



Solving EXAFS puzzle using reverse Monte Carlo simulations

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<https://www.facebook.com/EXAFSLab/>



Acknowledgements



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Dr. Janis Timoshenko



Dr. Aleksandr Kalinko

Dr. Edmund Welter



Talk Outline

- **History of synchrotron radiation research in Latvia**
 - Experiments → Effects → Data analysis
- **Advanced methods for X-ray absorption spectra interpretation**
 - Effect of disorder & multiple-scattering (MS)
- **Reverse Monte Carlo (RMC) simulations**
 - Capabilities and limitations
 - Crystalline germanium
 - Lattice dynamics in 2D compounds
- **RMC applications to multicomponent materials**
 - NiWO_4 - ZnWO_4 solid solutions
 - medium-entropy $(\text{MnNiCuZn})\text{WO}_4$ and a high-entropy $(\text{MnCoNiCuZn})\text{WO}_4$ tungstates
- **Conclusions**



Synchrotron radiation research in Latvia (I)

1982 - 93

1993 - 2006

2000 - ...

A. Kuzmin (1985)
MS

(1997)
MD

J. Timoshenko (2006)
RMC/MD

A. Kalinko (2007)
MD/DFT

A. Anspoks (2009)
MD/RMC

I. Jonane/Pudza (2013)
RMC/RIXS



Juris Purans (1982)

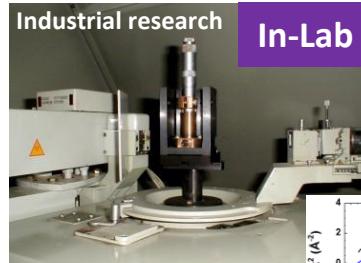
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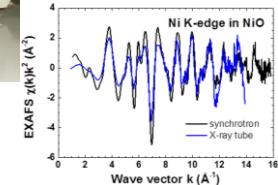
VEPP-4



LURE



1989-1997



PETRA III
Hamburg, Germany



MAX IV
Lund, Sweden



SOLEIL
Gif-sur-Yvette Cedex, France



ALBA
Cerdanyola del Vallès (Barcelona), Spain



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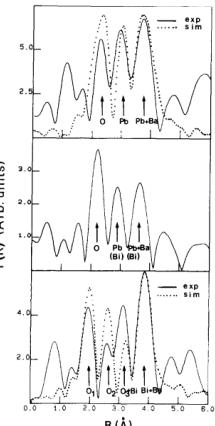
Synchrotron radiation research in Latvia (II)

1982 - 93

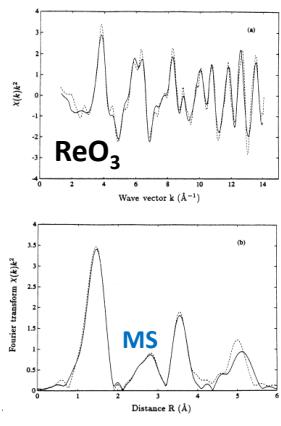
J. Purans
FT/SS

A. Kuzmin (1985)
MS

EXAFS OF THE SUPERCONDUCTING OXIDE $BaPb_x\cdot Bi_2O_3$
A. Balazsotti
Dipartimento di Fisica, Università di Roma II, 00173 Roma, Italy
A.P. Monastyrskii
Engineering Physics Institute, 115409 Moscow, U.S.S.R.
N. Metra
Scuola Normale Superiore, 56100 Pisa, Italy
J. Purans
Institute of Solid State Physics, Latvian University, 226063 Riga, Latvia
(Received 15 October 1983 by P. Basani)



PHYSICAL REVIEW B
VOLUME 41, NUMBER 5
1 FEBRUARY 1990
X-ray-absorption study of rhenium L_2 and L_3 edges in ReO_3 : Multiple-scattering approach
A. Kuzmin and J. Purans
Institute of Solid State Physics, Kengaraga 8, 296004 Riga, Latvia
M. Benito and C. R. Nardi
Istituto Nazionale di Fisica Nucleare, Casella Postale 13, 00044 Frascati, Italy
(Received 20 July 1990)



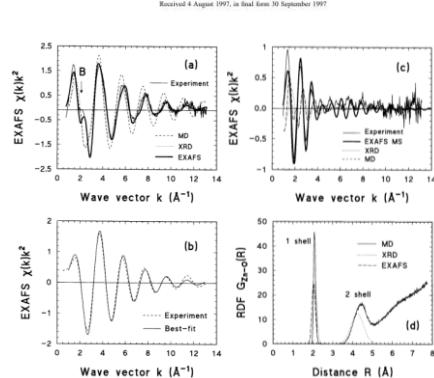
1993 - 2006

(1997)
MD

X-ray absorption spectroscopy and molecular dynamics studies of Zn^{2+} hydration in aqueous solutions

A. Kuzmin¹, S. Obst¹ and J. Purans²
¹ Institute of Solid State Physics, Kengaraga 8, LV-1063 Riga, Latvia
² Institute für Kristallographie, Freie Universität Berlin, Takustrasse 6, 14195 Berlin, Germany

Received 4 August 1997, in final form 30 September 1997



J. Timoshenko (2006)
RMC

Reverse Monte Carlo modeling of thermal disorder in crystalline materials from EXAFS spectra
Janis Timoshenko^a, Alexei Kuzmin, Juris Purans
Institute of Solid State Physics, University of Latvia, Kengaraga street 8, LV-1063 Riga, Latvia

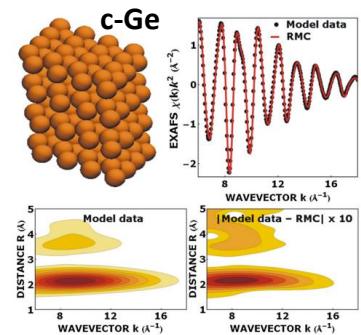


Study of the thermochromic phase transition in $CuMo_{1-x}W_xO_4$ solid solutions at the W L_3 -edge by resonant X-ray emission spectroscopy
Inga Pudza^{a,b}, Aleksandr Kalinko^{a,b}, Arturs Cintins^a, Alexei Kuzmin^{b,c}
^a Institute of Solid State Physics, University of Latvia, Kengaraga street 8, Riga, LV-1063 Latvia
^b Department of Chemistry and Center for Sustainable Systems Design, Paderborn University, Paderborn, Germany

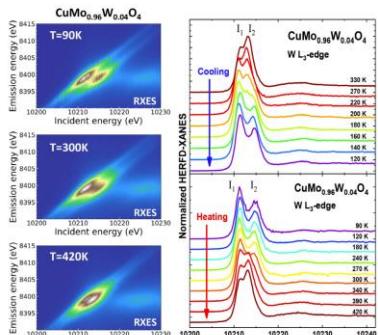


2000 - ...

A. Kalinko (2007)
MD/DFT



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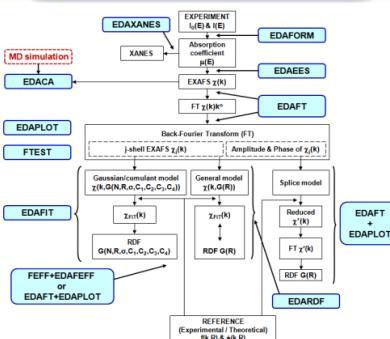
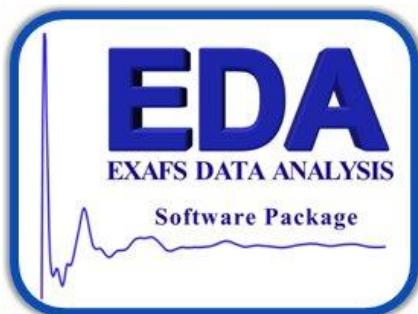
DEC VAX / Intel 8086/286

Intel 386/486

Intel® XEON



EXAFS analysis



A. Kuzmin,
Physica B 208&209 (1995) 175-176.

XAS data analysis in Latvia

Molecular Dynamics + EXAFS (MD-EXAFS)

EDACA

Author: Dr. phys. Alexei Kuzmin
Institute of Solid State Physics
University of Latvia
Kengaraga street 8, LV-1063 Riga, Latvia
Internet: <http://www.dragon.lv/edaca>
E-mail: a.kuzmin@cfi.lu.lv

Preface

X-ray absorption spectroscopy (XAS) at synchrotron radiation sources is a structural tool providing information on the local atomic and electronic structure around an atom of a particular type. Today XAS is successfully applied to a study of crystalline, nanocrystalline and disordered solids, liquids and gases in a wide range of external conditions defined by temperature, pressure, etc. The size of the region, probed by XAS, depends on the degree of thermal and static disorder present in a material and is limited by the mean-free path of the excited photoelectron. Typically the information reach region extended up to 3-10 Å around the absorbing atom.

An advantage of the XAS method is its sensitivity to many-atom distribution functions, giving rise to multiple-scattering (MS) contributions, and to correlation effects in atom dynamics. Note that accurate account of both effects is still challenging.

The time-scale (about $10^{-15}\text{--}10^{-16}$ s) of the X-ray absorption process is much shorter than the characteristic time (about $10^{-13}\text{--}10^{-14}$ s) of thermal vibrations. Therefore, the atoms may be considered as frozen at their instantaneous positions during a single photoabsorption process, and the total experimentally measured X-ray absorption spectrum corresponds to the configurational average of all atomic positions over the time of the experiment. This situation can be straightforwardly modelled combining the molecular dynamics (MD) simulation with the extended X-ray absorption fine structure (EXAFS) calculations, known as the MD-EXAFS approach.

Finally, the agreement between the experimental and configuration-averaged EXAFS spectra can be used to validate the accuracy of the interatomic potential (force-field) models employed in the MD simulations.

**A. Kuzmin and R.A. Evarestov,
J. Phys.: Condens. Matter 21 (2009) 055401.**

Reverse Monte Carlo (RMC) with Evolutionary Algorithm

Evolutionary Algorithm for EXAFS analysis

HOME METHOD DOWNLOADS APPLICATIONS

EvAX code:

SIMULATION-BASED ANALYSIS OF EXAFS DATA FOR CRYSTALLINE AND NANOCRYSTALLINE MATERIALS

This web-page is a home for a novel simulation-based scheme, developed to probe the local structural and thermal disorder in crystalline and nanocrystalline materials by analyzing fine structure of X-ray absorption spectra (EXAFS). We believe that the proposed method improves the accuracy of currently available approaches for EXAFS analysis, especially in the case of strongly distorted local environment. The method is implemented in freely available EvAX code (see Downloads section).

