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STUDIES OF LOCAL STRUCTURE RELAXATION IN NANOMATERIALS

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Abstract

The X-ray absorption spectroscopy is a unique tool for direct local structure determination which is suitable for any material starting from bulk crystals ending with nanomaterials, liquids and gasses.

In this study we have applied the extended x-ray absorption fine structure (EXAFS) spectroscopy to probe the atomic structure of NiO, $CoWO_4$, $CuWO_4$ and PbS nanoparticles. We have compared the atomic structure of these nanomaterials with that of the corresponding bulk compounds, in order to identify the atomic structure relaxation (changes in atomic structure) caused by a reduction of the particle size down to nanoscale.

We have adopted a recently developed complex modeling approach, combining *ab initio* multiplescattering EXAFS calculations with classical molecular dynamics (MD), further referenced as MD-EXAFS, to the nanomaterials. The advantage of the MD-EXAFS method is a significant reduction of a number of free model parameters, which are required to describe the structure and dynamics of nanoobjects. Thus, a set of the parameters is restricted to that related to the geometry of the nanoobject and to the force-field model utilized in the MD simulations. The novel approach has been tested on NiO nanoparticles and thin films. The obtained results allowed us to identify the amount and the role of the Ni vacancies in the structure relaxation of NiO.

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1. Introduction

1.1. Motivation

Nanomaterials are used in a broad range of applications, for example, in sensors, catalysts, fuelcells, energy harvesting, nano-electronics, optoelectronic, and photonics devices. It was noticed that physical properties of nanomaterials are different compared with that in the bulk. Since it is well known that most of the properties are determined by atomic structure, it is important to have an access to precise structural information for nanomaterials, which is challenging task [1].

Scientists have been studying structure of nanomaterials for more than 40 years. It was noticed that in metallic nanoparticles the interatomic distances decrease with decreasing the size of the particle [2, 3]. Such behavior is consistent with the predictions of the classical physics [4], stating that surface tension should increase with decreasing of the particle diameter. Thus, increasing surface tension creates more pressure to the particle volume that leads to the decreasing of the interatomic distances. At the same time metal oxides and other metal nanomaterials possess opposite behavior, their interatomic distances increase with decreasing size of nanoparticles [5, 6, 7, 8]. Different mechanisms have been proposed to explain this phenomena [9, 10, 11], but still the question, why metals and metal compounds show different behavior, is open. In this context, the accurate determination of the changes in atomic structure in nanomaterials is very important. Information about atomic structure allows to validate theoretical models for existing nanomaterials and predict new nanomaterials with desired properties.

Different experimental techniques have developed to study nanomaterials [1, 12, 13], but only two methods, namely total scattering [14] and x-ray absorption spectroscopy [15, 16], provide with direct access to the structural information in the whole sample. The advantage of x-ray absorption spectroscopy (XAS) is its chemical element selectivity, sensitivity to low element concentration and scalability down to nanoparticles and even molecules [17, 18, 19]. It allows to extract information on the local atomic structure around the absorbing atom including distances and mean-square relative displacements (MSRD).

1.2. Aim and objectives of the work

The aim of this work was to study changes in atomic structure (structure relaxation) that happen upon decreasing the size of the materials to nanoscale. In particular, we have studied structure relaxation in nanocrystalline nickel oxide (NiO), tungstates (MeWO₄, Me = Co, Cu), and lead sulfide (PbS) using extended X-ray absorption fine structure (EXAFS) experimental data.

In this work we have adopted a recently developed complex modeling approach [20], combining *ab initio* EXAFS calculations [19, 21] with classical molecular dynamics (MD), further referenced as MD-EXAFS, to the nanomaterials [22, 23]. The advantage of the MD-EXAFS method is a significant reduction of a number of free model parameters, which are required to describe the structure and dynamics of nanoobjects. The only parameters we need are related to the geometry of the nanoobject and to the force-field model used in the molecular dynamics simulations. All interatomic distances, bond angles, thermal and static disorder effects are obtained from MD simulations by calculating configuration averages from snapshots of instant atomic positions.

We have applied MD-EXAFS on nanocrystalline NiO and have reconstructed structural and dynamic information from experimental Ni K-edge EXAFS spectra up to the eighth coordination shell of nickel in nanocrystalline NiO taking into account the presence of defects, thermal disorder and structure relaxation in nanoparticles [22, 23].

1.3. Scientific novelty of the work

Conventional EXAFS data analysis is restricted by the photoelectron single-scattering approximation [24], which limits the obtained structural information with only the first or, in some cases, also the second coordination shell of the absorbing atom. At the same time, standard fitting procedure, including photoelectron multiple-scattering processes [25, 26], employs three model parameters (path degeneracy, length and MSRD) for each scattering path, that results in a huge number of correlated parameters rapidly exceeding the maximum number of the allowed independent parameters.

