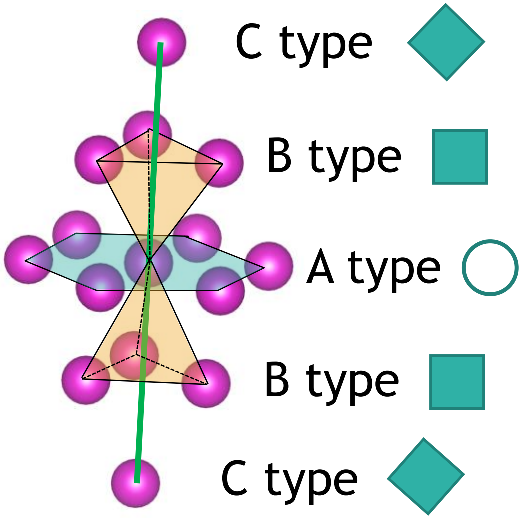
Cd
Zn



hcp

$a = b \neq c$

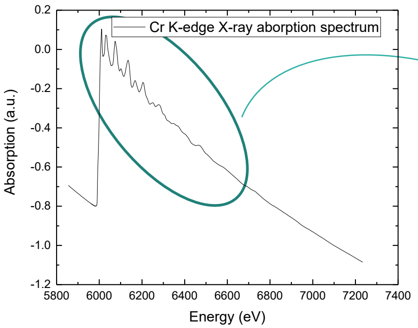
$90° = \alpha = \beta \neq \gamma = 120°$

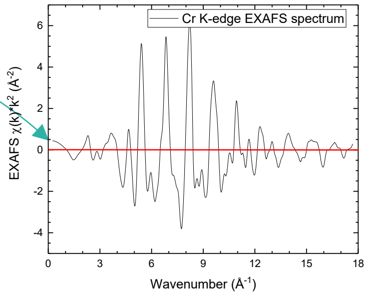


Wedig et al (2013), https://doi.org/10.1002/zaac.201300091

XAS EXPERIMENT AND OVERALL ANALYSIS ROUTE

DESY PETRA III P65 Beamline





Reverse Monte Carlo (RMC)

Analysis of coordinates

Or

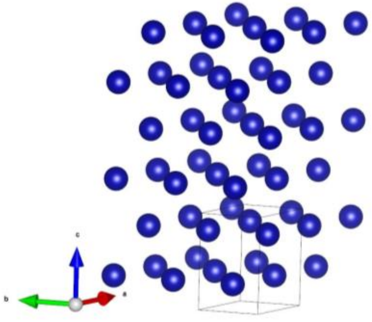
Analysis of Radial Distribution Functions (RDF)

Mean-square Relative Displacements (MSRDs)

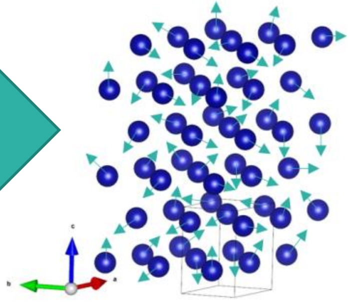
Welter et al (2019), https://doi.org/10.1063/1.5084603

DETAILS OF RMC SIMULATIONS

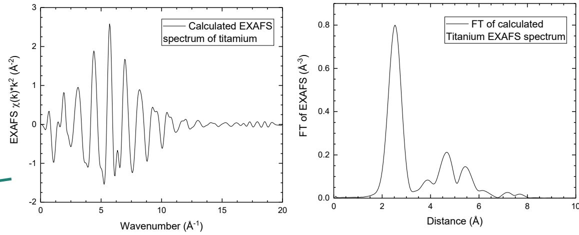
$$\chi(k) = \sum_{i=2}^{n} \chi_i(k) = \sum_{i=2}^{n} \sum_{j} A(k,R_j) \sin\left(2kR_j + \Phi(k,R_j)\right)$$



RMC (EvAX)

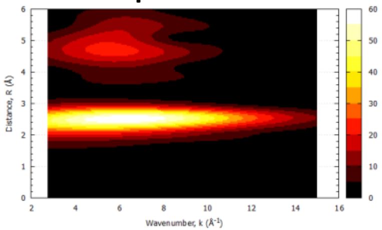


EXAFS calc (FEFF 8.5L)