[READ MORE](#)

WHY TO TRY EVAX?



MULTIPLE-SCATTERING EFFECTS

To benefit from structural information, hidden in the contribution of multiple-scattering effects and of distant coordination shells, EvAX code provides great flexibility for treating all important scattering paths with user-specified precision.

[READ MORE](#)



EVOLUTIONARY ALGORITHM

The optimization process that employs the power of evolutionary algorithm allows much more efficient exploration of the possible configuration space and makes feasible advanced analysis of complex compounds with low symmetry even with only decent computational resources available.

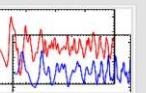
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WAVELET TRANSFORM

The representation of EXAFS spectra in k- and R-spaces simultaneously using Morlet wavelet transform allows one to obtain more information from the same experimental data and to have much better control over the difference between the experimental and calculated EXAFS data.

[READ MORE](#)



ANALYSIS OF EXAFS AT SEVERAL EDGES

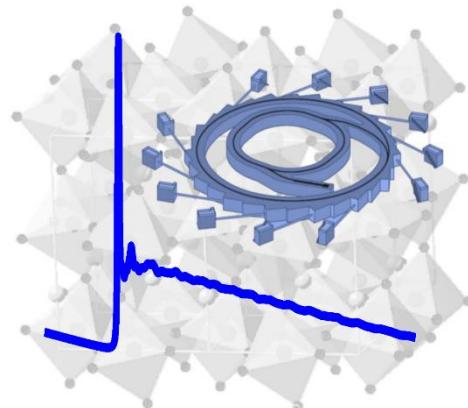
EvAX code allows to construct an unambiguous single structure model, consistent with EXAFS data, acquired at several absorption edges.

[READ MORE](#)

J. Timoshenko, A. Kuzmin, J. Purans,
J. Phys.: Condens. Matter 26 (2014) 055401.

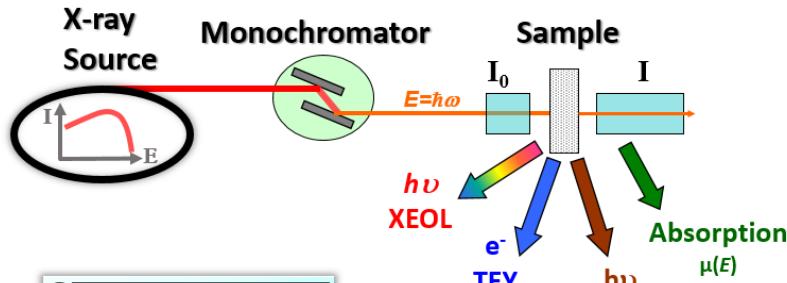
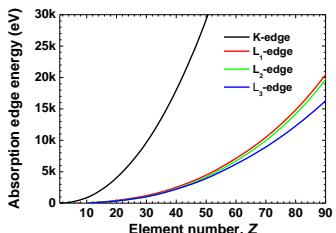


Advanced methods for X-ray absorption spectra interpretation



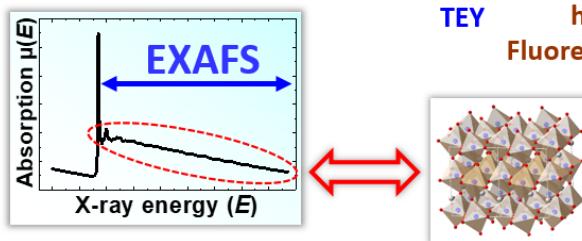
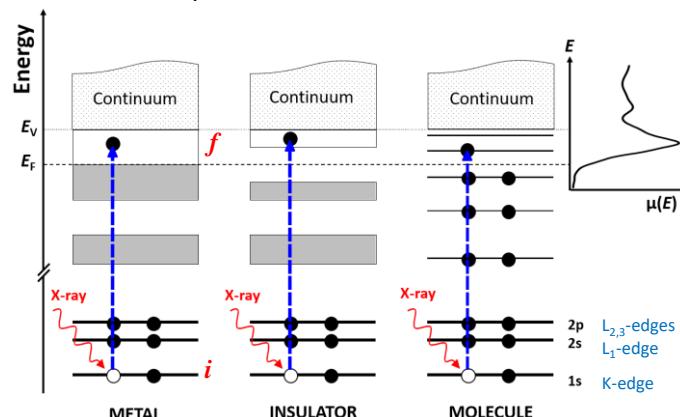
Basics of X-ray absorption spectroscopy (XAS)

X-rays:
soft (<5 keV)
hard (>5 keV)



Fermi's Golden Rule:

$$\mu(E) \propto \sum_f |\langle f | \hat{H} | i \rangle|^2 \delta(E_f - E_i - \hbar\omega)$$



Characteristic time of X-ray absorption process:

$$t_{ab} \sim 10^{-15}-10^{-16} \text{ s}$$

Characteristic time of thermal vibrations:

$$t_{th} \sim 10^{-13}-10^{-14} \text{ s}$$

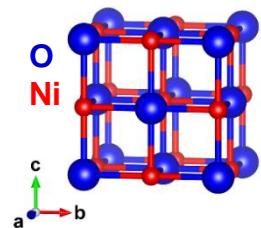
$$\mu(E) = \frac{1}{x} \ln \left(\frac{I_0(E)}{I(E)} \right)$$

$$\mu(E) \propto \frac{I_{\text{fluo}}(E)}{I_0(E)}$$

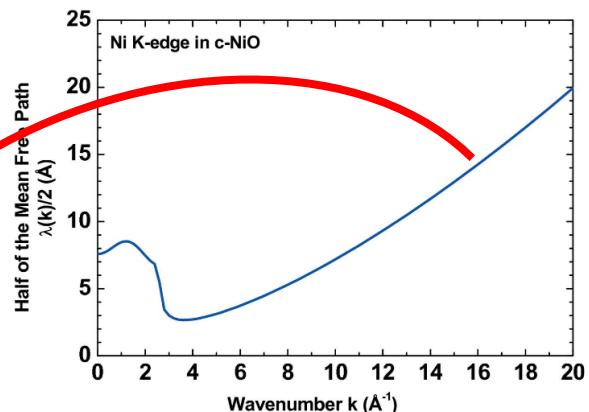
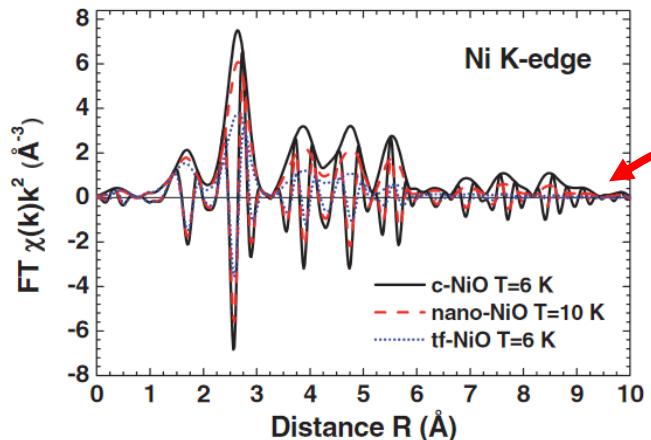
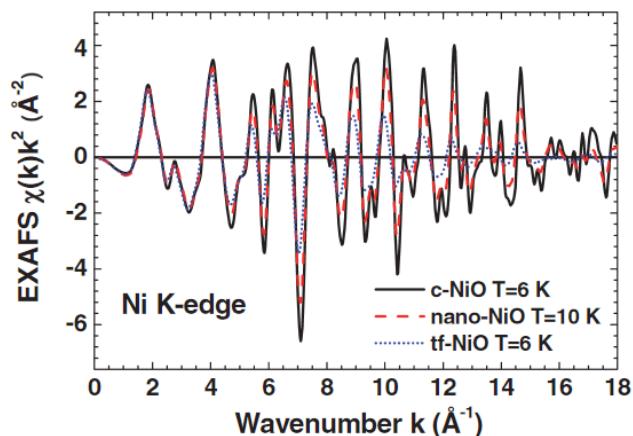
$$\mu(E) \propto \frac{I_{\text{TEY}}(E)}{I_0(E)}$$

$$\mu(E) \propto \frac{I_{\text{XEOL}}(E)}{I_0(E)}$$

- Atoms are frozen during X-ray absorption
- Static & thermal disorder contribute similarly



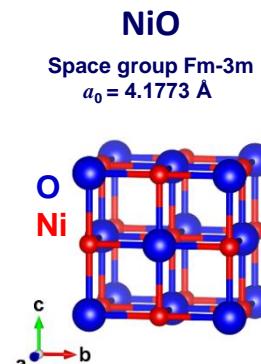
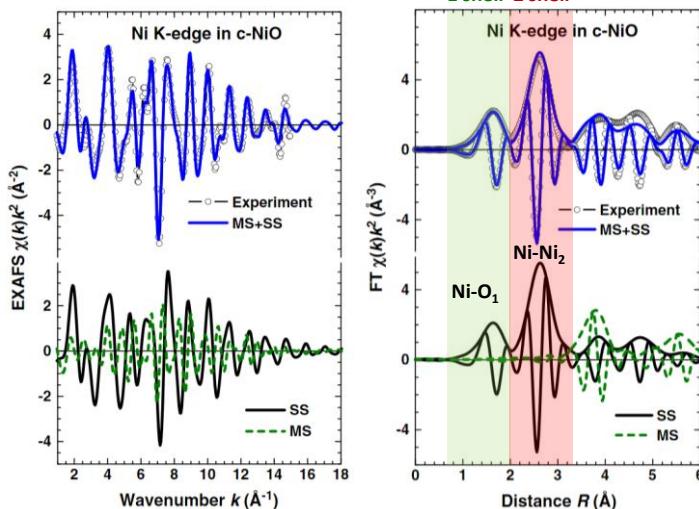
How local is X-ray absorption spectroscopy? The case of NiO: $T = \sim 10$ K



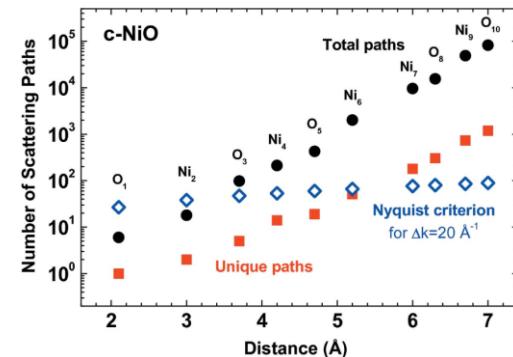
A. Anspoks, A. Kalinko, R. Kalendarev, A. Kuzmin, Phys. Rev. B 86 (2012) 174114.