Recently developed MD-EXAFS method [20] overcomes these limitations and allows one to use all information hidden in the EXAFS spectra, including all contributions from the photoelectron multiplescattering events. Also the method requires only few force-field parameters to describe the interatomic interactions in a compound.

We have extended MD-EXAFS method to the case of nanomaterials. It allows us to account for atomic structure relaxation, thermal disorder, nanoobject size and the presence of defects. This method enables us direct comparison of experimental EXAFS spectrum with the model one taking into account all coordination shells of the absorbing atom and the multiple-scattering effects. The agreement between experimental and theoretical EXAFS spectra is used as a criterion for the force-field model reliability.

The study of the local atomic structure around nickel atoms in nickel oxide (NiO) nanocrystalline powder and thin films has been performed using Ni K-edge EXAFS and interpreted using MD-EXAFS method [22, 27, 28]. It was found that in nanocrystalline NiO there is noticeable structure relaxation, which results in an expansion of the Ni–Ni bonds and a contraction of the nearest neighbor Ni–O bonds as well as an increase of the static disorder probed by the mean-square relative displacement (MSRD). At the same time, the lattice dynamics, also probed by the MSRD, is close in both micro- and nanocrystalline NiO in the temperature range from 10 to 300 K. It was shown using the MD-EXAFS method that the structure relaxation inside NiO nanoparticles is due to the presence of Ni vacancies [22, 23].

The study of the local atomic structure around tungsten and metal atoms in MeWO₄ (Me = Co, Cu) nanoparticles has been performed using the W L₃-edge and Me K-edge EXAFS and Raman spectroscopy. It was found that atomic structure of nanosized MeWO₄ relaxes compared with microcrystalline phase, leading to large and particular distortion of the WO₆ octahedra. In nanoparticles tungsten atoms have stronger and shorter bonds with the nearest four oxygen atoms, whereas other two oxygens become weakly bound. It is also shown that the relaxation is affected by the Me²⁺ ion type.

Pb L_3 - edge EXAFS results indicate strong structure relaxation in led sulfide (PbS) nanoparticles compared to microcrystalline PbS. The analysis of radial distribution functions (RDF) for Pb–S and Pb– Pb atom pairs revealed that they have non-Gaussian shape, indicating strong anharmonic Pb–S interaction, average Pb–S distance in the first coordination shell decreases, but the average Pb–Pb distance in the second coordination shell increases. This effect is similar to that found in NiO.

1.4. Author's contribution

The majority of the work has been done at the Institute of Solid State Physics, University of Latvia. X-ray absorption spectroscopy measurements were performed at HASYLAB/DESY (Hamburg, Germany) using synchrotron radiation produced by the DORIS~III storage ring.

The author has been participated in the nanopowder preparation and their characterization by Raman spectroscopy and x-ray diffraction.

The MD-EXAFS implementation for nano-compounds and corresponding computer code has been developed by the author.

The molecular dynamics simulations, the analysis of the experimental EXAFS data and the advanced modeling of EXAFS spectra (including MD-EXAFS) have been performed by the author at the Latvian SuperCluster facility LASC.

The results of this work have been presented at 8 international conferences and 4 international schools during 2009-2013 and discussed at the scientific seminar at the Institute of Solid State Physics, University of Latvia on April 20, 2013. Main results have been published in 6 SCI papers and 3 SCI papers are accepted, but not published yet.

2. EXAFS data analysis and simulations

To use the full power of the multiple-scattering EXAFS theory, we employed a recently developed simulation method [20], combining *ab initio* multiple-scattering EXAFS calculations with classical molecular dynamics (MD), further referenced as MD-EXAFS. This approach allows us to reconstruct the local environment of the absorbing atom, which contains not only single-scattering, but also multiple-scattering contributions, at the same time taking into account thermal disorder, structure relaxation and presence of defects.

An implementation of the MD-EXAFS scheme for nanoparticles is given in Fig.2.1. [22, 23] The goal of the first stage is to find force-field (FF) parameters which give the mean values of interatomic distances for the first coordination shells being in agreement with those obtained from the conventional analysis of the experimental EXAFS spectrum or other structural analysis. Only those model nanoparticles which give this agreement within the desired precision are passed to the second step. The goal of the second step is to fine-tune FF parameters in order to minimize the residual between configuration-averaged multiple-scattering EXAFS spectrum of the model nanoparticle and experiment. One should find the model nanoparticle which gives the minimal residual value. After second phase one can use MD data to find all necessary properties of the selected model nanoparticle.

