International Workshop on Recent Advances and Future Trends in EXAFS Spectroscopy

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STUDIES OF NICKEL OXIDE LATTICE DYNAMICS ACROSS MAGNETIC PHASE TRANSITION USING X-RAY ABSORPTION SPECTROSCOPY

LATVIJAS UNIVERSITĀTES
CIETVIELU FIZIKAS INSTITŪTS

INSTITUTE OF SOLID STATE PHYSICS
UNIVERSITY OF LATVIA

Julija Lukasevica, Alexei Kuzmin

RESEARCH PLAN

Literature data

MSRD values

RDF

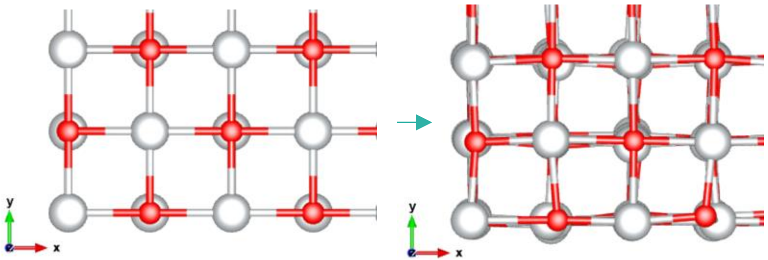
Sample

EXAFS experiment NiO

EvAX

Reverse Monte Carlo simulations

EvAX



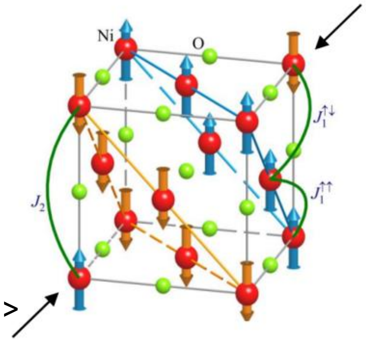
NiO

- The highest magnetic phase transition temperature (T_N = 525 K) among all transition metal monoxides:

  αNiO → βNiO

  Antiferromagnetic → Paramagnetic

  Rhombohedral (R-3m) → Cubic (Fm-3m)



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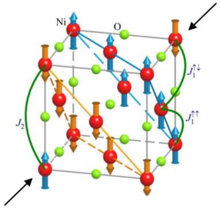
- Use in semiconductors, electronics, rechargeable batteries, sensors and detectors, catalysis and pharmacy. Potential application for ensuring the magnetic stability of data carriers at temperatures well above room temperature.

STUDIED SAMPLES



Polycrystalline stoichiometric NiO

- Green
- Magnetic phase transition expected at T_N=525 K

αNiO → βNiO

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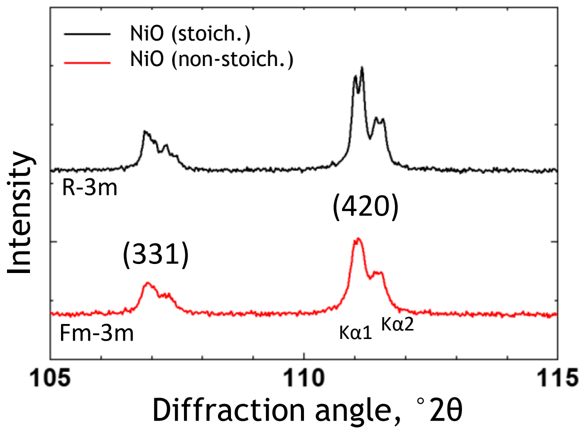
Polycrystalline non-stoichiometric NiO

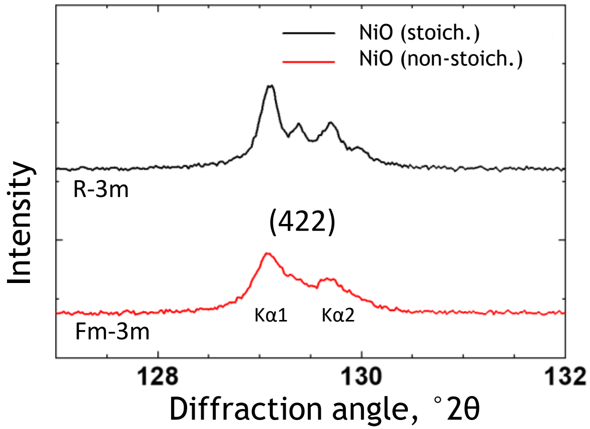
- Black
- $Ni_{1-x}O$, x << 1
- No phase transition expected

βNiO

Paramagnetic

Cubic (Fm-3m)