EXAFS challenges: analysis of distant coordination shells

- 1 The analysis of the distant coordination shells must take into account the **multiple-scattering (MS)** and **disorder** effects.



- 2 A number of parameters in the model increases rapidly upon an increase of analyzed region size around the absorbing atom. This problem is especially relevant for disordered and nanocrystalline materials.



Number of scattering paths vs independent parameters N_{par} :

$$N_{\text{par}} = \frac{2\Delta k \Delta R}{\pi}$$

A. Anspoks and A. Kuzmin,
J. Non-Cryst. Solids 357 (2011) 2604.

A. Kuzmin and J. Chaboy, IUCrJ 1 (2014) 571.



Why do we need advanced methods of EXAFS analysis?

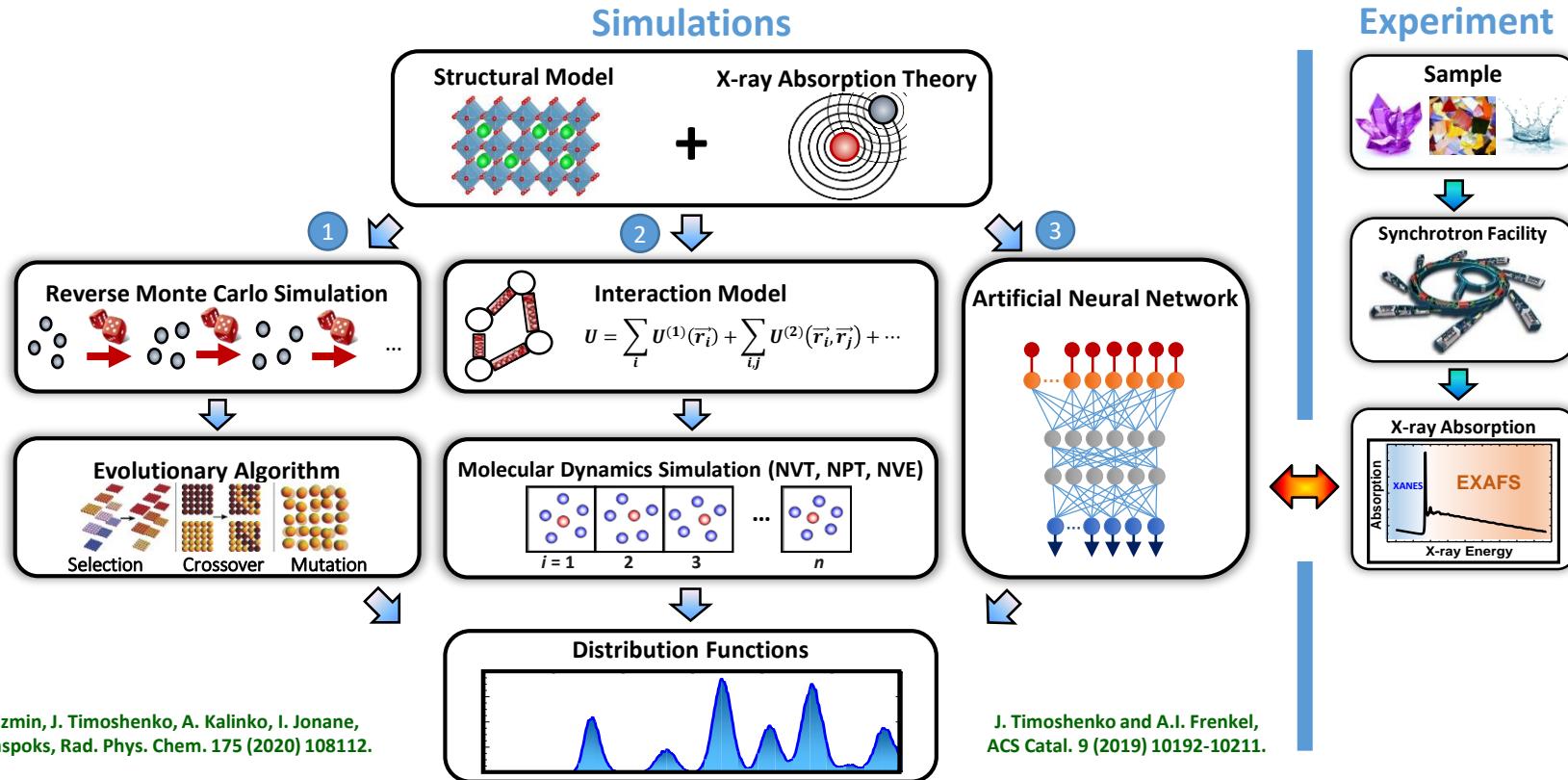
- To account properly for disorder effects.
- To perform reliable analysis of distant coordination shells.
- To determine bond-angle distribution functions.
- To extract structural information in some specific cases (nanoparticles).
- To validate other theoretical simulations as molecular dynamics or DFT calculations.

[1] A. Kuzmin and J. Chaboy, EXAFS and XANES analysis of oxides at the nanoscale, IUCrJ 1 (2014) 571.

[2] A. Kuzmin, J. Timoshenko, A. Kalinko, I. Jonane, A. Anspoks, Treatment of disorder effects in X-ray absorption spectra beyond the conventional approach, Rad. Phys. Chem. 175 (2020) 108112.



Advanced methods of XAS analysis using atomistic simulations



Reverse Monte Carlo (RMC) method: 1st paper

Molecular Simulation, 1988, Vol. 1, pp. 359–367 © 1988 Gordon and Breach Science Publishers S.A.
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REVERSE MONTE CARLO SIMULATION: A NEW TECHNIQUE FOR THE DETERMINATION OF DISORDERED STRUCTURES

R.L. MCGREEVY

Clarendon Laboratory, Parks Road, Oxford, OX1 3PU, UK

L. PUSZTAI

Laboratory of Theoretical Chemistry, Department of Chemistry, L. Eotvos
University, H-1088 Budapest, Hungary

(Received March 1988)

We have developed a new technique, based on the standard Monte Carlo simulation method with Markov chain sampling, in which a set of three dimensional particle configurations are generated that are consistent with the experimentally measured structure factor, $A(Q)$, and radial distribution function, $g(r)$, of a liquid or other disordered system. Consistency is determined by a standard χ^2 test using the experimental errors. No input potential is required, we present initial results for liquid argon. Since the technique can work directly from the structure factor it promises to be useful for modelling the structures of glasses or amorphous materials. It also has other advantages in multicomponent systems and as a tool for experimental data analysis.

Radial Distribution Function

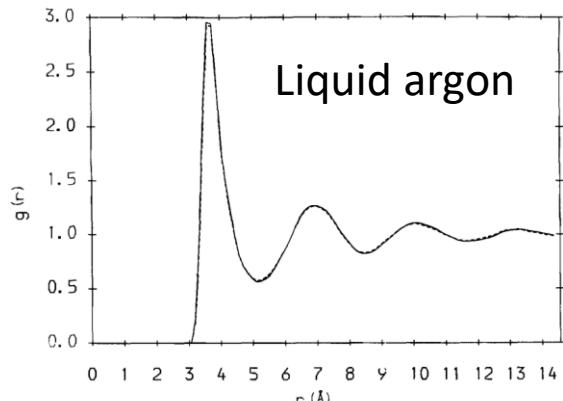


Figure 1 Radial distribution function $g(r)$ for liquid argon; comparison of experiment [3] (solid line) and RMC calculation (broken line).

Structure factor

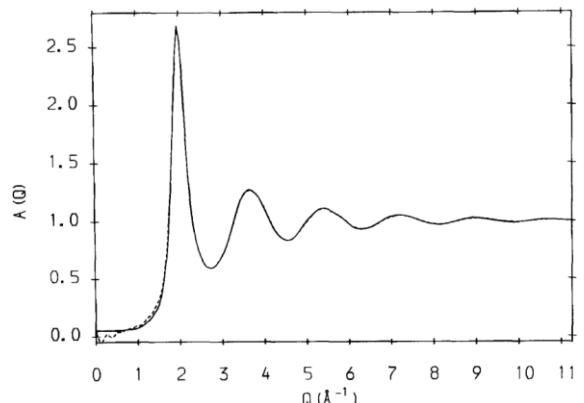


Figure 2 Structure factor $A(Q)$ for liquid argon; comparison of experiment [3] (solid line) and RMC calculation (broken line).

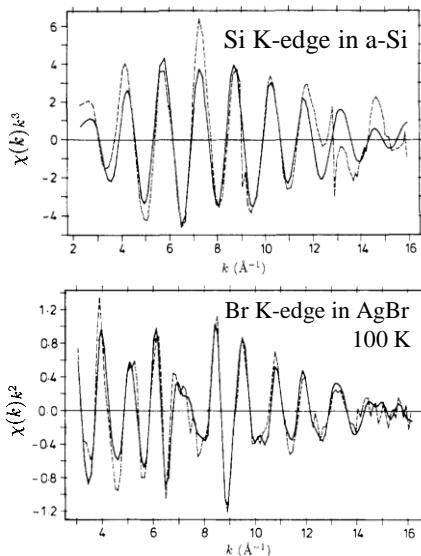
R. L. McGreevy & L. Pusztai, Reverse Monte Carlo Simulation: A New Technique for the Determination of Disordered Structures, Molecular Simulation, 1 (1988) 359–367.