The advantage of the MD-EXAFS method is a significant reduction of a number of free model parameters, which are required to describe the structure and dynamics of nano-objects. Only actual parameters are related to geometry (size and shape) and force-field model used in molecular dynamics simulations. All interatomic distances, bond angles, thermal and static disorder effects, and an influence of defects are obtained from MD simulations by calculating configuration averages from snapshots of instant atomic positions.



Figure 2.1. The scheme of MD-EXAFS calculations [22, 23].

3. Experimental

3.1. Sample preparation and characterization

Non-stoichiometric nanocrystalline $Ni_{1-x}O$ powder (nano-NiO) was produced by the precipitation method [32], based on a reaction of aqueous solutions of $Ni(NO_3)_2 \cdot 6H_2O$ and NaOH, followed by subsequent annealing of the precipitate in air at 250°C.

Non-stoichiometric nanocrystalline Ni_{1-x}O thin films were produced using reactive dc-magnetron sputtering of metallic nickel target and were deposited on three substrates (silicon, glass and polyimide tape). The film deposition was performed at three Ar/O₂ ratios equal to 0/100 (TF1), 50/50 (TF2) and 90/10 (TF3). Thus obtained thin films have dark brown color, suggesting the presence of nickel vacancies [33-36].

Commercial microcrystalline NiO powder (c-NiO, Aldrich, 99%), having green color, was used for comparison.

Nanocrystalline lead sulfide (nano-PbS) sample was synthesized using the method described in [37] and kindly provided to us by Dr. Boriss Polyakov. Microcrystalline PbS was commercial powder from Aldrich (99.9% trace metals basis).

MeWO₄ (Me = Co, Cu) nanoparticles were synthesized using co-precipitation technique by the reaction of Co(NO₃)₂·6H₂O or CuSO₄·5H₂O and Na₂WO₄·2H₂O at room temperature (20°C), pH=8 [38, 39]. We used "as prepared" nanopowders, which were x-ray amorphous or nanocrystalline.

Microcrystalline MeWO₄ powders were produced by annealing of "as-prepared" powders at 800°C for 4-8 h in air.

The crystallinity of samples was characterized by x-ray diffraction (XRD) using PANalytical diffractometer, Model X-Pert Pro MPD. It has high resolution vertical goniometer equipped with long fine focus ceramic tube, type PW3373/00, Cu anode, wavelength $\lambda = 0.154$ nm, max. P = 2.2 kW, U = 60 kV and PIXcel wide dynamic range solid-state detector.

Morphology of the films was characterized by scanning electron microscopy (SEM) using Carl Zeiss EVO 50 XVP electron microscope. Tungsten cathode was used as a source of electrons. The accelerating voltage was 25 kV.

Micro-Raman scattering spectra were collected in back-scattering geometry at 20°C using a confocal microscope with spectrometer "Nanofinder-S" (SOLAR TII, Ltd.). The measurements were performed through Nikon Plan Apo $20 \times$ (NA=0.75) optical objective. DPSS laser (532 nm, 150 mW cw) was used as the excitation source, and the Raman scattering spectra were dispersed by 1800 grooves/mm diffraction grating, having a resolution of about 2.5 cm⁻¹ and mounted in the 520 mm focal length monochromator. The elastic laser light component was eliminated by the edge filter (Semrock LP03-532RE). Peltier-cooled back-thinned CCD camera (ProScan HS-101H, 1024×58 pixels) was used as a detector.

3.2. X-ray absorption spectroscopy

X-ray absorption spectra were measured in transmission mode at the HASYLAB/DESY C bending-magnet beamline. The storage ring DORIS III operated at E = 4.44 GeV and $I_{max} = 140$ mA. The x-ray radiation was monochromatized by a 40 % detuned Si(111) double-crystal monochromator, and the beam intensity was measured using two ionization chambers filled with argon and krypton gases.

To achieve the absorption edge jump value $\Delta \mu \approx 1$, the proper amount of the sample powder was deposited on Millipore nitrocellulose membrane filter and fixed by Scotch tape, whereas a stack of simultaneously sputtered thin films was used. The relevant metal foil was used as the reference sample to control monochromator stability.

The Oxford Instruments liquid helium flow cryostat was used to maintain the required sample temperature, usually 6-300 K. The temperature was stabilized to within ± 0.5 degrees during each experiment.

4. Results and Discussion

4.1. Microcrystalline and nanosized NiO

Nickel oxide (NiO) is antiferromagnetic material [40] with the Neel temperature $T_N = 523$ K. It has cubic rock-salt structure (*Fm-3m*) above T_N , undergoing weak cubic-to-rhombohedral distortion (*R-3m*) below T_N due to the magnetostriction effect. NiO is known to be *p*-type semiconductor, having an oxygen excess due to the presence of nickel vacancies [33, 36]. Nickel vacancies are indicated by Rutherford back scattering measurements [34], by microthermogravimetric techniques [42], by Hall mobility measurements [33], and by *ab initio* calculations [36].