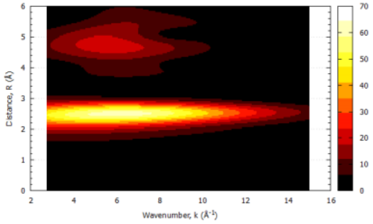


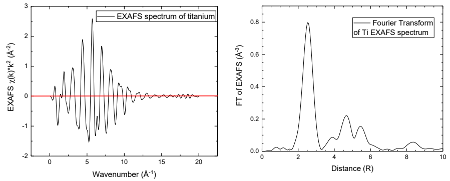
Calculated data

Experiment



Calculations





Experimental data

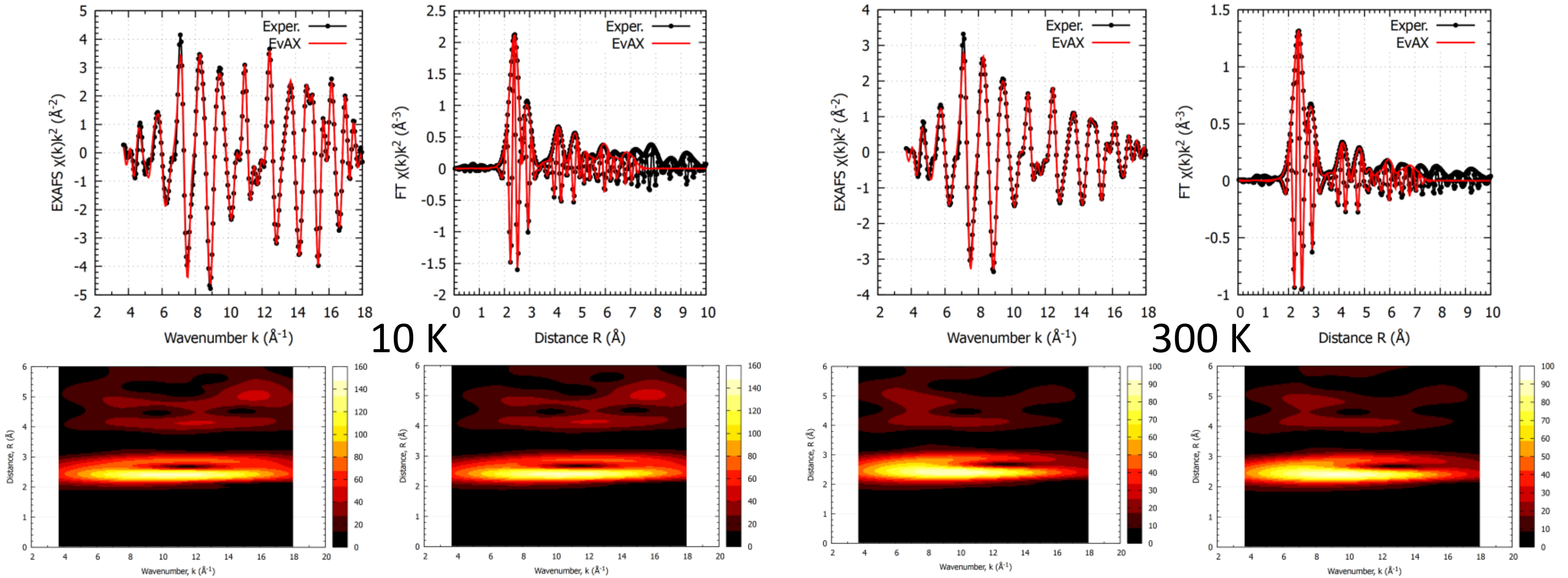
Accept or reject new structure

+ evolutionary algorithm

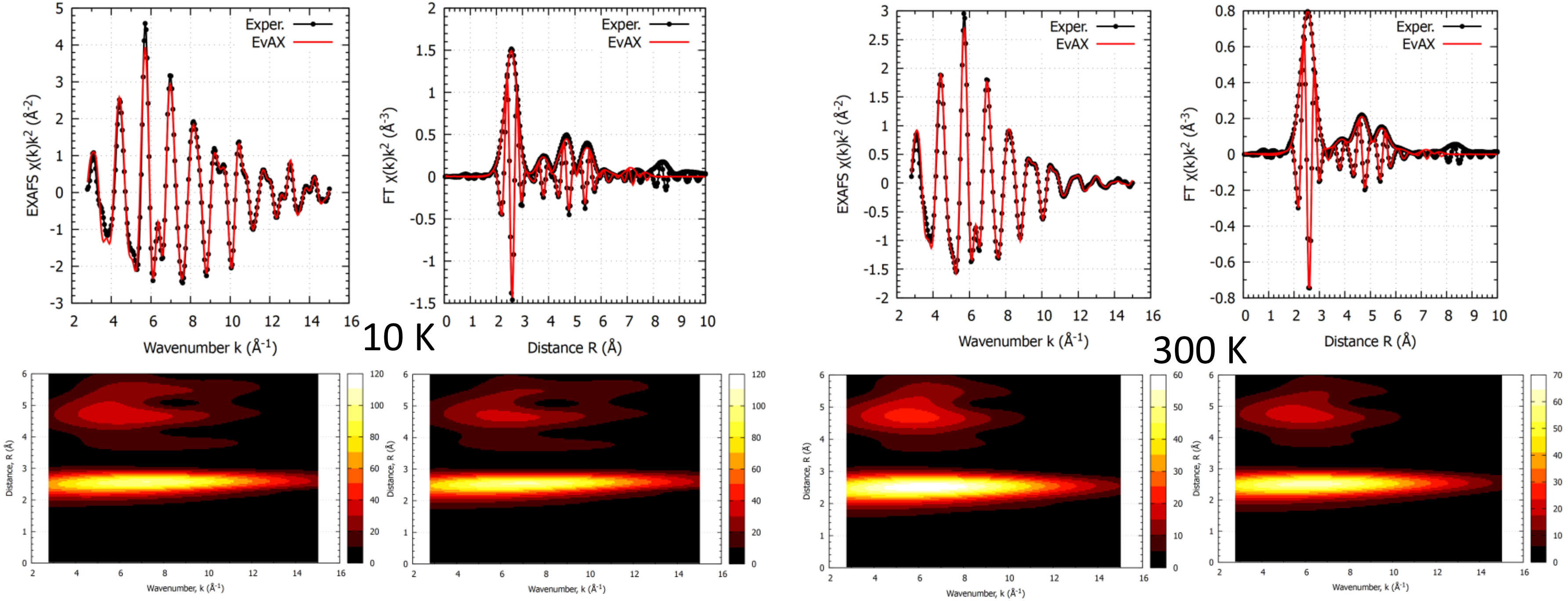
Simultaneously compare in R and k space

Rehr et al, https://doi.org/10.1103/RevModPhys.72.621
Timoshenko et al (2014), Doi: 10.1088/0953-8984/26/5/055401.