Comparison of polycrystalline NiO diffraction patterns

https://doi.org/10.1515/zna-1991-0606

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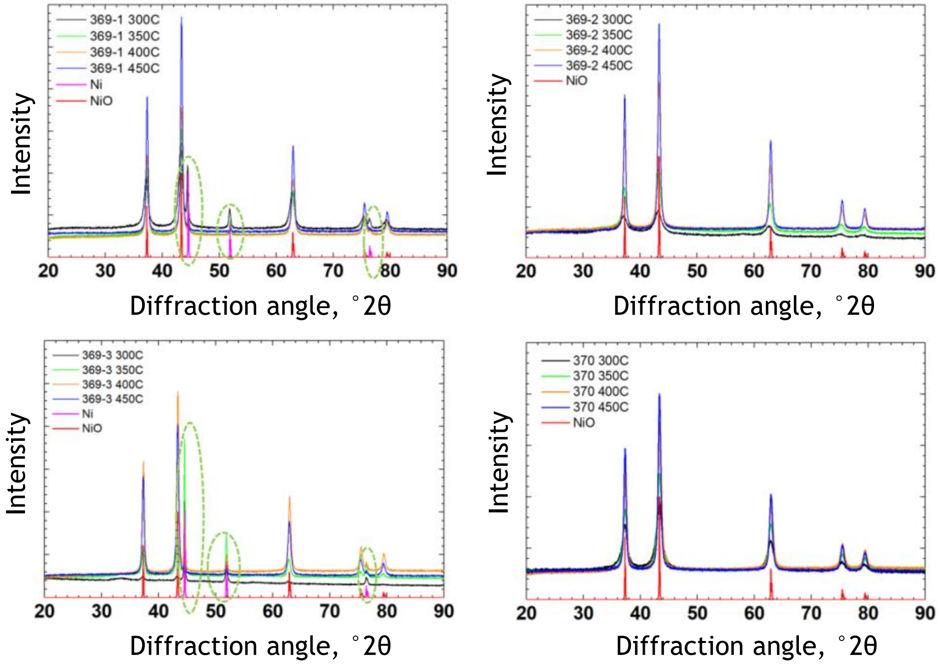
Nanoctrystalline NiO

- Several aerogel samples
- 6,1±0,1 nm
  7,3±0,1 nm
- Studied at room temperature

STUDIED SAMPLES



Diffraction patterns of different aerogel series

Nanoctrystalline NiO

- Several aerogel samples
- 6,1±0,1 nm
  7,3±0,1 nm
- Studied at room temperature

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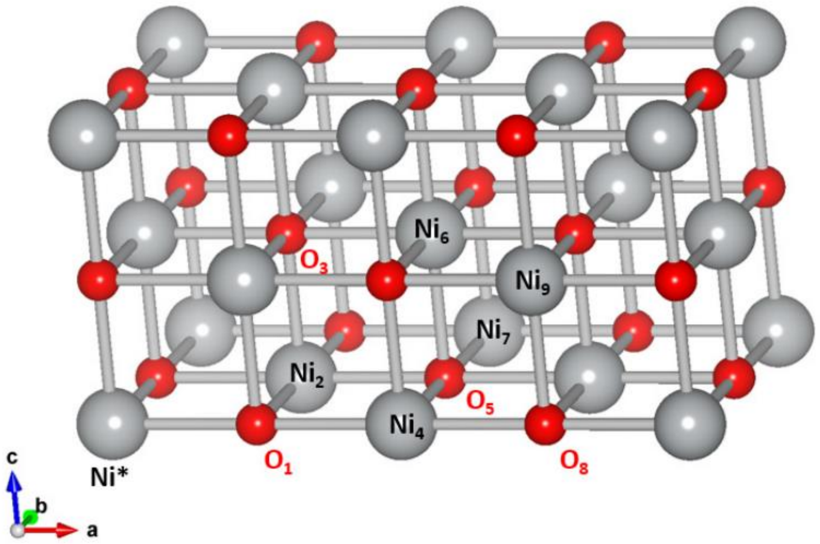
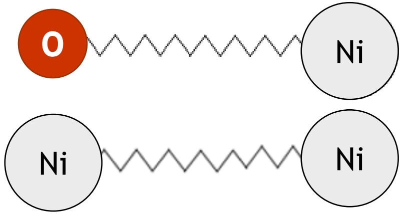
LATTICE DYNAMICS



NiO structure with studied atomic pairs

MSRD(NiO) = MSD (Ni) + MSD (O) – DCF(NiO) (1)