Upon size reduction down to nanoscale, the influence of crystallite surface increases leading to atomic structure relaxation. An expansion of lattice volume has been found in nanosized NiO by x-ray diffraction [43-46]. This phenomenon is in line with the general behaviour of nanosized metal oxides [5, 9, 10] and in the case of nickel oxide was tentatively explained in [43, 46] by a negative pressure due to the repulsive interaction of the parallel surface defect dipoles at small particle sizes. The unit cell volume in NiO nanoparticles becomes equal to that in the bulk nickel oxide for crystallite size above about 20 to 30 nm, taking into account the accuracy of the lattice constant determination in [43-46].

The crystallinity of our samples was characterized by x-ray diffraction (XRD). The structure of all samples correspond to cubic NiO. Using the Scherrer's method, and assuming the cubic crystallites shape, we have found that the average size of nanocrystallites was 6.2 ± 1.8 nm in the nanopowder and 6 ± 1 nm (TF3), 12 ± 1 nm (TF2) and 17 ± 1 nm (TF1) in the thin films. So the XRD data suggest that the crystallinity of the films is influenced by the sputtering atmosphere, i.e. Ar/O₂ ratio, and the nanocrystallites in the thin film TF3 are smaller than in the nanopowder.



Figure 4.1. Low temperature (T = 10 K) Ni K-edge EXAFS spectra $\chi(k)k^2$ and their Fourier transforms (FTs) for c-NiO, nano-NiO and TF3. There is noticeable signal damping upon a decrease of the size of particles (going from c-NiO to nano-NiO and, next, to TF3). Note also a small shift of the peak positions in FTs to larger distances upon a decrease of the particle size.



Figure 4.2. Left panel: Temperature dependence of the mean-square relative displacements (MSRD) ($\Delta\sigma^2(T) = \sigma^2(T) - \sigma^2(c - NiO, T = 6K)$) for the first (Ni-O₁) and second (Ni-Ni₂) coordination shells in c-NiO, nano-NiO and TF3. The Debye models are shown by lines. Right panel: Temperature dependence of the average interatomic distances in the first (Ni-O₁, labeled with full markers) and second (Ni-Ni₂, labeled with open markers) coordination shells of nickel in c-NiO (squares), nano-NiO (circles) and TF3 (triangles).

The low temperature (T = 10 K) experimental Ni K-edge EXAFS spectra $\chi(k)k^2$ and their Fourier transforms (FT) for selected NiO samples are shown in Fig.4.1. When comparing these spectra with the particle size estimations from XRD data, one can see that the damping of the signal increases upon decreasing of the particle size. Also one can notice the shift of the FT peak positions starting from the second peak to the larger distances upon a decrease of the crystallite size. This indicates clearly the lattice volume expansion in nanocrystalline NiO.

The difference between temperature dependencies of the MSRDs (Fig.4.2) for nano- and microcrystalline NiO samples remains nearly constant in the whole range of temperatures in both the first and second coordination shells. The constant difference gives clear evidence of the static disorder in nanocrystalline NiO, which is induced by a relaxation of its atomic structure. At the same time, the thermal disorder contribution into the MSRD is close in all samples but differs for the first and second coordination shells, as expected. It can be well approximated by the Debye model [47].

The average second shell distance $R_2(Ni-Ni_2)$ in nanoparticle samples is longer by ~0.008 Å in nano-NiO and by ~0.015 – 0.18 Å in NiO thin films than that in microcrystalline c-NiO at all temperatures (Fig. 4.2). On the contrary to the second shell behavior, the average first shell $R_1(Ni-O_1)$ distance in all nanocrystalline samples is shorter compared with microcrystalline NiO (Fig. 4.2). This interesting result has been found by us [27, 28] in nanosized NiO powder at room temperature and is confirmed in a wide temperature range for differently prepared NiO nanocrystalline samples [22, 23]. This can be a result of the non-uniform relaxation of the atomic structure (distances) in nanoparticles. One obvious example is the interatomic distances on the surface. This phenomenon should be studied in more details, by using advanced methods of EXAFS analysis.

To reveal the fine details of the structure relaxation in NiO nanocrystallites, we used a more rigorous approach [20, 22, 23, 27, 28] based on the MD-EXAFS method [20].