RMC-EXAFS approach: Earlier works

Reverse Monte Carlo simulation for the analysis of EXAFS data

S J Gurman[†] and R L McGreevy[‡]

[†] Department of Physics, University of Leicester, Leicester LE1 7RH, UK
[‡] Clarendon Laboratory, Parks Road, Oxford OX1 3PU, UK



High temperature EXAFS experiments on liquid KPb alloys analysed with the reverse Monte Carlo method

W. Bras^{a,b,*}, R. Xu^c, J.D. Wicks^{d,l}, F. van der Horst^c, M. Oversluizen^{a,b}, R.L. McGreevy^c, W. van der Lugt^c

^aNetherlands Organisation for Scientific Research (NWO), The Netherlands

^bSERC Daresbury Laboratory, Warrington WA4 4AD, UK

^cLaboratory for Solid State Physics, Groningen University, Nijenborgh 18, 9747 AG Groningen, The Netherlands

^dClarendon Laboratory, Parks Road, Oxford, OX1 3PU, UK

*Studsvik Neutron Research Laboratory, Uppsala University, S-611 82 Nyköping, Sweden

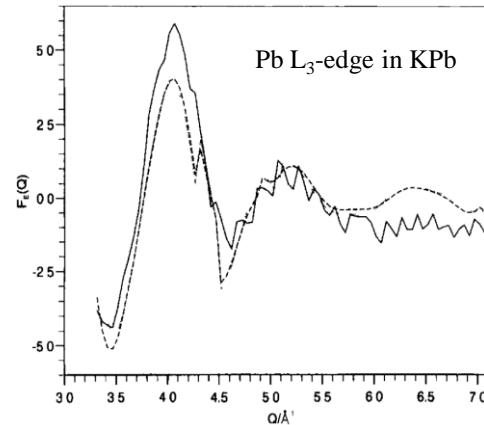


Fig. 4. EXAFS data, $F_E(Q)$, for molten KPb (solid line) compared to the RMC fit with 100% Zintl ions maintained (dotted line)

Modelling the Structure and Ionic Conduction of $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ Glasses

J. D. Wicks,¹ L. Börjesson,² G. Bushnell-Wye,³ W. S. Howells⁴ and R. L. McGreevy⁵

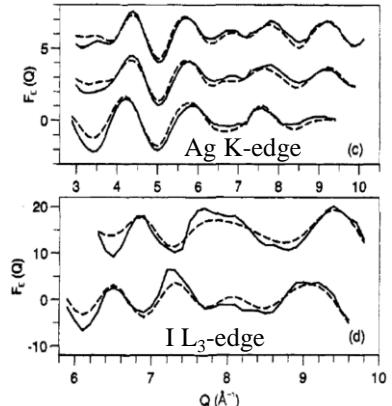
¹ Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

² Department of Physics, Royal Institute of Technology, S-100 44 Stockholm, Sweden

³SRS Daresbury Laboratory, Warrington, Cheshire WA4 4AD, UK

⁴ISIS Science Division, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK

⁵Studsvik Neutron Research Laboratory, S-611 82 Nyköping, Sweden



Experimental data (solid curves) and RMC fits (broken curves) for $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ (top to bottom) $x = 0.5, 0.3$ and 0.0 . EXAFS at (c) the Ag K-edge and (d) the I L_3 -edge.

[1] S.J. Gurman and R.L. McGreevy, *J. Phys.: Condens. Matter* **2** (1990) 9463-9473.

[2] W. Bras, R. Xu, J.D. Wicks, F. van der Horst, M. Oversluizen, R.L. McGreevy, W. van der Lugt, *Nucl. Instrum. Meth. Phys. Res. A* **346** (1994) 394-398.

[3] J.D. Wicks, L. Börjesson, G. Bushnell-Wye, W.S. Howells, R.L. McGreevy, *Physica Scripta* **T57** (1995) 127-132.



Available software for RMC-EXAFS simulations

RMC-GNXAS [1], RMCprofile [2], RMC++/RMC_POT++ [3], EvAX [4]

- [1] A. Di Cicco, A. Trapananti, *J. Phys. Condens. Matter* 17 (2005) S135.
- [2] M.G. Tucker, D.A. Keen, M.T. Dove, A.L. Goodwin, Q. Hui, *J. Phys.: Condens. Matter* 19 (2007) 335218.
- [3] O. Gereben, L. Pusztai, *J. Computat. Chem.* 33 (2012) 2285.
- [4] J. Timoshenko, A. Kuzmin, J. Purans, *J. Phys.: Condens. Matter* 26 (2014) 055401.

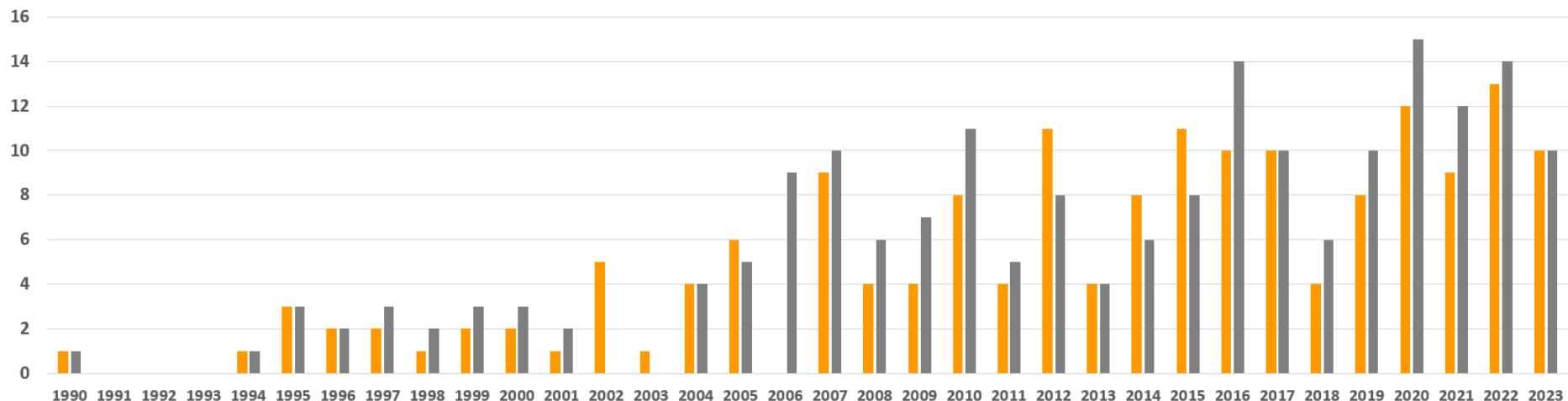
SpecSwap-RMC [5], EPSR-RMC [6]

- [5] M. Leetmaa, K.T. Wikfeldt, L.G.M. Pettersson, *J. Phys.: Condens. Matter* 22 (2010) 135001.
- [6] D.T. Bowron, *Pure Appl. Chem.* 80 (2008) 1211.

rmcxas [7]

- [7] M. Winterer, *J. Appl. Phys.* 88 (2000) 5635.

Publications on reverse Monte Carlo simulations of EXAFS



Scopus

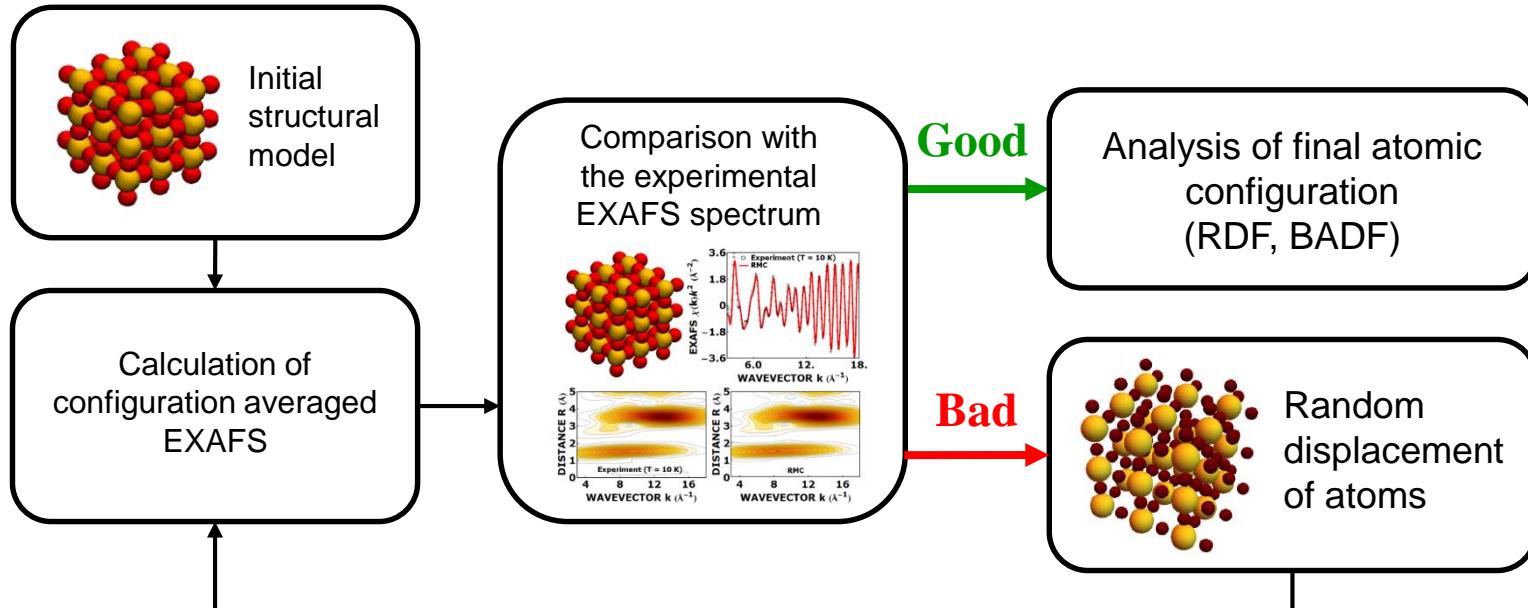
170

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Reverse Monte Carlo simulations of EXAFS spectra (RMC-EXAFS)



[1] R.L. McGreevy and L. Pusztai, Mol. Simul. 1 (1988) 359.