RMC FIT FOR MOLYBDENUM FOIL (BCC) AT 10 AND 300 K



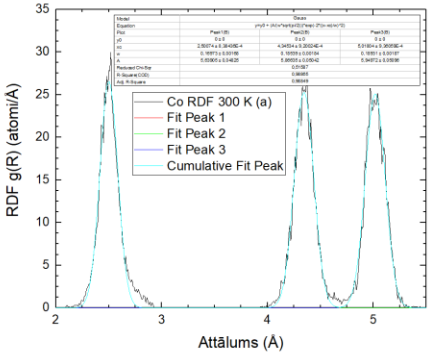
RMC FIT FOR TITANIUM FOIL (HCP) AT 10 AND 300 K



DATA ANALYSIS AFTER RMC

1

Analysis of RDF



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

A – number of atoms in a component
x_c – interatomic distance
σ^2 – **MSRD**

How to define atomic pair types?

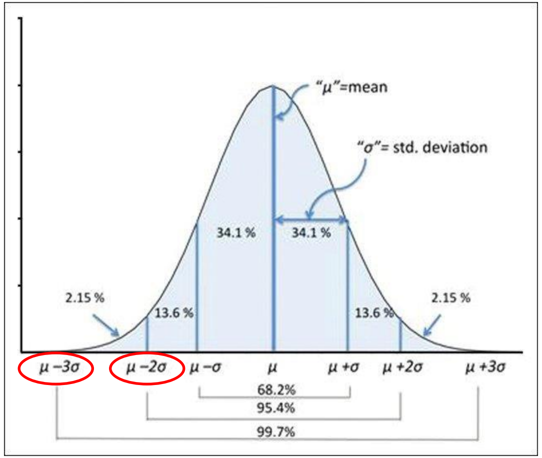
First way:
From final structure

Second way:
From equilibrium structure

2

Analysis of coordinates

$$\boldsymbol{MSRD} = \frac{1}{N}\sum_{k}^{N}(R_k - \bar{R})^2$$



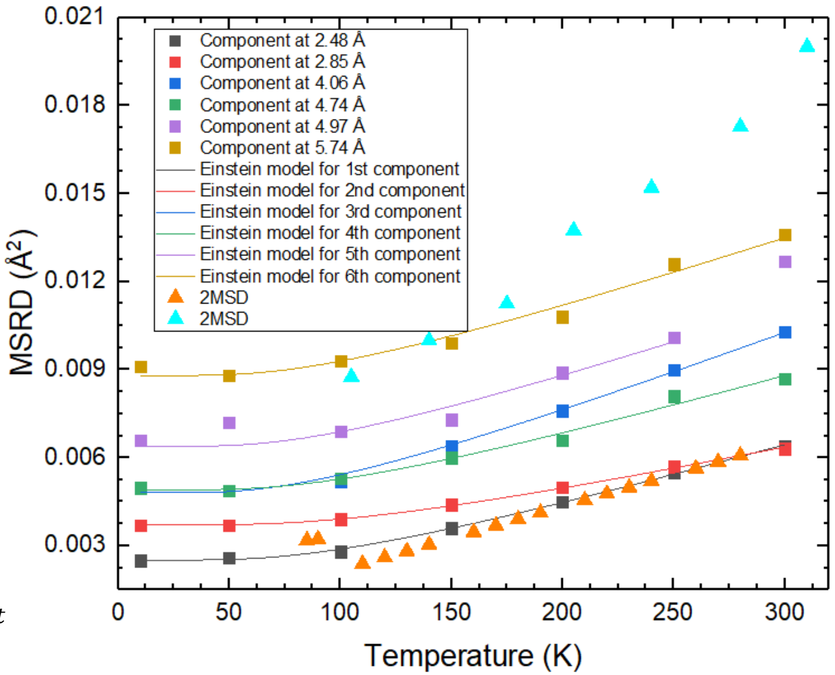
MSRD DEPENDENCE ON TEMPERATURE FOR Cr-Cr ATOMIC PAIRS (BCC)

Errors:
x axes ± 2 K
y axes ± 0.0005 Å²

Sample	Distance, Å	Pair type	Force constant, N/m
Bcc Cr	2,48	-	62,4 ± 0,8
	2,85		84 ± 1
	4,06		48 ± 1
	4,74		63 ± 2
	4,97		54 ± 4
	5,74		54 ± 3

$$\sigma^2(T) = \frac{\hbar}{2\mu\omega_E}\coth\left(\frac{\hbar\omega_E}{2k_BT}\right) + \sigma_{st}^2$$

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



Literature: MSD from phonon density of states

▲ 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. https://doi.org/10.1107/S010876739600089X