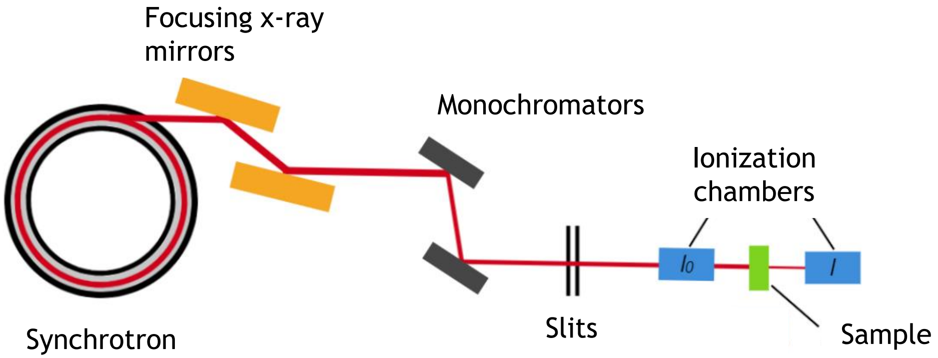
DCF – displacement correlation function



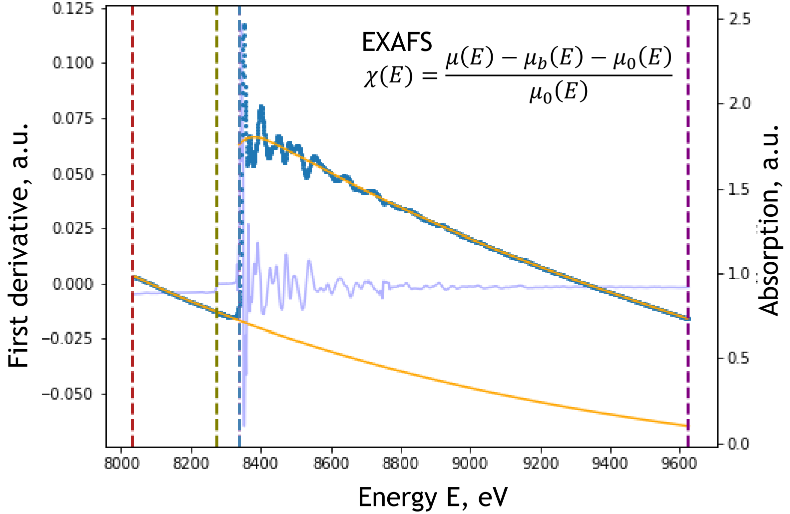
$$\sigma_E^2(T) = \frac{\hbar}{2\mu\omega_E}\coth\left(\frac{\hbar\omega_E}{2k_B T}\right) + \sigma_{st}^2 \quad (2)$$

$$\mathrm{MSRD} = \sigma^2$$

XAS EXPERIMENT



$$\mu(E) = \frac{1}{d}\ln\left(\frac{I_0}{I}\right) \quad (3)$$

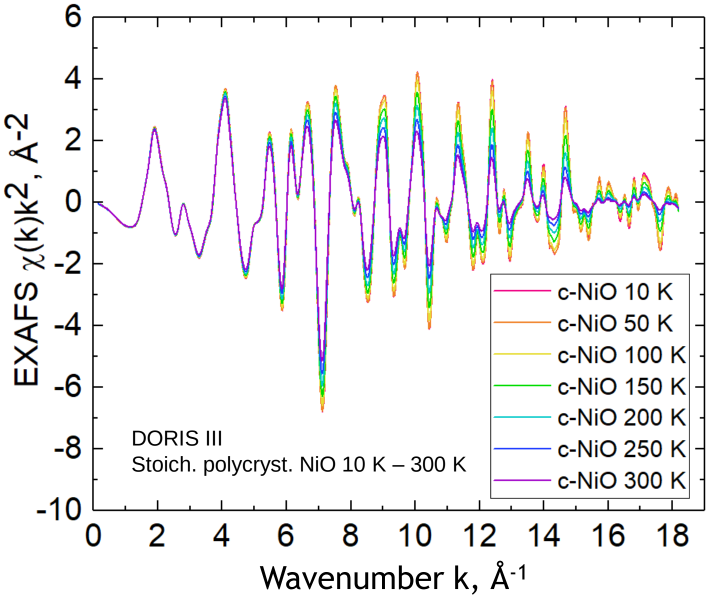


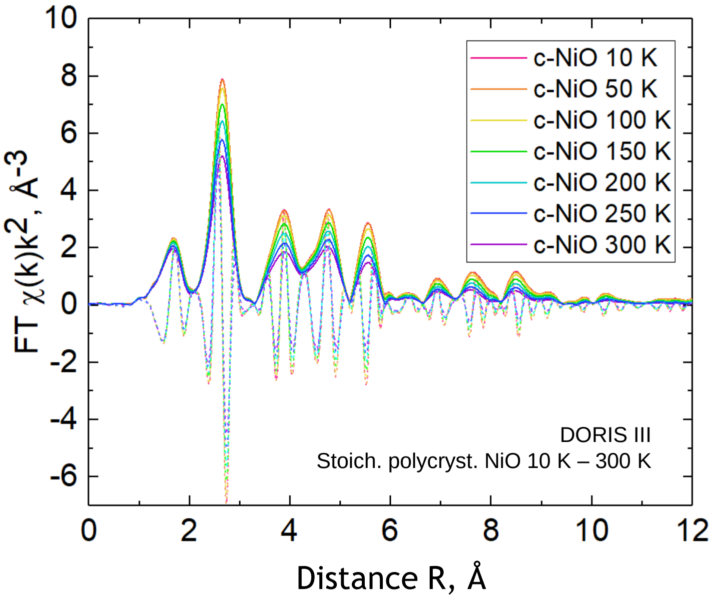
Ni k edge XAS of polycrystalline stoichiometric NiO (300K)

$$\chi(E) = \frac{\mu(E) - \mu_b(E) - \mu_0(E)}{\mu_0(E)} \quad (4)$$

$\chi(E)$ - EXAFS spectrum
$\mu(E)$ - experimentally obtained signal
$\mu_b(E)$ - background from other absorption edges
$\mu_0(E)$ - atomic absorption