[2] J. Timoshenko, A. Kuzmin, J. Purans, J. Phys.: Condens. Matter 26 (2014) 055401.

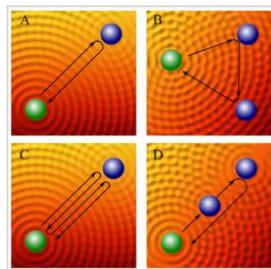


Reverse Monte Carlo method with Evolutionary Algorithm

EvAX code was developed by Dr. Janis Timoshenko

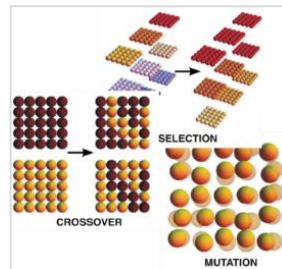
J. Timoshenko, A. Kuzmin, J. Purans, J. Phys.: Condens. Matter 26 (2014) 055401.

J. Timoshenko, A. Kuzmin, J. Purans, Comp. Phys. Commun. 183 (2012) 1237-1245.



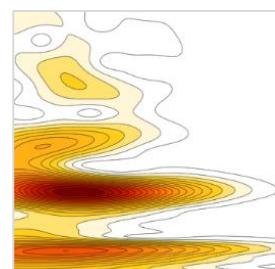
Multiple-scattering
approximation

Reliable analysis of distant shells,
PDF and BADF



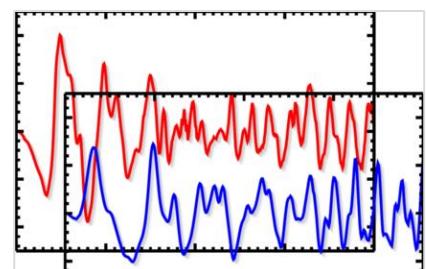
Evolutionary
algorithm for
optimization

Fast with good
convergence



Wavelet transform for
spectra comparison
in k and R space

More reliable solution



EXAFS spectra at several edges

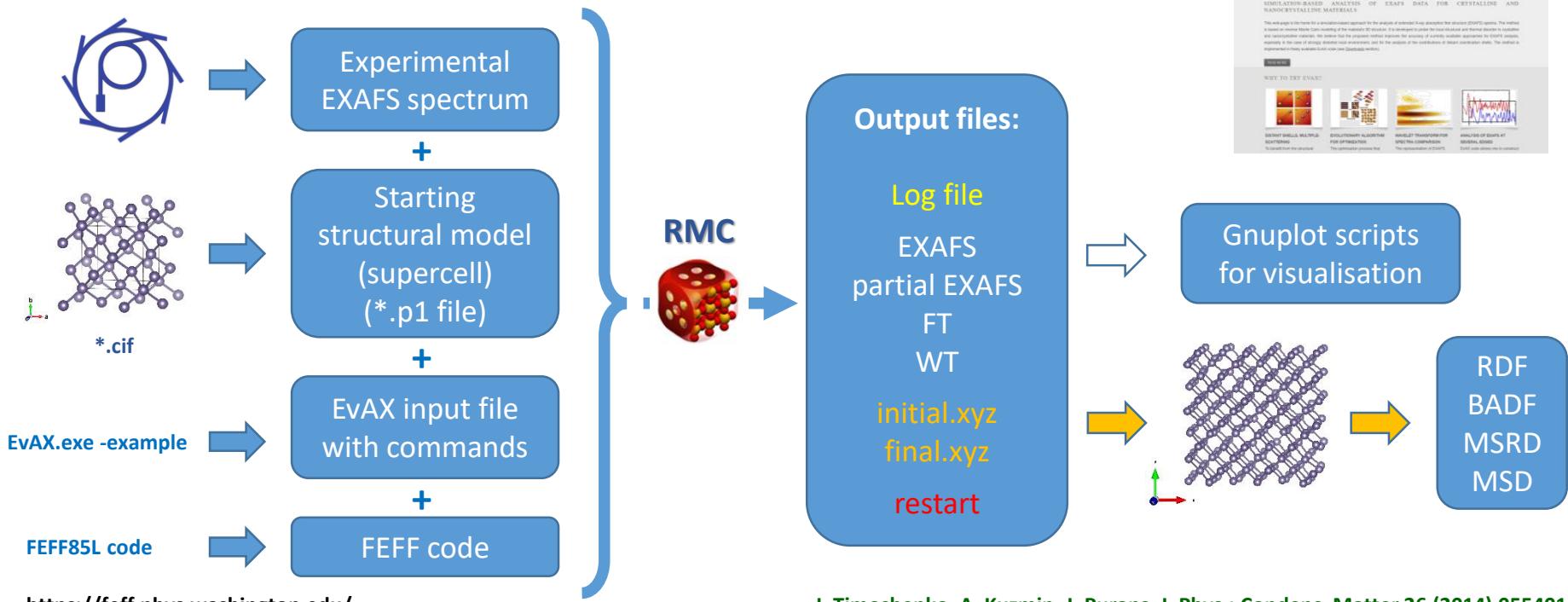
One structural model

<http://www.dragon.lv/evax/>



Reverse Monte Carlo (RMC) simulation using the EvAX code

<http://www.dragon.lv/evax/>



J. Timoshenko, A. Kuzmin, J. Purans, J. Phys.: Condens. Matter 26 (2014) 055401.

Fourier and wavelet transforms of EXAFS $\chi(k)$

Fourier transform:

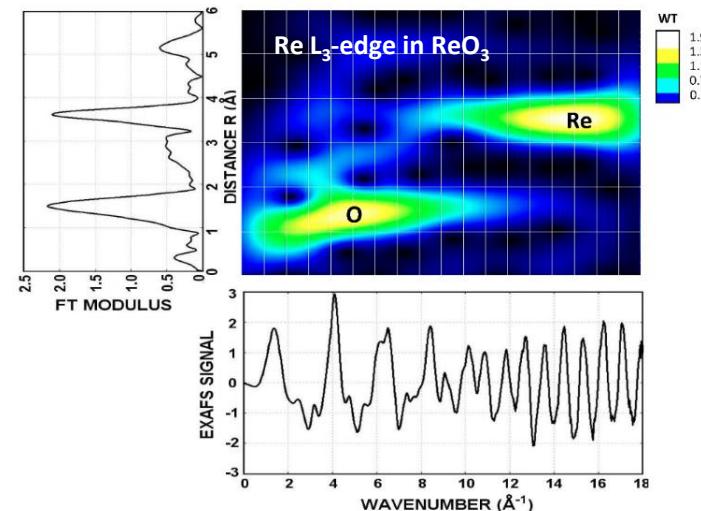
$$\text{FT}(R) = \sqrt{\frac{2}{\pi}} \int_{k_{min}}^{k_{max}} k^n \chi(k) W(k) e^{-2ikR} dk$$

$W(k)$ is the window function

Wavelet transform:

$$\text{WT}(k, R) = \left(\frac{R}{R_0}\right)^{1/2} \int_{k_{min}}^{k_{max}} (k')^n \chi(k') \phi\left(\frac{k' - k}{R_0/R}\right) dk'$$

$\phi(k) = e^{-2ikR_0} e^{-k^2/\sigma_0^2}$ is the Morlet wavelet



Fourier transform is a **1-dimensional integral transformation** providing information on the EXAFS signal behavior in **R -space**.

Wavelet transform is a **2-dimensional integral transformation** providing information on the EXAFS signal behavior in both **k and R spaces**.

J. Timoshenko and A. Kuzmin, Wavelet data analysis of EXAFS spectra, Comp. Phys. Commun. 180 (2009) 920-925.



RMC simulations using the EvAX code for crystalline Ge

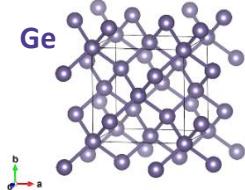
Calculation time for this example is about 6 min on 6-core CPU.

Crystalline Germanium:

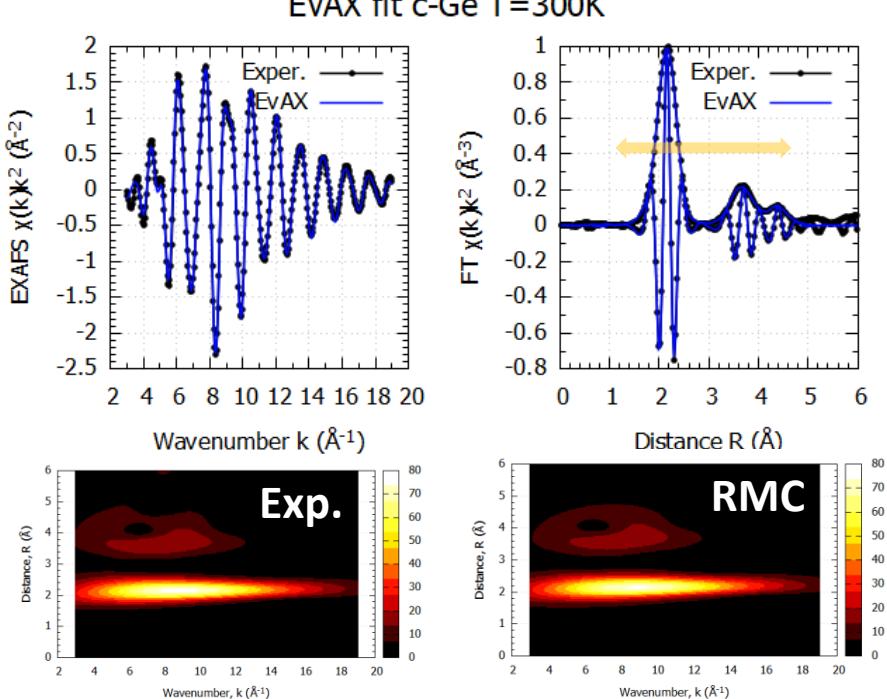
Lattice constant:

$$a = 5.657 \text{ \AA}$$

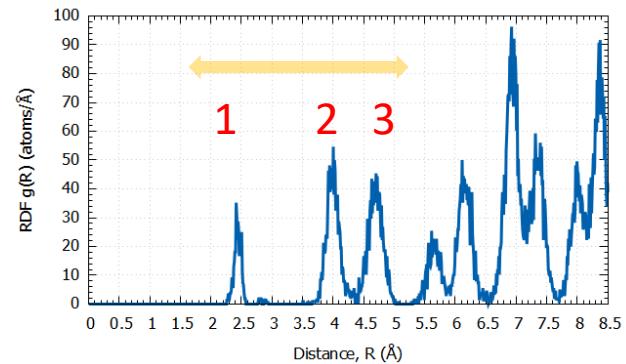
Space group Fd-3m



R(Ge-Ge):
 $4 \times 2.45 \text{ \AA}$
 $12 \times 4.00 \text{ \AA}$
 $12 \times 4.69 \text{ \AA}$