Figure 4.3. Comparison of the experimental (solid lines) and configuration-averaged (dashed lines) Ni K-edge EXAFS spectra $\chi(k)k^2$ and their Fourier transforms (FTs) for nano-NiO and TF3. The theoretical data correspond to the nanoparticle models which give the best fit to the experimental spectra (nano-NiO: N = 9 corresponding to $L \approx 3.6$ nm, $C_{vac} = 0.4$ % corresponding to 12 vacancies, Z_{Ni} =+1.976, Z_{O} =-1.968; tf-NiO: N=4 corresponding to $L \approx 1.5$ nm, $C_{vac} = 1.6$ % corresponding to 4 vacancies, Z_{Ni} =+1.925, Z_{O} =-1.895).

Crystalline NiO was modeled in the isothermal-isobaric ensemble (NPT) with constant pressure and temperature using the supercell size 6x6x6 and 3D periodic boundary conditions [22]. Nanosized nickel oxide particles were simulated in the canonical ensemble (NVT) using cubic shape clusters LxLxL placed in a large empty box, which corresponds to the free NiO particle in a vacuum [22]. They were generated from cubic rocksalt-type unit cell having the symmetry *Fm-3m* (space group 225) and containing 4 nickel and 4 oxygen atoms. The cluster size was up to L = 40a₀, where a₀ = 4.1773 Å is lattice parameter of c-NiO.

Our force-field (FF) potential model included two-body central force interactions between atoms *i* and *j* described by a sum of the Buckingham and Coulomb potentials. The Buckingham potential parameters *A*, ρ , and *C* were taken from simulations of c-NiO [28, 48] using the formal charges of ions $(Z_{\text{Ni}} = +2.0 \text{ for nickel atoms and } Z_{\text{O}} = -2.0 \text{ for oxygen atoms})$ and reproduce well such properties of bulk crystal as lattice constant, elastic constants, bulk modulus and static dielectric constant [28]. In this study we selected the charge of nickel atoms Z_{Ni} as the optimization parameter to minimize the residual between experimental and calculated EXAFS signals. All other Buckingham potential parameters were left unchanged. Nickel vacancies were generated by randomly removing Ni atoms from the ideal model particle, ensuring their homogeneous distribution [22]. Thus, each model particle now is characterized by its size *L* and the number of nickel vacancies N_{vac} . The charge of oxygen atoms Z_{O} was calculated to maintain electroneutrality of the system.

As a result, we found that there is a clear minimum in the dependence of the residual on the particle size and vacancy concentration, which determines the sought model nanoparticle. Thus, only comparison between the experimental and configuration-averaged EXAFS spectra, using the full potential of the multiple-scattering theory, allowed us to select the best nanoparticle model, which also fulfills conditions of the first step. The experimental and final theoretical EXAFS spectra are compared in Fig.4.3, showing good agreement in both k and R space for NiO nanocrystalline powder and thin film samples.

The nanoparticle model, having the size $L \approx 3.6$ nm and the vacancy concentration $C_{\text{vac}} = 0.4$ %, gives the best fit to the experimental EXAFS spectrum for the NiO nanocrystalline powder sample (nano-NiO). The same procedure was applied to the experimental data of NiO thin film samples.

4.2. MeWO₄ nanoparticles and microcrystalline samples

Crystalline CoWO₄, NiWO₄ un ZnWO₄ have monoclinic (*P2/c*) wolframite-type structure built from distorted WO₆ and MeO₆ octahedra joined by edges into infinite zigzag chains, consisting of octahedral units of the same type and running parallel to *c*-axis [49]. Crystalline CuWO₄ has close structure but lower triclinic (*P-1*) symmetry due to the strong first-order Jahn-Teller (FOJT) distortion induced by Cu²⁺ 3d⁹ electronic configuration [51].

In this study we have explored a size-induced relaxation of the local structure in CoWO₄ and CuWO₄, having two distinct structure types, by extended x-ray absorption fine structure (EXAFS) spectroscopy, x-ray powder diffraction and micro-Raman spectroscopy, extending recent results of our laboratory for nanosized NiWO₄ [52] and ZnWO₄ [39, 53, 54], thus, allowing us to elucidate in more details the effect of size, temperature and transition metal type.

The XRD patterns for as-prepared tungstates have strongly broadened Bragg peaks, thus indicating their nanocrystalline structure. The powders become microcrystalline upon annealing in air at 800°C [53], transforming into wolframite-type phase.

X-ray absorption spectroscopy has been used to analyze the first coordination shell, which contains only single-scattering contributions, singled out by the back-FT procedure in the range of $\approx 0.8-2.2$ Å. To extract structural information, the first shell EXAFS contributions $\chi(k)k^2$ were best-fitted using a modelindependent approach [30, 31] allowing the reconstruction of the true radial distribution function (RDF) G(R), in this case corresponding to the distribution of the distances between oxygen and metal atoms within metal-oxygen octahedra.