XAS EXPERIMENT RESULTS

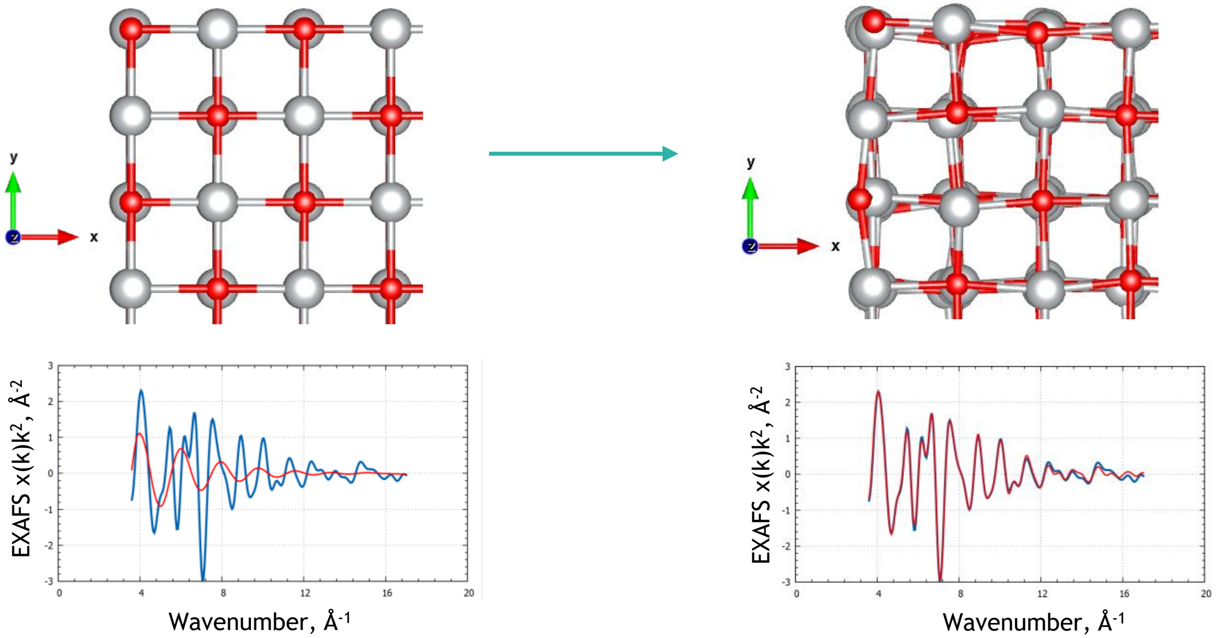




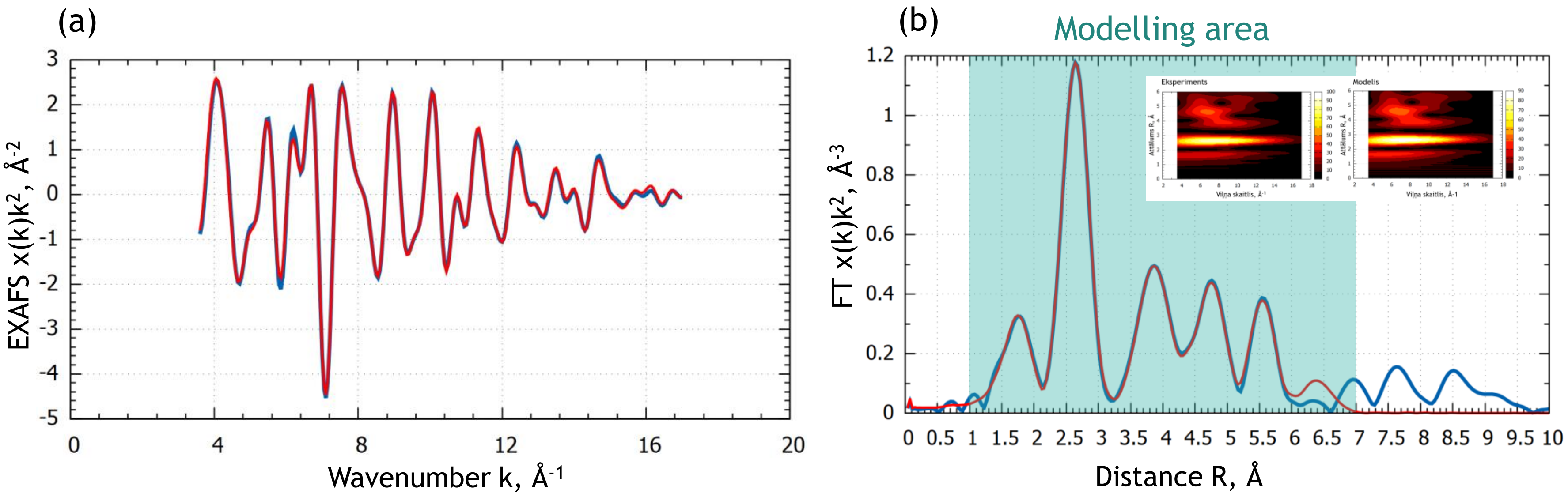
Ni K edge EXAFS x(k)k² spectra of polycrystalline stoichiometric NiO (a), FT of NiO Ni k edge EXAFS (b)