RMC supercell: $3 \times 3 \times 3$



$$R_1 = 2.46 \text{ \AA}$$

$$\text{MSRD}_1 = 0.0037 \text{ \AA}^2$$

$$R_1(\text{XRD}) = 2.4497 \text{ \AA}$$

$$R_2 = 4.00 \text{ \AA}$$

$$\text{MSRD}_2 = 0.011 \text{ \AA}^2$$

$$R_2(\text{XRD}) = 4.0039 \text{ \AA}$$

$$R_3 = 4.69 \text{ \AA}$$

$$\text{MSRD}_3 = 0.014 \text{ \AA}^2$$

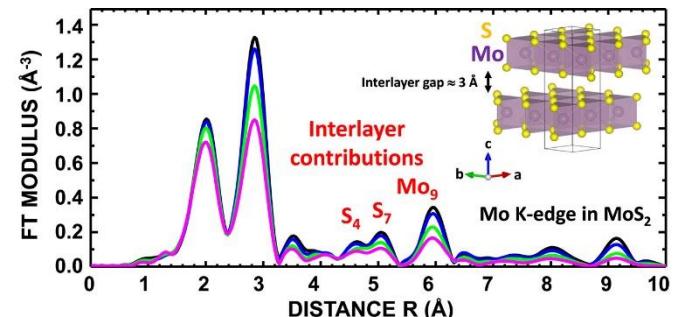
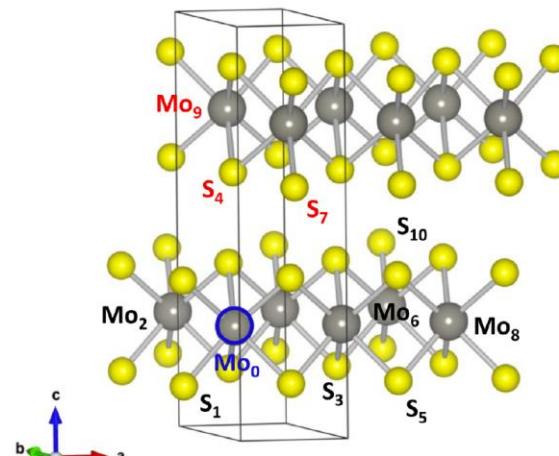
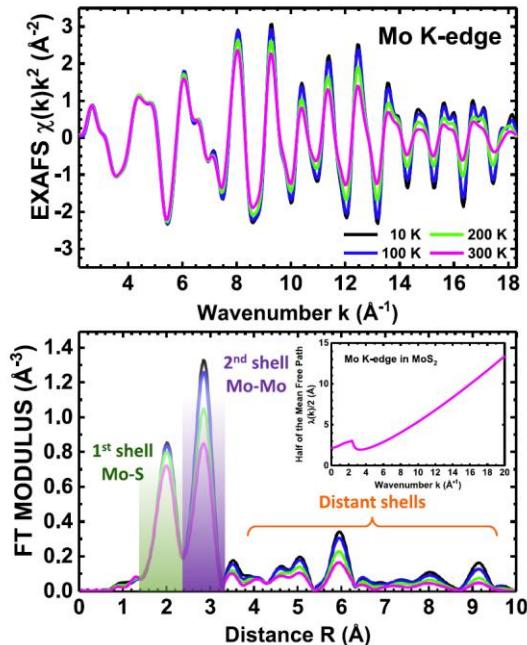
$$R_3(\text{XRD}) = 4.6909 \text{ \AA}$$

$$\text{MSD} = 0.02 \text{ \AA}^2$$

$$\text{MSD}(\text{XRD}) = 0.022 \text{ \AA}^2$$

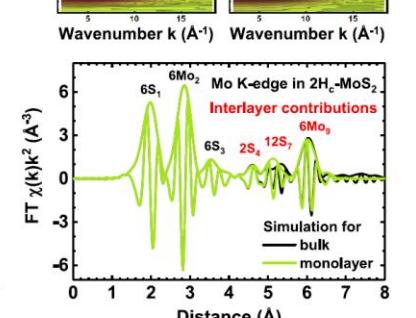
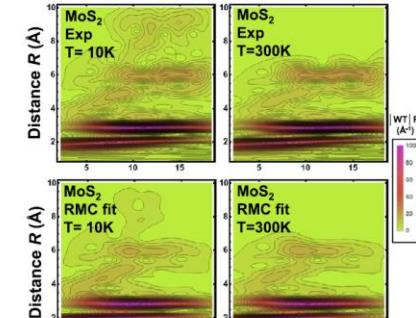
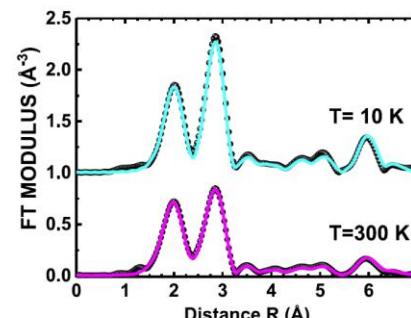
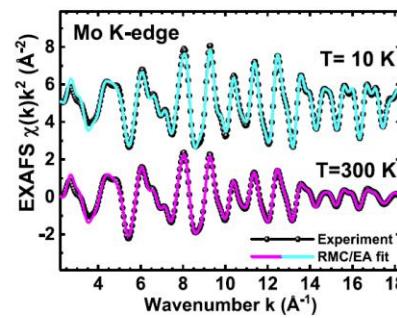
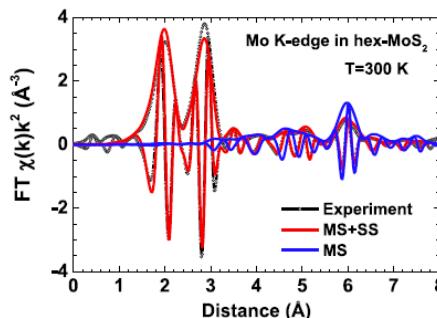
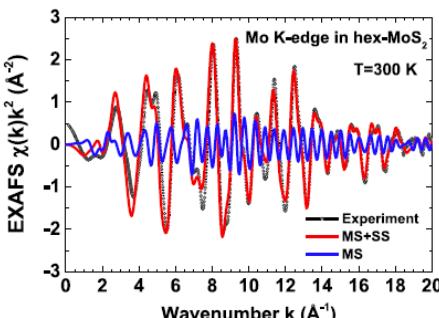
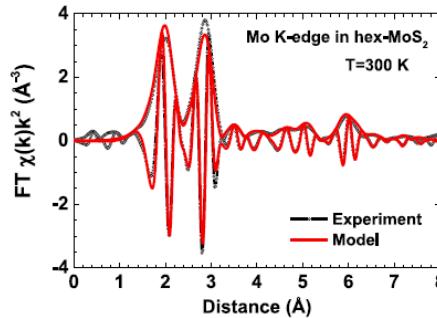
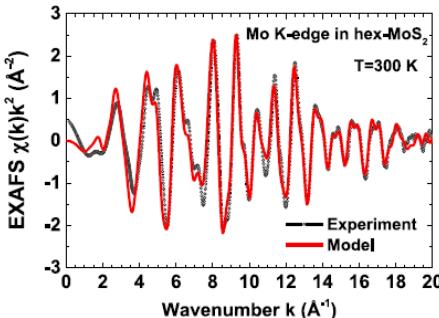
N. M. Butt et al., Acta Crystallogr. A 44, 396 (1988).

Unraveling the interlayer and intralayer coupling in two-dimensional layered MoS₂



I. Pudza, D. Bocharov, A. Anspoks, M. Krack, A. Kalinko, E. Welter, A. Kuzmin, Mater. Today Commun. 35 (2023) 106359.

Unraveling the interlayer and intralayer coupling in two-dimensional layered MoS₂



Ab initio MD simulation

RMC fit

I. Pudza, D. Bocharov, A. Anspoks, M. Krack, A. Kalinko, E. Welter, A. Kuzmin, Mater. Today Commun. 35 (2023) 106359.

Unraveling the interlayer and intralayer coupling in two-dimensional layered MoS₂