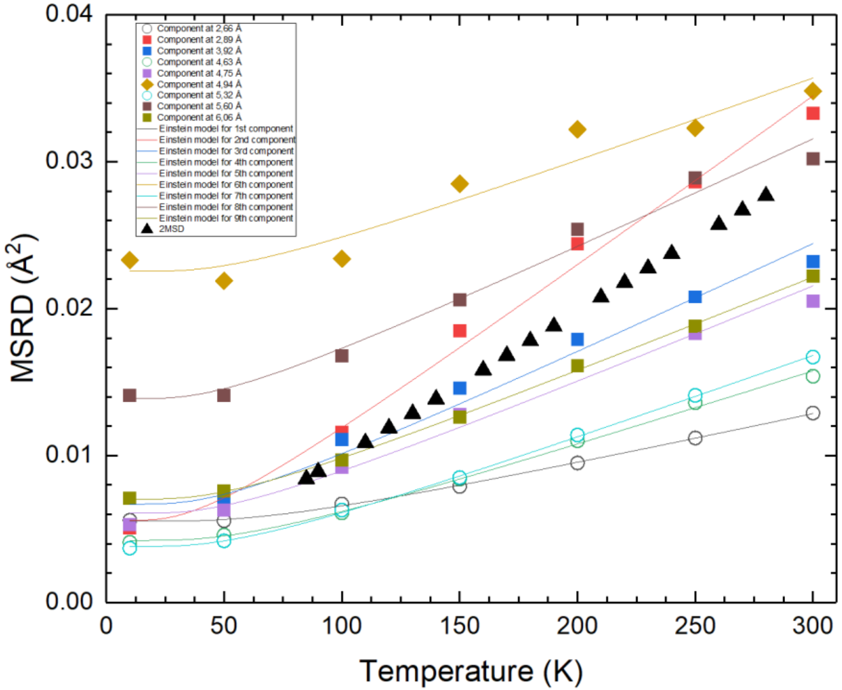
▲ Singh, N.; Sharma, P. K. Debye-Waller Factors of Cubic Metals. *Phys. Rev. B* **1971**, *3* (4), 1141–1148. https://doi.org/10.1103/PhysRevB.3.1141.

MSRD DEPENDENCE ON TEMPERATURE FOR Zn-Zn ATOMIC PAIRS (HCP)

Sample	Distance, Å	Pair type	Force constant, N/m
Zn	2,66	A	29,3 ± 0,4
	2,89	B	11,8 ± 0,4
	3,62	B	18,3 ± 1,1
	4,63	A	26,7 ± 0,5
	4,75	B	20,6 ± 1,1
	4,94	C	23 ± 2
	5,32	A	24,1 ± 0,2
	5,60	B	18,4 ± 1,0
	6,06	B	21,1 ± 0,2

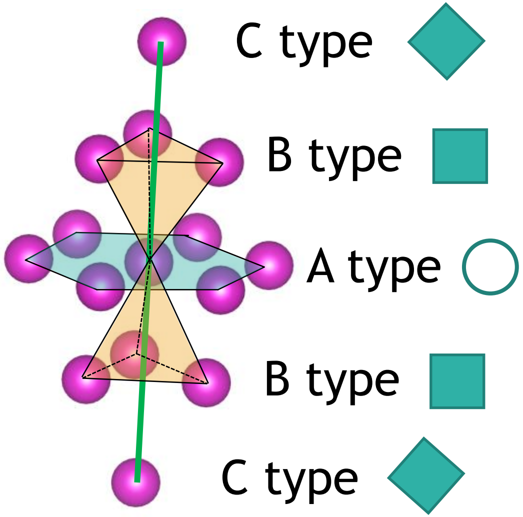
$$\sigma^2(T) = \frac{\hbar}{2\mu\omega_E}\coth\left(\frac{\hbar\omega_E}{2k_B T}\right) + \sigma_{st}^2$$

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



$c/a = 1.86$
$c/a_i = 1.63$

Errors:
x axes ± 2 K
y axes ± 0.002 Å²



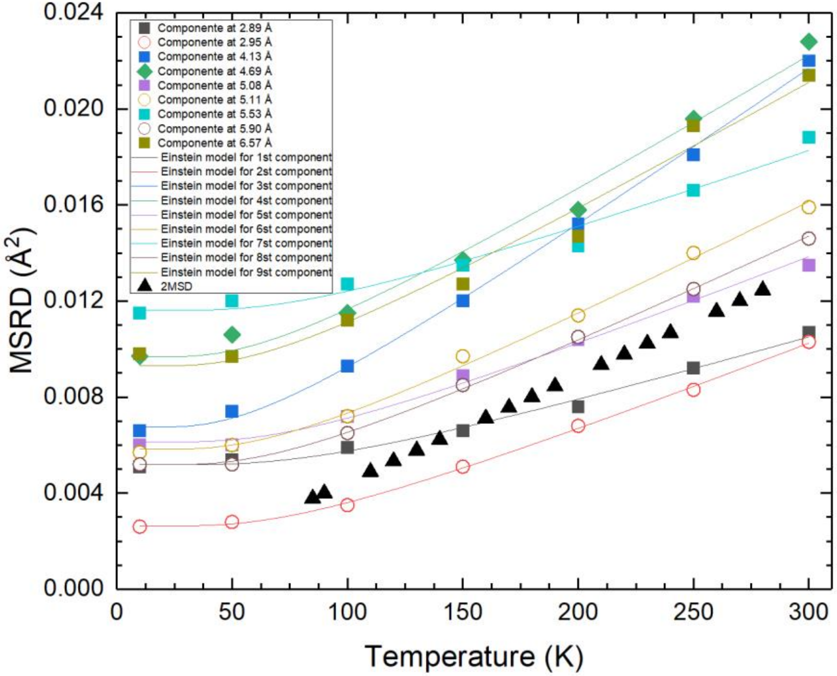
https://doi.org/10.1107/S010876739600089X

MSRD DEPENDENCE ON TEMPERATURE FOR Ti-Ti ATOMIC PAIRS (HCP)