RMC PRINCIPLE

EvAX



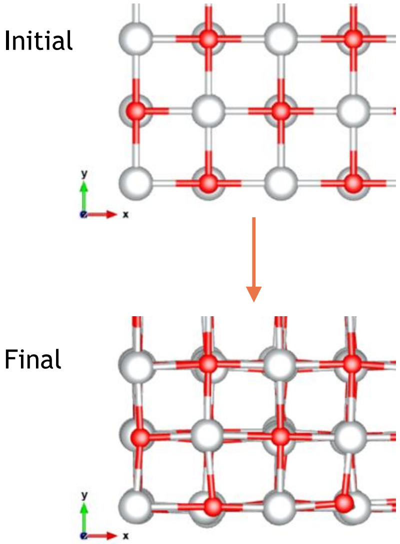
EXPERIMENT-MODEL FIT

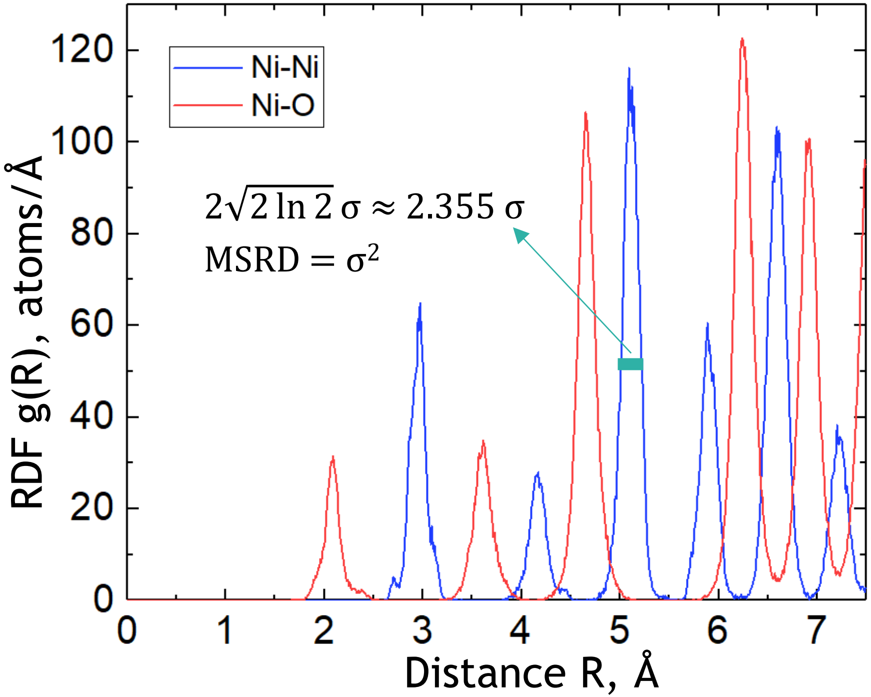


Comparison of the experimental (blue line) and RMC simulated (red line) Ni K-edge EXAFS spectra x(k)k2 (a) and their Fourier transforms (b) at 300 K

RMC RESULT - RDF

Supercell fragments from RMC:

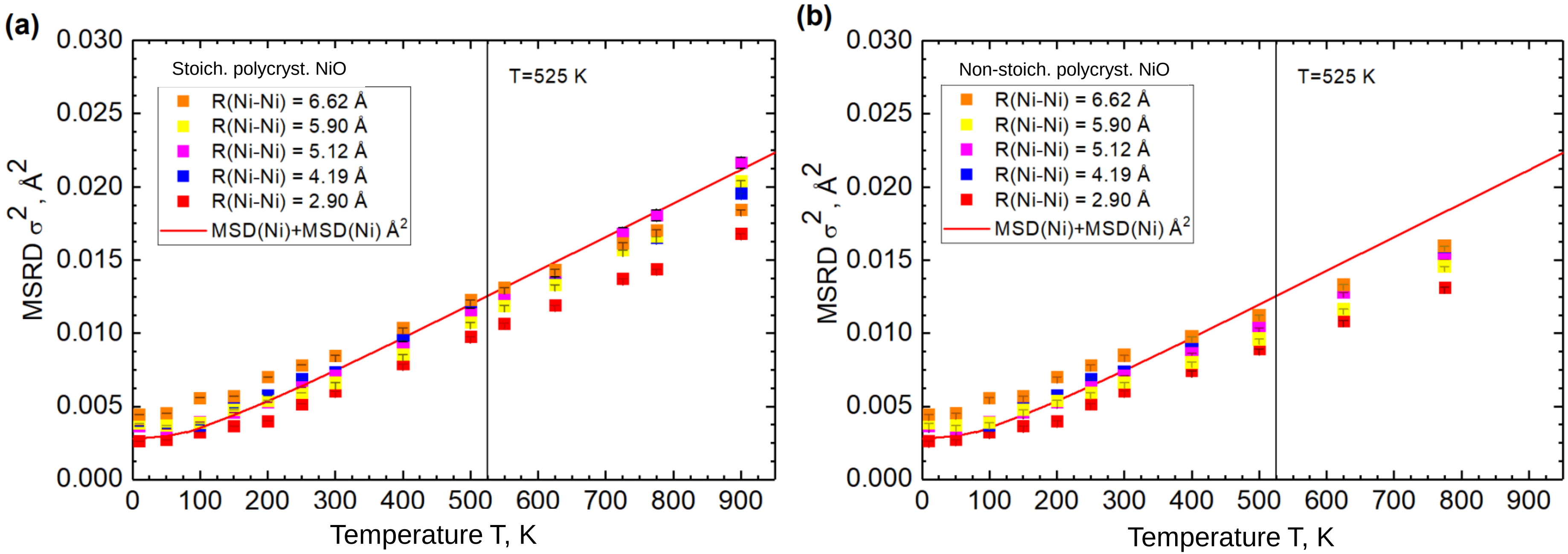




RDF for Ni-Ni and Ni-O atomic pairs of polycrystalline stoichiometric NiO obtained as the result of RMC