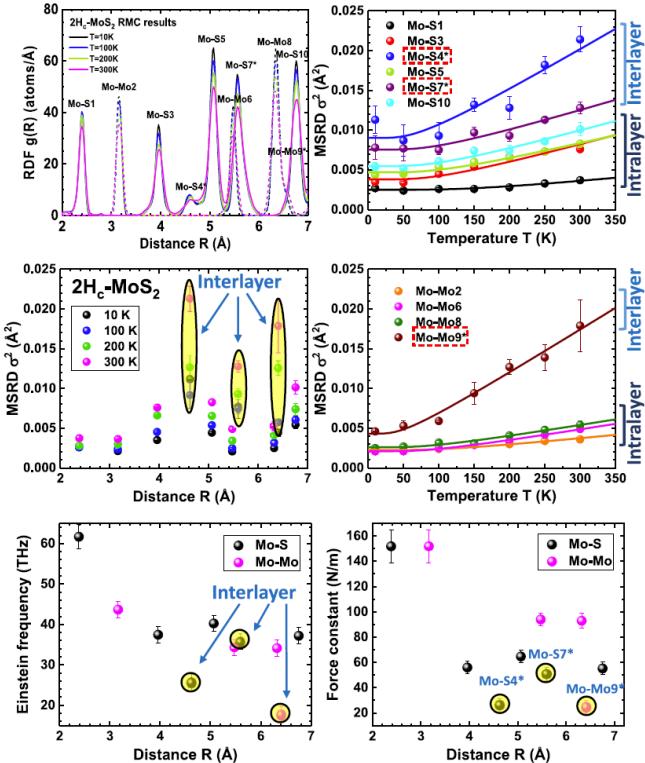


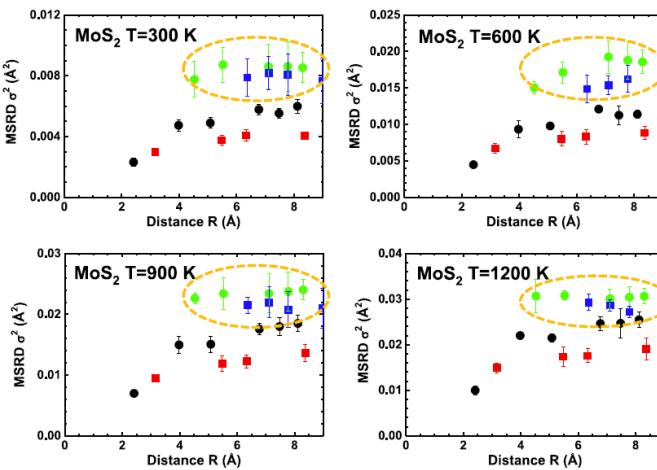
Table 1

Values of Mo-S and Mo-Mo interatomic distances for the first ten coordination shells of molybdenum calculated from the crystallographic structure of 2H_c-MoS₂ [55]. Interlayer distances are given in bold. The values of characteristic Einstein frequencies (ω_E) and the effective force constants (κ) obtained from the RMC analysis are also given.

Atom pair	Distance (\AA)	ω_E (THz)	κ (N/m)
Mo ₆ -S ₁	2.37	62 ± 3	152 ± 13
Mo ₆ -Mo ₂	3.16	44 ± 2	152 ± 13
Mo ₆ -S ₃	3.95	38 ± 2	56 ± 5
Mo ₆ -S ₄	4.64	26 ± 2	26 ± 5
Mo ₆ -S ₅	5.06	40 ± 2	65 ± 5
Mo ₆ -Mo ₆	5.48	34 ± 2	94 ± 5
Mo ₆ -S ₇	5.62	36 ± 2	51 ± 5
Mo ₆ -Mo ₈	6.32	34 ± 2	93 ± 6
Mo ₆ -Mo ₉	6.41	18 ± 2	25 ± 5
Mo ₆ -S ₁₀	6.75	37 ± 2	55 ± 5

$$\sigma_{\text{th}}^2 = \langle u_A^2 \rangle + \langle u_B^2 \rangle - 2 \langle u_A u_B \rangle$$

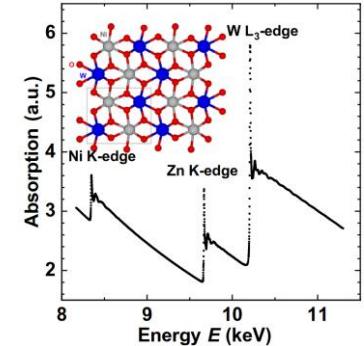
MSRD MSD MSD
or
Debye-Waller factor



Interactions between neighbouring layers in 2D compounds can be probed by EXAFS!

I. Pudza, D. Bocharov, A. Anspoks, M. Krack, A. Kalinko, E. Welter, A. Kuzmin, Mater. Today Commun. 35 (2023) 106359.

Dimerization of nickel ions in NiWO_4 and $\text{Zn}_c\text{Ni}_{1-c}\text{WO}_4$ solid solutions

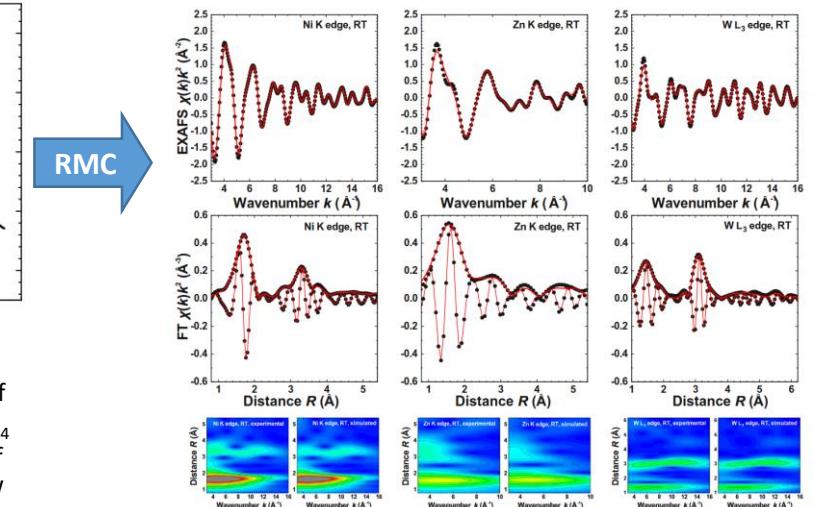


X-ray absorption spectrum of microcrystalline $\text{Zn}_{0.6}\text{Ni}_{0.4}\text{WO}_4$ spanning across the range of the Ni and Zn K-edges and W L_3 -edge at 300 K.

Antiferromagnetic NiWO_4

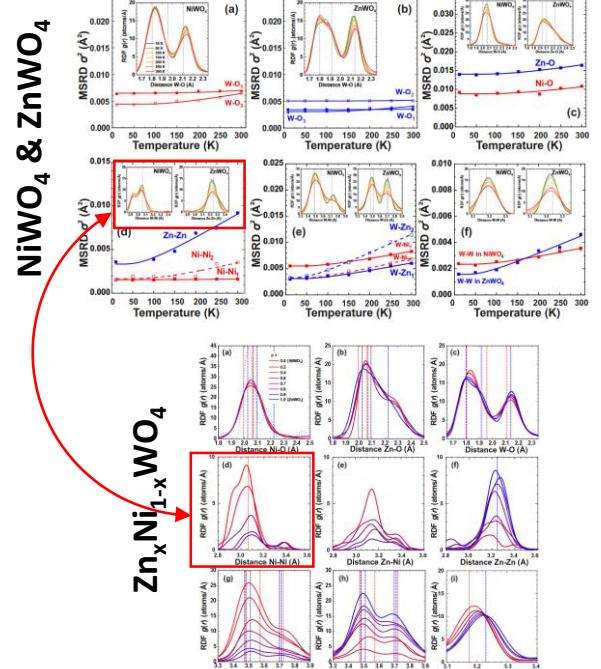
$T_{\text{Néel}} = 60\text{-}67 \text{ K}$

**P2/c (13)
monoclinic**



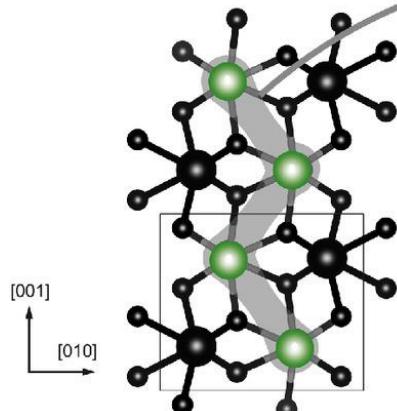
Experimental (black dots) and simulated (solid lines) extended X-ray absorption fine structure (EXAFS) spectra $\chi(k)k^2$ of $\text{Zn}_{0.6}\text{Ni}_{0.4}\text{WO}_4$ solid solution at the Ni and Zn K-edges and W L_3 -edge (top row), their Fourier transforms (FTs) (middle row) and wavelet transforms (bottom row) at 300 K.

G. Bakradze, A. Kalinko, A. Kuzmin, Evidence of dimerization of nickel ions in NiWO_4 and $\text{Zn}_c\text{Ni}_{1-c}\text{WO}_4$ solid solutions probed by EXAFS spectroscopy and reverse Monte Carlo simulations, *Acta Mater.* 217 (2021) 117171.

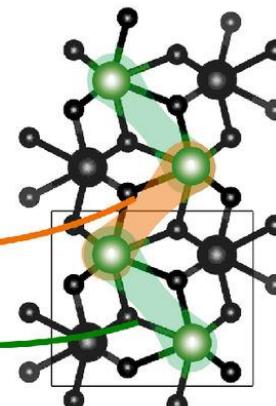
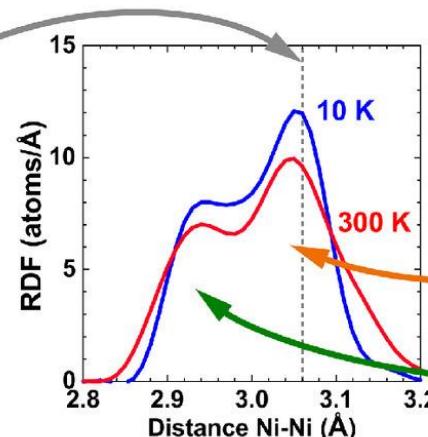


Dimerization of nickel ions in NiWO_4 and $\text{Zn}_c\text{Ni}_{1-c}\text{WO}_4$ solid solutions

XRD of NiWO_4 : no Ni^{2+} dimers
single Ni-Ni distance



EXAFS-RMC of NiWO_4 : Ni^{2+} dimers
two distinct Ni-Ni distances



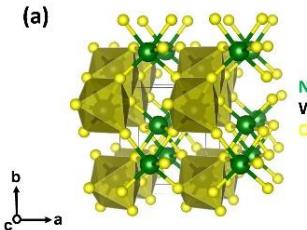
- Dimerization of Ni^{2+} ions within quasi-one-dimensional zigzag chains of $[\text{NiO}_6]$ octahedra was evidenced in NiWO_4 in the whole studied temperature range. It manifests itself as the splitting of the Ni–Ni radial distribution function into two separate peaks.
- The effect is further preserved in solid solutions $\text{Zn}_c\text{Ni}_{1-c}\text{WO}_4$ for $c \leq 0.6$, which is related to the probability to find two Ni^{2+} ions in neighbouring positions.