Sample	Distance, Å	Pair type	Force constant, N/m
Ti	2,89	B	48,3 ± 1,6
	2,95	A	36,2 ± 0,4
	4,13	B	20,5 ± 0,3
	4,69	C	23,8 ± 1,0
	5,08	B	35,8 ± 1,1
	5,11	A	28,1 ± 0,6
	5,53	B	40 ± 3
	5,90	A	30,0 ± 0,3
	6,57	B	25,1 ± 1,5

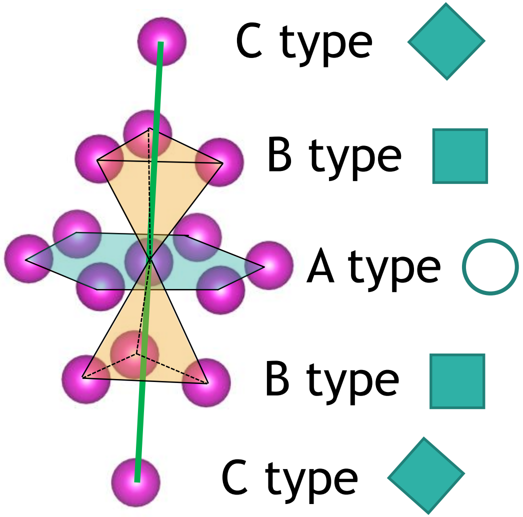
$$\sigma^2(T) = \frac{\hbar}{2\mu\omega_E}\coth\left(\frac{\hbar\omega_E}{2k_B T}\right) + \sigma_{st}^2$$

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



c/a = 1.59
c/a_i = 1.63

Errors:
x axes ± 2 K
y axes ± 0.001 Å²

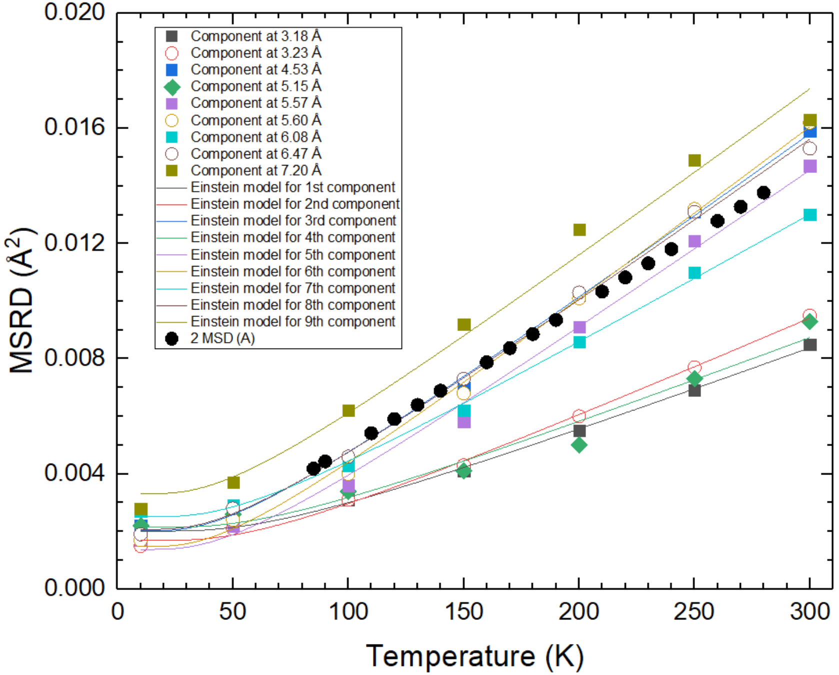


MSRD DEPENDENCE ON TEMPERATURE FOR Zr-Zr ATOMIC PAIRS (HCP)

Sample	Distance, Å	Pair type	Force constant, N/m
Zr	3,18	B	46,7 ± 0,7
	3,23	A	39,5 ± 0,8
	4,53	B	23,7 ± 0,4
	5,15	C	45 ± 3
	5,57	B	24,7 ± 0,8
	5,60	A	22,6 ± 0,5
	6,08	B	30,2 ± 0,5
	6,47	A	24,1 ± 0,4
	7,20	B	23,3 ± 1,2

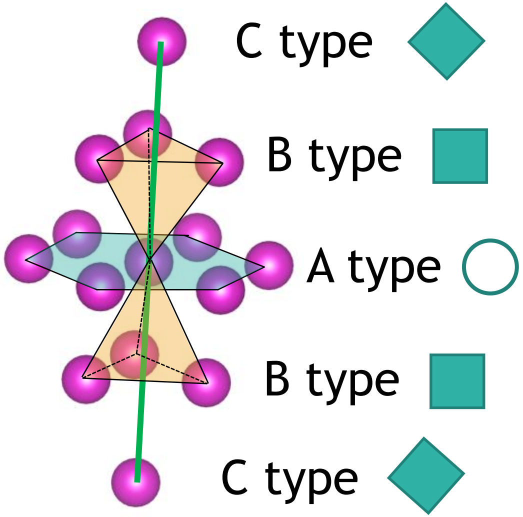
$$\sigma^2(T) = \frac{\hbar}{2\mu\omega_E}\coth\left(\frac{\hbar\omega_E}{2k_BT}\right) + \sigma_{st}^2$$

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



$c/a = 1.59$
$c/a_i = 1.63$

Errors:
x axes ± 2 K
y axes ± 0.002 Å²



https://doi.org/10.1107/S010876739600089X

CONCLUSION ABOUT FIRST PART

- The use of partial Radial Distribution Functions (RDF) enabled the analysis of overlapping components, corresponding to various atomic pair types
- The anisotropy of local lattice dynamics in hcp metals is influenced by c/a ratio and can be observed from MSRD dependence on temperature