MSRD VALUES FOR Ni-Ni PAIRS

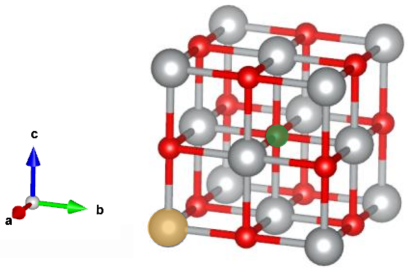
$MSRD_{AB}=MSD_A+MSD_B-DCF_{AB}$

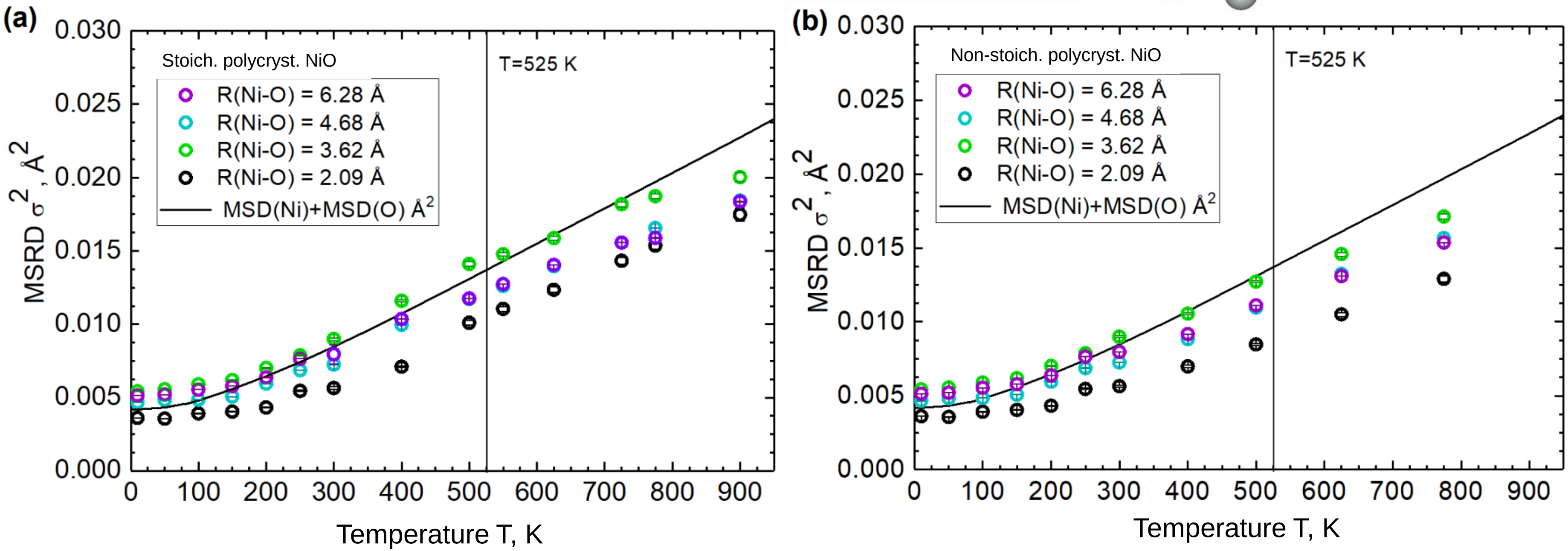


Temperature dependence of obtained MSRD values for Ni-Ni pairs for polycrystalline stoichiometric (a) and non-stoichiometric (b) NiO

https://doi.org/10.1107/S0108767399007114

MSRD VALUES FOR Ni-O PAIRS





Temperature dependence of obtained MSRD values for Ni-O pairs for polycrystalline stoichiometric (a) and non-stoichiometric (b) NiO