G. Bakradze, A. Kalinko, A. Kuzmin, Evidence of dimerization of nickel ions in NiWO_4 and $\text{Zn}_c\text{Ni}_{1-c}\text{WO}_4$ solid solutions probed by EXAFS spectroscopy and reverse Monte Carlo simulations, *Acta Mater.* 217 (2021) 117171.

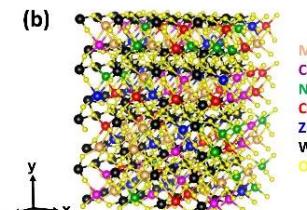


Medium- and High-Entropy Tungstates AWO_4 (A=Mn, Co, Ni, Cu, Zn)

P2/c (13)
monoclinic



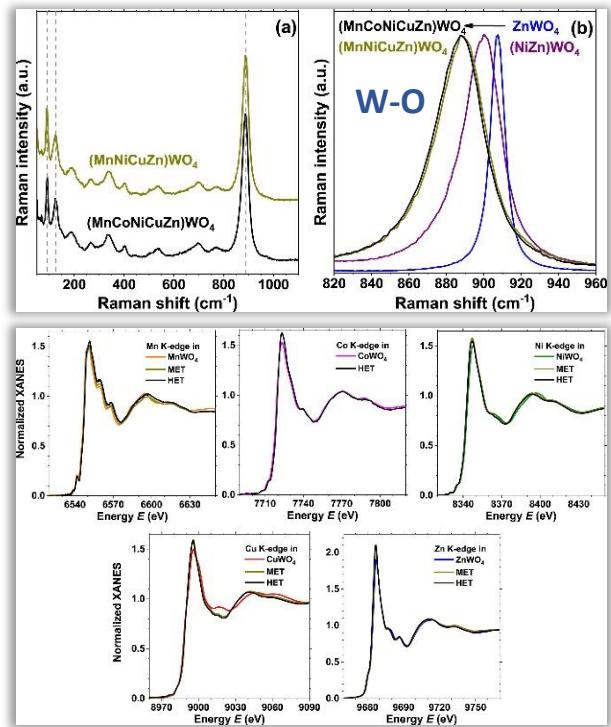
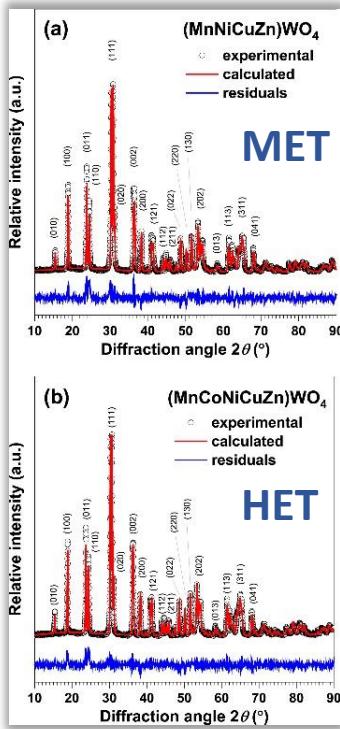
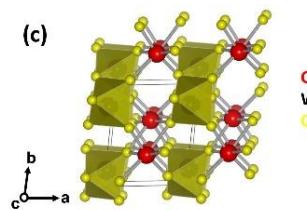
P2/c (13)
monoclinic



P-1 (2)
triclinic



Jahn-Teller
distortion



G. Bakradze, E. Welter, A. Kuzmin, Peculiarities of the local structure in new medium- and high-entropy, low-symmetry tungstates, *J. Phys. Chem. Solids* 172 (2023) 111052.

Medium- and High-Entropy Tungstates AWO_4 ($\text{A}=\text{Mn, Co, Ni, Cu, Zn}$)

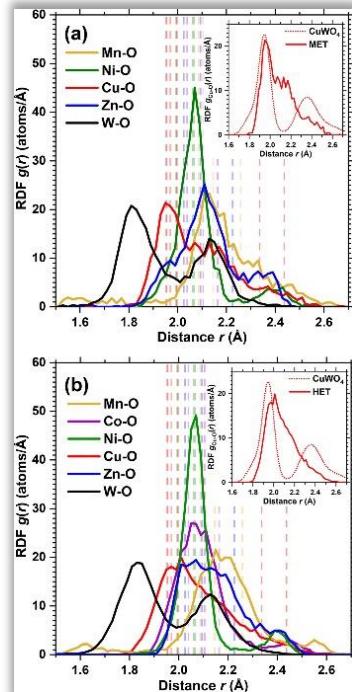
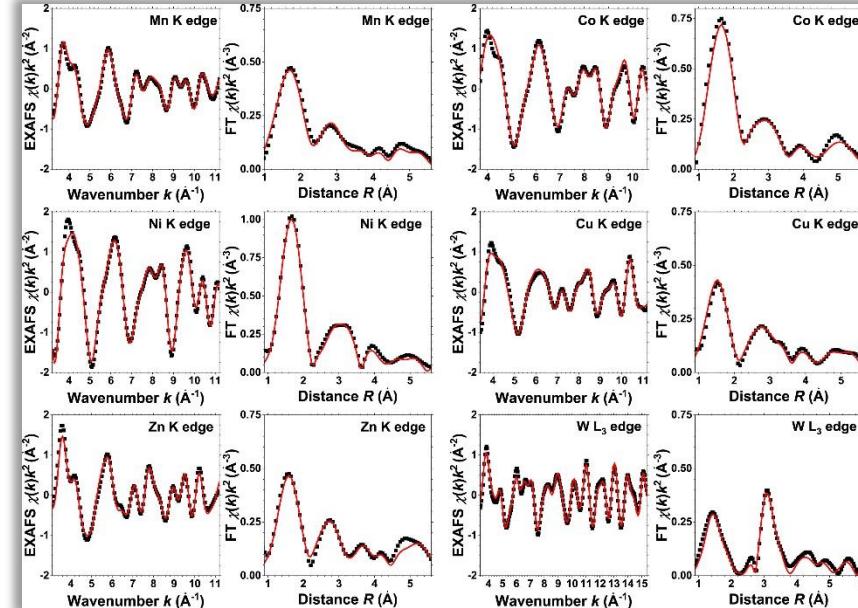


Table 1. Jahn-Teller distortion parameter, σ_{JT} (Å), for different octahedra in medium-entropy tungstate (MET) $(\text{MnNiCuZn})\text{WO}_4$ and high-entropy tungstate (HET) $(\text{MnCoNiCuZn})\text{WO}_4$ at 10 K.

	MET	HET
$[\text{MnO}_6]$	0.163 ± 0.092	0.152 ± 0.090
$[\text{CoO}_6]$	–	0.102 ± 0.052
$[\text{NiO}_6]$	0.091 ± 0.057	0.085 ± 0.056
$[\text{CuO}_6]$	0.140 ± 0.051	0.131 ± 0.049
$[\text{ZnO}_6]$	0.122 ± 0.046	0.115 ± 0.043
$[\text{WO}_6]$	0.159 ± 0.033	0.161 ± 0.038

Conclusions:

- Ni^{2+} ions have regular octahedral environment.
- Mn^{2+} , Co^{2+} , and Zn^{2+} ions have distorted octahedral environment.
- $[\text{Cu}^{2+}\text{O}_6]$ octahedra are less distorted than expected for a Jahn-Teller centre.

G. Bakradze, E. Welter, A. Kuzmin, Peculiarities of the local structure in new medium- and high-entropy, low-symmetry tungstates, *J. Phys. Chem. Solids* 172 (2023) 111052.



Conclusions

Advantages of the RMC method:

- A natural way to include disorder (static and dynamic, also anharmonic) into EXAFS simulations taking into account multiple-scattering effects.
- Reliable interpretation of EXAFS far beyond the first coordination shell is possible.
- Analysis at several absorption edges is possible in multicomponent compounds.
- Information on atom-atom and bond-angle distributions and correlations can be obtained.
- Constraints can be easily incorporated to account for information from other experiments (diffraction, total scattering, etc) or chemical/geometrical information (bond-lengths, bonding angles, coordination, energetics, etc).

Peculiarities of the RMC method:

- RMC gives the most disordered solution.
- Several simulations are often required for good statistics.
- RMC is sensitive to noise.
- One should be careful with the size of the simulation box.



Thank you for your attention!

<http://www.dragon.lv/exafs/>

EXAFS Lab

Institute of Solid State Physics, University of Latvia

About

EXAFS Spectroscopy Laboratory (EXAFS Lab) has been re-established at the Institute of Solid State Physics, University of Latvia in 2020 and focuses on the study of materials structures using modern experimental and theoretical methods, employing also high performance cluster computing. Until 2017 the Lab was headed by Dr hab. phys. J. Purans.

Our experimental possibilities include but are not limited to several techniques such as synchrotron-radiation X-ray absorption spectroscopy (XAS/EXAFS/XANES), confocal spectromicroscopy (CM) and X-ray diffraction (XRD).

We use advanced theoretical calculations and simulations of experimental data to gain insight on the structure-property relationships in materials.

Our laboratory is also involved in the teaching process at the University of Latvia and provides students with opportunities to participate in research activities during Bachelor, Master and Doctoral level programs.

Highlights

- X-ray Absorption Spectroscopy
- X-ray Diffraction
- Confocal Microscopy
- Molecular Dynamics
- Reactive Force Fields
- Machine Learning
- Quantum Chemistry

Projects

- Projects
- Products
- Equipment
- Collaboration

For students

- Theses
- Software

Links

- Cluster
- Cool Links
- Silicate

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EXAFS Spectroscopy Laboratory
Institute of Solid State Physics
Kengaraga street 8
LV-1000 Riga
LATVIA

Large Visitor Map

Website Statistics

EXAFS Spectroscopy Lab

Structure Microscopy

Modelling & Simulations Large-scale facilities

Spectroscopy

Education for the future "Microscopy and spectroscopy characterization (theory and lab)"

FLPP
FUNDAMENTAL AND
APPLIED RESEARCH
PROJECTS

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The work was supported by the Latvian Council of Science project No. Izp-2022/1-0608.



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The new COST program "European Materials Informatics Network" (EuMINe) is dedicated to the development, engineering and improvement of materials based on materials informatics, artificial intelligence (AI) and data-centric technologies.

The action period is from 24/10/2023 to 23/10/2027.