A comparison of the reconstructed RDFs (Fig. 4.4) obtained at 10 K and 300 K in CuWO₄ suggests that the effect of thermal disorder leads to some peak broadening and is relatively small, in particular, in nanopowders where static relaxation dominates. Both RDFs $G_{W-O}(R)$ and $G_{Me-O}(R)$ (Me = Co, Ni, Cu, Zn) for microcrystalline tungstates agree well with data from the corresponding crystallographic structure.

In CoWO₄ and NiWO₄ the six oxygen atoms of MeO₆ octahedra contribute into one broad peak, centered at ~2.08 Å in the RDF $G_{\text{Co-O}}(R)$ and at ~2.05 Å in the RDF $G_{\text{Ni-O}}(R)$, but the six oxygens of the WO₆ octahedra are divided into two groups of four (at ~1.83 Å) and two (at ~2.15 Å) atoms [55].

Chemical bonding in microcrystalline tungstates can be successfully probed by Raman spectroscopy, providing an access to the half of vibrational modes (Fig. 4.5). An increase of the stretching W-O frequency from 882 cm⁻¹ in CoWO₄ to 905 cm⁻¹ in ZnWO₄ indicates some strengthening of tungsten-oxygen bonds [57], which compete with the Me-O bonding. Note that the corresponding W-O bond lengths are almost the same (~1.79 Å) in the four tungstates [55, 56].

Nanocrystalline tungstates are much weaker Raman scatterers (Fig. 4.5): the only visible broad band at ~955 cm⁻¹ was attributed previously to the double tungsten-oxygen W=O bonds at the nanoparticle surface [53]. The band has a single-peak shape in CoWO₄, NiWO₄ and ZnWO₄, but has more complex structure in CuWO₄, suggesting the presence of slightly inequivalent non-bridging W=O bonds. A well-known correlation [57] between the force constant (or stretching frequency) and the length of the W-O bond suggests the W=O bond length of about 1.7 Å.



Figure 4.4. The reconstructed RDFs *G(R)* for the first coordination shell of tungsten and transition metals in microcrystalline (solid lines) and nanocrystaline (dashed lines) MeWO₄ (Me = Co, Ni, Cu, Zn). The data for NiWO₄ and ZnWO₄ are taken from [39].



Figure 4.5. Left panel: Raman scattering spectra of microcrystaline and nanocrystaline MeWO₄ (Me = Co, Ni, Cu, Zn) powders. The position of the main band at 955 cm⁻¹ in nanosized tungstates is indicated by dashed vertical line. Measurements were performed at 20°C. Right panel: the dependence of the main Raman band for microcrystaline MeWO₄ from the atomic number of the Me atom.

In fact, the existence of short tungsten--oxygen bonds in nanopowders is clearly visible in the RDFs $G_{W-O}(R)$ (Fig. 4.4). In general, the WO₆ octahedra distortion originates from strong electron-lattice coupling, which leads to the second-order Jahn-Teller (SOJT) effect due to a covalent interaction of

empty 5*d* orbitals in W⁶⁺ ions with filled 2*p* orbitals in the oxygen atoms [58]. An additional contribution into the WO₆ octahedron deformation comes from competing interaction of oxygens with the 3*d* transition metal ions. It manifests most strongly in CuWO₄, where the axial distortion of CuO₆ octahedra is stabilized by the first-order Jahn-Teller (FOJT) effect caused by the 3*d*⁹ electron configuration of Cu²⁺ ions [51]. As a result, the RDFs $G_{Cu-O}(R)$ have close shape in both microcrystalline and nanocrystalline powders, and the difference between the RDFs $G_{W-O}(R)$ is caused mainly by peak broadening.

In CoWO₄, NiWO₄ and ZnWO₄, the bonding between 3d and oxygen ions is less rigid, so that their local environment is able to relax in nanopowders, giving more freedom to tungsten ions to adapt themselves. Therefore, tungsten ions are able to attract four nearest oxygens, thus enhancing the distortion of WO₆ octahedral.

4.3. Microcrystalline and nanosized PbS

Lead sulfide (PbS) is an IV-VI semiconductor, having cubic sodium chloride type structure (space group *Fm-3m*, lattice constant $a_0 = 5.936$ Å [59]) and rather small bandgap ($E_g = 0.42$ eV at T = 300 K [60]), which is very suitable for infrared detection applications. Optical properties of PbS nanocrystals strongly depend on their size and shape, and the quantum confinement effect leads to an increase of effective band gap E_g to values beyond 1 eV. Therefore, nanosized PbS is a promising material for harvesting visible and infrared radiation and other opto-electronic applications [61].

There is limited number of X-ray absorption spectroscopy (XAS) studies of local structure in crystalline PbS [62-64] and no such studies for nanosized PbS. Therefore, we have performed the Pb L_3 -edge XAS study of local environment both in microcrystalline and nanocrystalline PbS with the goal to estimate the relaxation of the local atomic structure around lead atoms due to a reduction of crystallites size.