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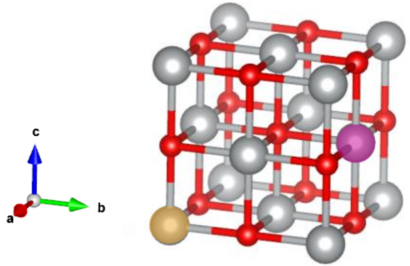
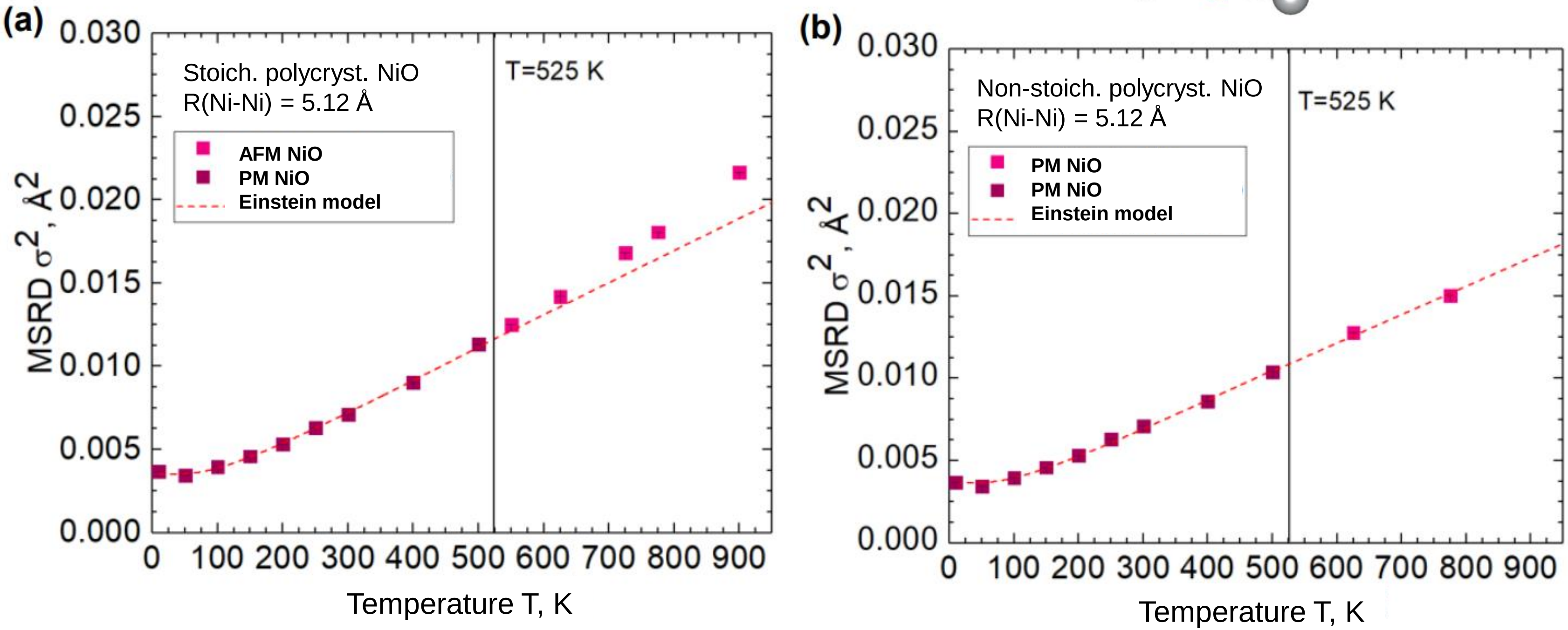
For Ni-O3 atomic pairs a reduced correlation of atomic motion was observed in a wide temperature range from 10 K to 900 K

MSRD VALUES FOR Ni-Ni PAIRS

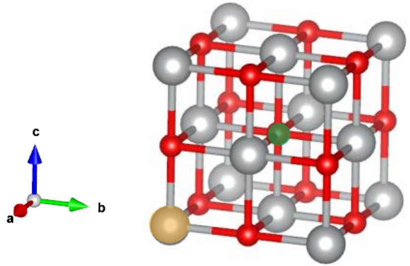


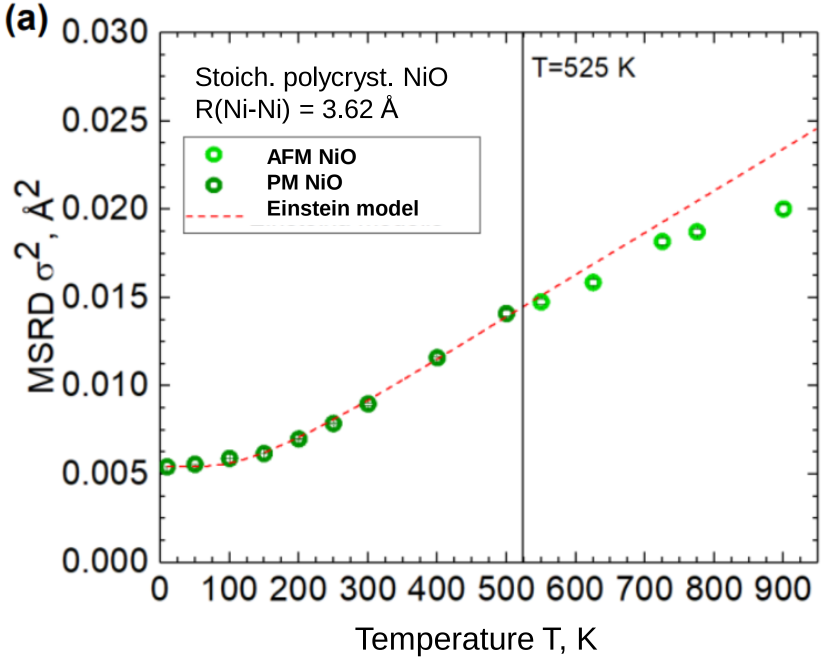


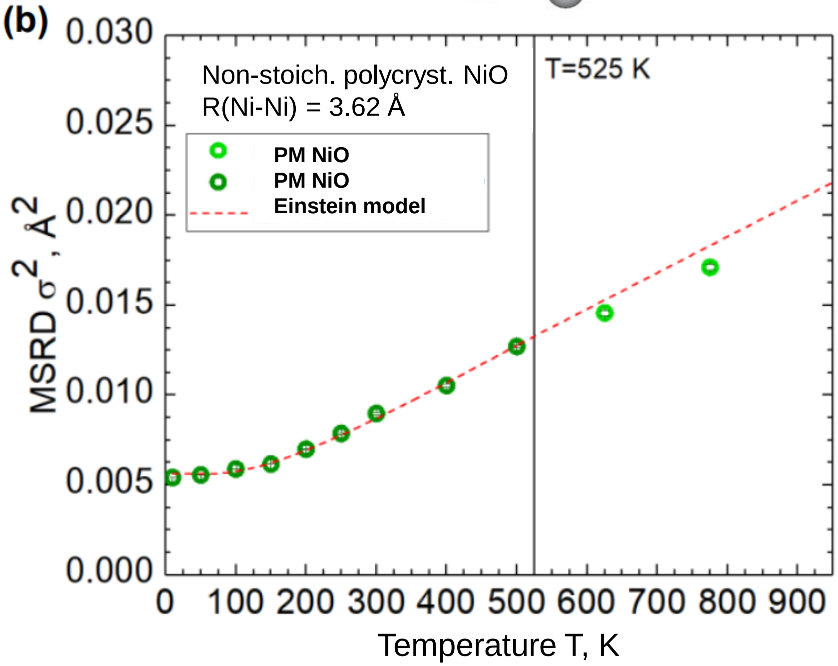
Approximation of Ni-Ni (5.12 Å) atomic pair MSRD values with Einstein Model