THIN CHROMIUM LAYER ON A SUBSTRATE

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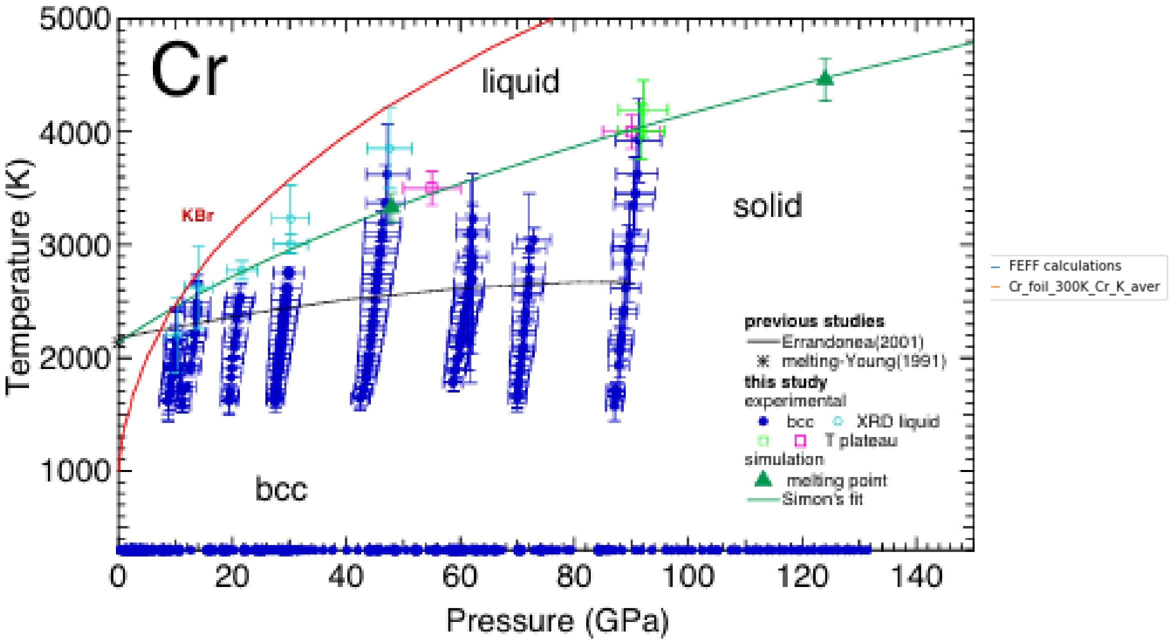
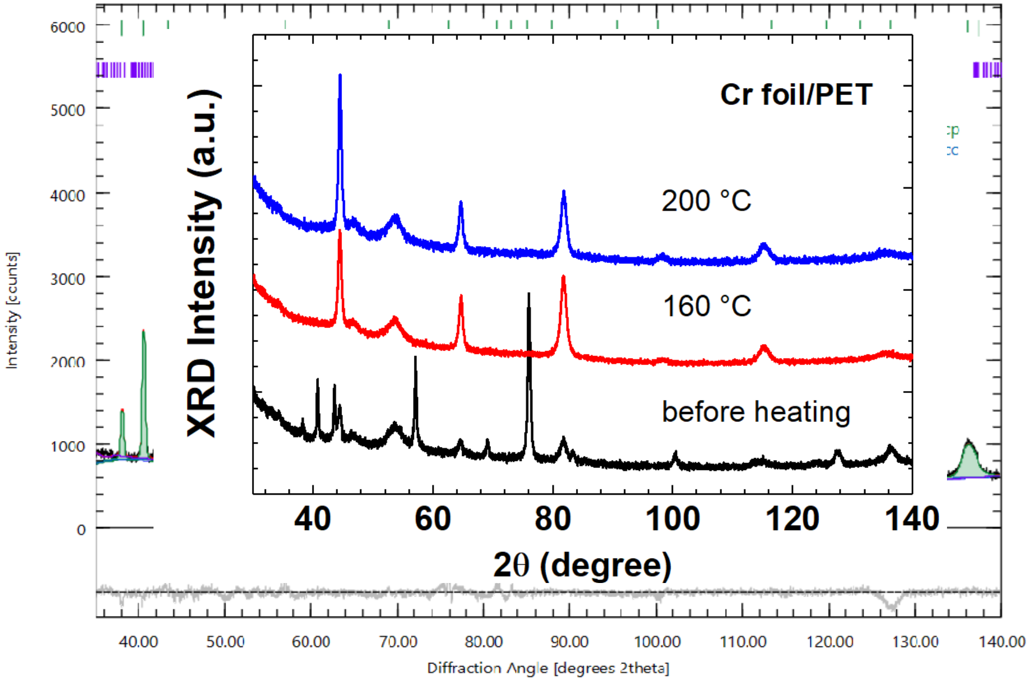
NOTHING WAS WRONG UNTIL…