Optical absorption spectra of our nanocrystalline PbS show well defined excitonic peak centered at about 1.63 eV (760 nm). There are well known relations linking particle size with optical band gap E_g [65] and position of the excitonic peak [66]. So, we estimated the average size of nanoparticles in nano-PbS to be about 3 nm.

The experimental Pb L₃-edge EXAFS spectra and their Fourier transforms for c-PbS and nano-PbS at T = 300 K indicate strong structure relaxation in nanosized PbS, observed as a small phase shift of the EXAFS signal and a change in the peak positions and amplitudes in FT. The phase shift of the EXAFS signal is well noticeable at k > 5 Å⁻¹ and indicates changes in interatomic distances of nano-PbS compared with c-PbS. In the Fourier transforms of the EXAFS spectra we can clearly recognize several peaks. The first peak at 2.4 Å is most pronounced and is due to the single-scattering signal from sulphur atoms in the first coordination shell of lead atoms (Pb-S₁). The signal from the second next coordination shell (Pb-Pb₂) is split into two peaks with the maxima at 3.5 Å and 4.2 Å. Next peaks in the Fourier transforms have very strong influence of the multiple-scattering signals, which are mixed with the next coordination shells of lead atoms (Pb-S₃ and Pb-Pb₄). Therefore, the analysis of the first two coordination shells of Pb can be performed within the single-scattering approximation.

The results reveal the noticeable structure relaxation in nano-PbS. The average distance in nano-PbS between the nearest neighbors (Pb-S₁) becomes smaller by -0.02 Å and the distance between next neighbors (Pb-Pb₂) increases by +0.01 Å compared with c-PbS (the error is ±0.01 Å). At the same time, we can see significant increase of the mean-square relative displacement (MSRD) values for both coordination shells in nano-PbS ($\sigma^2_{Pb-S1} = 0.021$ Å² and $\sigma^2_{Pb-Pb2} = 0.028$ Å²) compared with c-PbS ($\sigma^2_{Pb-S1} = 0.017$ Å² and $\sigma^2_{Pb-Pb2} = 0.020$ Å²) (the error is ±0.001 Å²).

RDF reconstruction was done using the same theoretical amplitudes and phases for Pb-S and Pb-Pb atom pairs as those obtained by FEFF8 [29] and used in the standard fitting procedure. As a result, non-Gaussian form of RDFs has been revealed in both c-PbS and nano-PbS (Fig. 4.6). The RDF asymmetry is caused by lone pair $6s^2$ electrons, which are responsible for high polarizability of Pb ions and anharmonic Pb-S interatomic potential. In Fig. 4.6 one can see a comparison of the reconstructed RDFs with those obtained within the Gaussian approximation. RDF reconstruction confirms the structure relaxation in nano-PbS sample, where the average Pb-S₁ distance decreases, whereas the average Pb-Pb₂ distance slightly increases compared with c-PbS. This effect is similar to that in metal oxides.



Figure 4.6. Left panel: The experimental Pb L₃-edge EXAFS spectra $\chi(k)k^2$ and their Fourier transforms (FTs) for c-PbS and nano-PbS at T = 300 K. Right panel: Radial distribution function (RDF) reconstruction for c-PbS and nano-PbS obtained using theoretical phases and amplitudes. Dotted lines show RDF approximation with the Gaussian shape obtained by the standard EXAFS fitting procedure for the first two coordination shells.

Conclusions

In this thesis we have employed the extended X-ray absorption fine structure (EXAFS) method to study experimentally and using complex modeling approach the phenomenon of atomic structure relaxation upon a decrease of the size of particles down to nanoscale in nickel oxide (NiO), tungstates (MeWO₄, Me = Co, Cu) and lead sulfide (PbS).

A recently developed complex modeling approach [20], combining *ab initio* EXAFS calculations [19, 21] with classical molecular dynamics (MD), further referenced as MD-EXAFS, has been adopted to nanomaterials [22, 23]. The advantage of the MD-EXAFS method is a significant reduction of a number of free model parameters, which are required to describe the structure and dynamics of nanoobjects [20, 22]. The only parameters we need are related to the geometry of the nanoobject and to the force-field model used in the molecular dynamics simulations. All interatomic distances, bond angles, thermal and static disorder effects are obtained from MD simulations by calculating configuration averages from snapshots of instant atomic positions.