In stoichiometric NiO, it is possible to observe changes in the amplitudes of thermal oscillations of Ni-Ni and Ni-O atom pairs during the magnetic phase transition with EXAFS spectroscopy

MSRD VALUES FOR Ni-O PAIRS



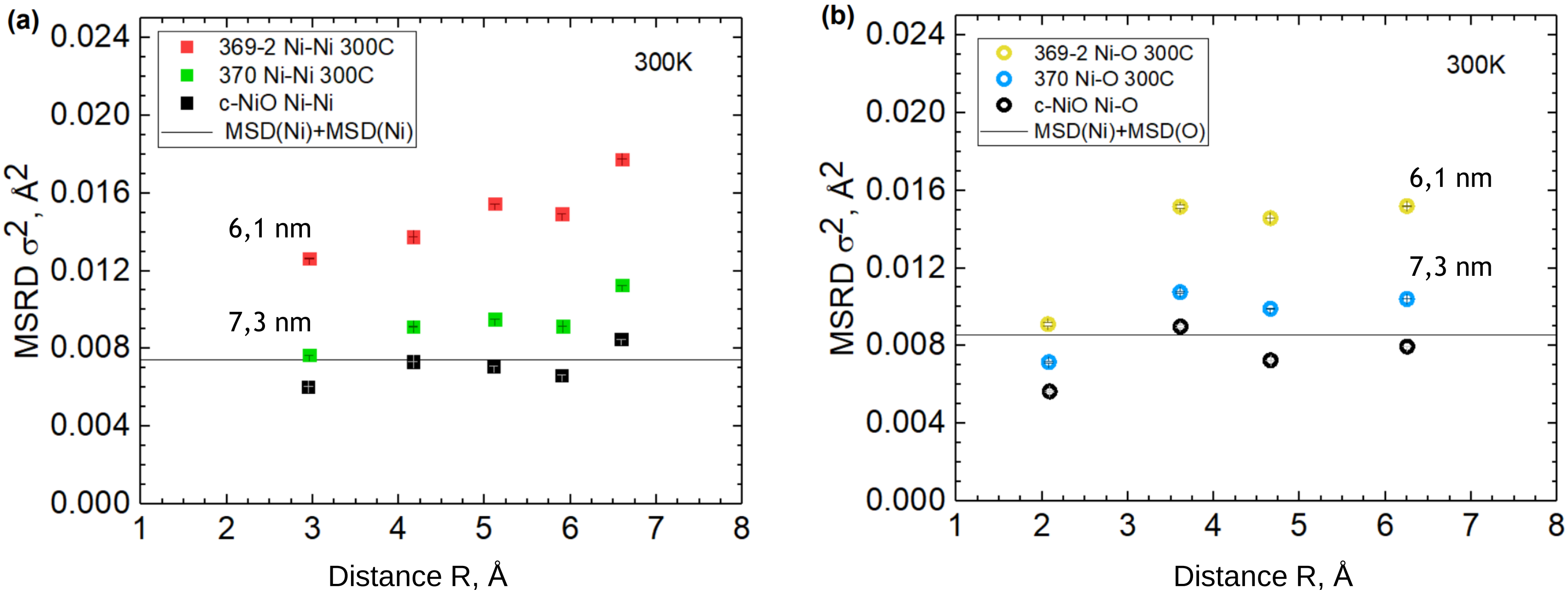




Approximation of Ni-O (3.62 Å) atomic pair MSRD values with Einstein Model

In stoichiometric NiO, it is possible to observe changes in the amplitudes of thermal oscillations of Ni-Ni and Ni-O atom pairs during the magnetic phase transition with EXAFS spectroscopy

MSRD VALUES FOR NANOCRYSTALLINE NiO



Obtained MSRD values for different Ni-Ni (a) and Ni-O (b) atomic pairs as a function of interatomic distance for nanocrystalline NiO samples

Ni-Ni and Ni-O atomic pair absolute MSRD values for nanocrystalline NiO samples are higher than in crystal

CONCLUSIONS

1. In stoichiometric NiO, it is possible to observe changes in the amplitudes of thermal vibrations of Ni-Ni and Ni-O atomic pairs during the magnetic phase transition with EXAFS spectroscopy.
2. Reduced correlation of atomic motion was observed for Ni-O3 atomic pairs in a wide temperature range from 10 K to 900 K. This can be explained by the strong anisotropy of the thermal atomic motion of O3 atoms.
3. The absolute MSRD values of Ni-Ni and Ni-O atomic pairs in nanocrystalline NiO are higher than in the crystal due to static disorder caused by atomic relaxation near the nanoparticle surface.

FLPP
FUNDAMENTAL AND APPLIED RESEARCH PROJECTS

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THANK YOU!

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