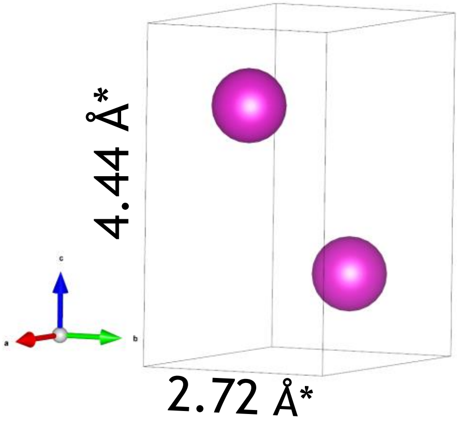
Cr 2 μm + 125 μm
Polyester substrate



XRD ANALYSIS BY RIETVELD REFINMENT



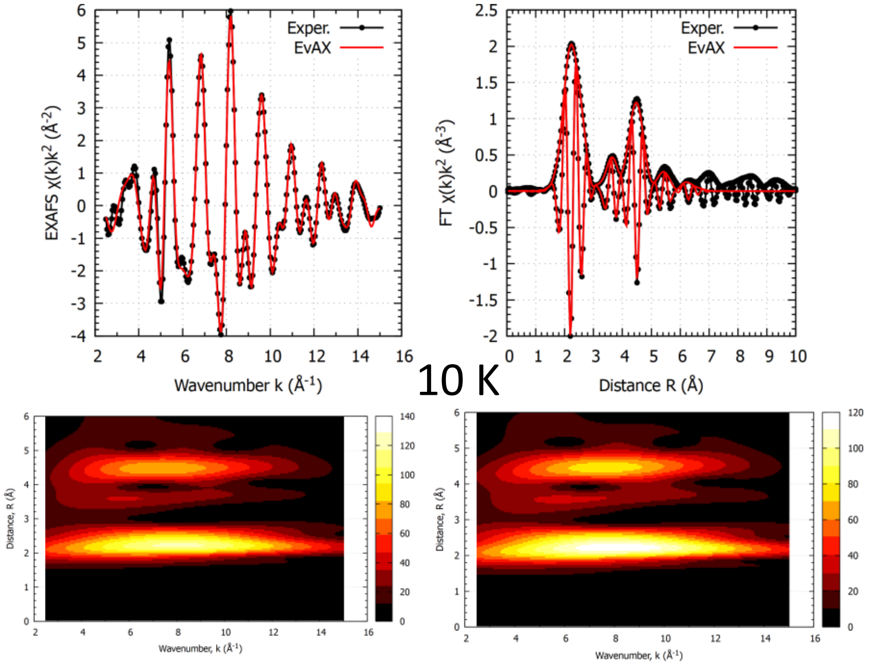
c/a = 1.63



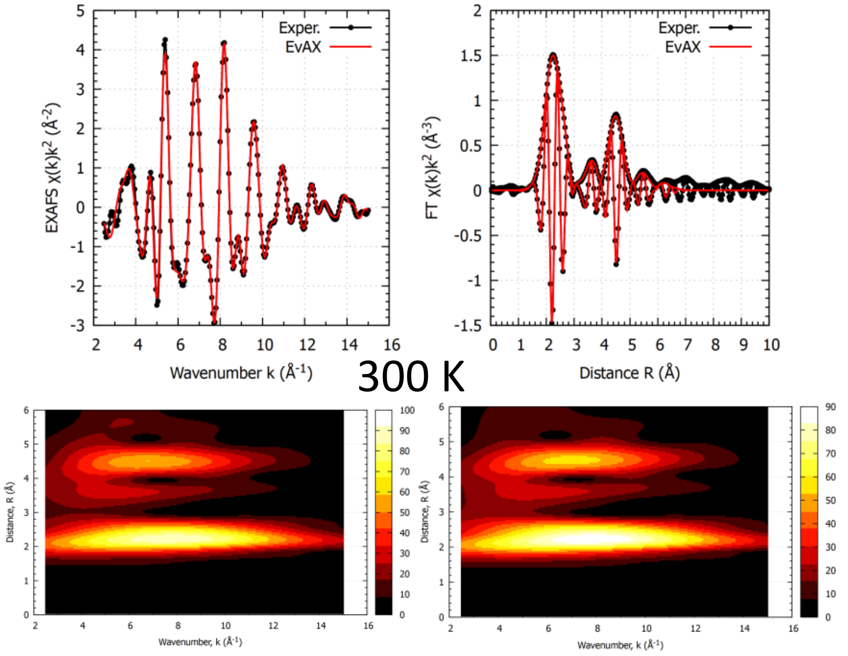
*Rounded data

Error ± 0.00001

RMC FIT FOR CHROMIUM FOIL (BCC) AT 10 AND 300 K

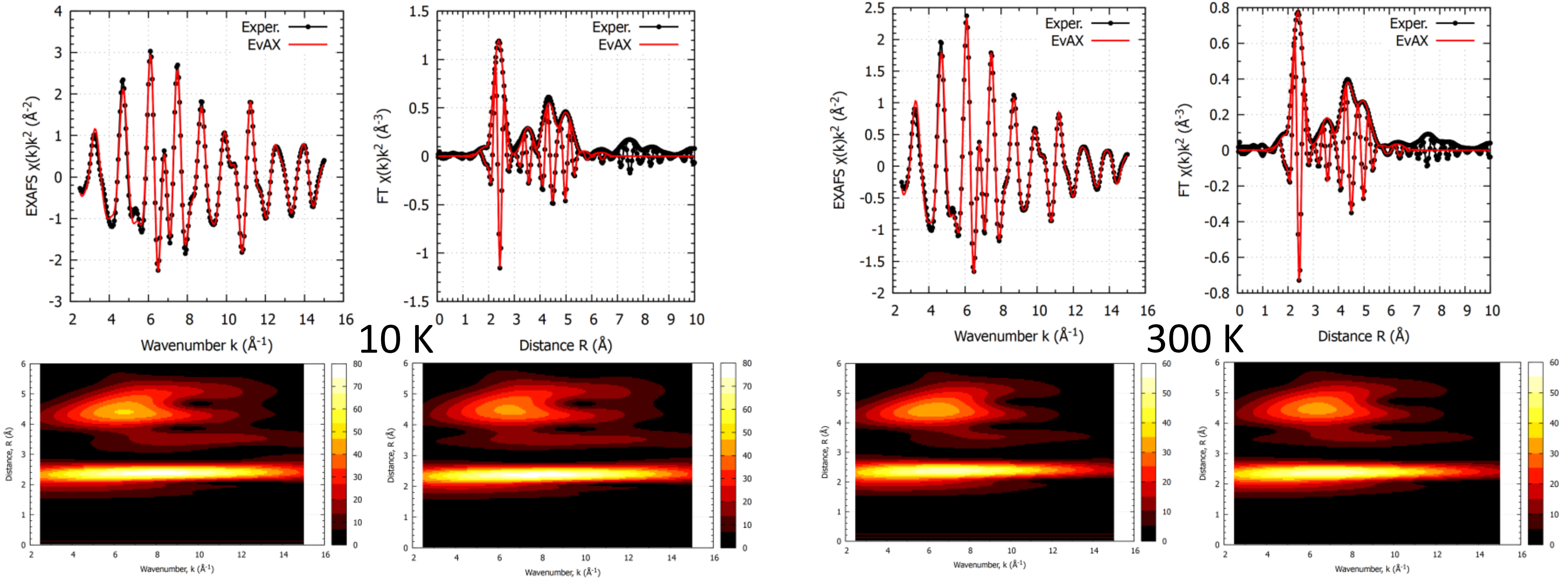


10 K



300 K

RMC FIT FOR CHROMIUM FOIL (HCP) AT 10 AND 300 K

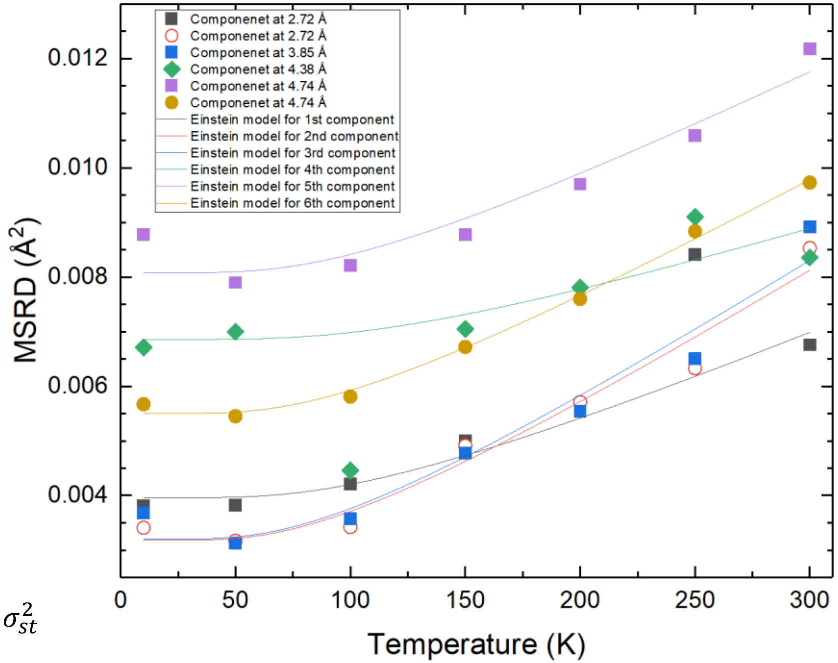


MSRD DEPENDENCE ON TEMPERATURE FOR Cr-Cr ATOMIC PAIRS (HCP)

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

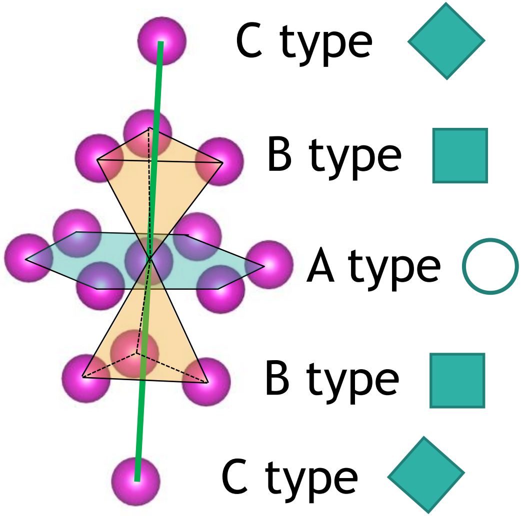
Sample	Distance, Å	Pair type	Force constant, N/m
Hcp Cr	2,72	B	53 ± 2
	2,72	A	69 ± 7
	3,85	B	53 ± 2
	4,38	C	34 ± 5
	4,74	B	64 ± 7
	4,74	A	70 ± 3

$$\sigma^2(T) = \frac{\hbar}{2\mu\omega_E}\coth\left(\frac{\hbar\omega_E}{2k_BT}\right) + \sigma_{st}^2$$



$c/a = 1.63$
$c/a_i = 1.63$

Errors:
x axes ± 2 K
y axes ± 0.002 Å²



CONCLUSIONS FROM SECOND PART

- Substrate-induced phase transition from bcc to hcp phase was detected in thin chromium foil on polyester substrate. This effect is analogous to that produced by the application of negative pressure
- Contrary to the anisotropic local lattice dynamics typically observed in hexagonal close-packed metals, hcp chromium exhibits isotropic behavior

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THANKS FOR YOUR ATTENTION!

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