Here we have used the MD-EXAFS method to reconstruct the structure of nanocrystalline NiO from experimental Ni K-edge EXAFS spectra taking into account the presence of defects, thermal disorder and structure relaxation in nanoparticles [22, 23]. It was found that there is noticeable structure relaxation in nanocrystalline NiO, which results in an expansion of the Ni-Ni distances in the second coordination shell of nickel atoms and in a contraction of the nearest neighbour Ni-O bonds as well as in an increase of the static disorder, evidenced by the mean-square relative displacement (MSRD) parameter. At the same time, the lattice dynamics, also probed by the MSRD, is close in both micro- and nanocrystaline NiO in the temperature range from 10 to 300 K. It was shown using the MD-EXAFS method that the structure relaxation inside NiO nanoparticles is due to the presence of Ni vacancies [22, 23].

The MD-EXAFS method, based on classical MD and rather simply pair atomic potentials, is not applicable to the materials, whose structure is strongly influenced by the electronic or quantum effects. Therefore, we have employed more conventional analysis scheme to nanosized tungstates and lead sulfide.

The study of the local atomic structure of tungsten and divalent metal atoms in nanosized MeWO₄ (Me = Co, Cu) has been performed using the W L₃-edge and Me K-edge EXAFS and Raman spectroscopy. It was found that atomic structure of MeWO₄ relaxes compared with microcrystalline phase, leading to large and particular distortion of the WO₆ octahedra. In nanoparticles tungsten atoms have stronger and shorter bonds with the nearest four oxygen atoms, whereas other two oxygens become weakly bound. This result contradicts to the general rule stating that the lattice of nanoparticles gets distorted in such a way that the crystal symmetry tends to increase [8]. In tungstates we can see that the asymmetry parameter increases upon decreasing the size of the particles. It is also shown that the relaxation is affected by the Me²⁺ ion type.

Finally, Pb L_3 -edge EXAFS results indicate strong structure relaxation in nanosized lead sulfide (PbS) compared to microcrystalline PbS. The analysis of radial distribution functions (RDF) for Pb-S and Pb-Pb atom pairs revealed that they have non-Gaussian shape, indicating strong anharmonic Pb-S interaction. We found that the average Pb-S distance in the first coordination shell of lead atoms decreases, but the average Pb-Pb distance in the second coordination shell increases. This effect is similar to that found in NiO.

To conclude, we have demonstrated that x-ray absorption spectroscopy is a suitable tool for the investigation of structure relaxation phenomena in nanosized materials. Moreover, when combined with advanced simulation methods, the technique allows one to obtain additional original information (for example, concentration of vacancies) not accessible within conventional data analysis procedure.

Main theses

- A method, combining classical molecular dynamics simulations with *ab initio* multiple-scattering EXAFS calculations (MD-EXAFS method), has been extended to the case of nanoparticles. It allows one to account for the effect of nanoparticle size, atomic structure relaxation, thermal disorder and the presence of defects using rather simple force-field model, based on the pair interatomic potentials with a few free parameters. Such approach allows straightforward incorporation of disorder effects into the multiple-scattering formalism and, thus, to perform the analysis of EXAFS spectra beyond the first coordination shell.
- In nanosized NiO (in powders and thin films) there is noticeable structure relaxation, which results in an expansion of the Ni-Ni₂ bonds and a contraction of the Ni-O₁ bonds as well as an increase of the static disorder probed by the mean-square relative displacement (MSRD). At the same time, the lattice dynamics, also probed by the MSRD, is close in both microcrystaline and nanosized NiO in the temperature range from 10 to 300 K. It was shown using the MD-EXAFS method that the main source of the structure relaxation inside <u>NiO</u> nanoparticles is the presence of Ni vacancies.
- The atomic structure of nanosized $MeWO_4$ (Me = Co, Cu) relaxes compared with microcrystalline phase, leading to a large and particular distortion of the WO₆ octahedra. Tungsten atoms make stronger and shorter bonds with nearest four oxygen atoms, whereas other two oxygens remain weakly coordinated to tungsten. It is also shown that the relaxation is affected by the Me²⁺ ion type.

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Author's publication list

Main publications:

- 1. A. Anspoks, A. Kalinko, R. Kalendarev, A. Kuzmin, Atomic structure relaxation in nanocrystalline NiO studied by EXAFS spectroscopy: Role of nickel vacancies. *Physical Review B* 86 (2012) 174114:1-11.
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Participation in schools with posters

- A. Anspoks, R. Kalendarev, A. Kuzmin, Structure, morphology and dynamics of Ni_{1-x}O thin films, X. Research Course on New X-ray Sciences "Ultrafast X-ray science", March 28-31, 2011, Hamburg, Germany.
- A. Anspoks, A. Kuzmins, A. Kalinko, Local structure relaxation and lattice dynamics in polycrystalline and nanocrystalline NiO, PSI Summer School 2011 - Phase Transitions, August 14-22, 2011, Zug, Switzerland.
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- A. Anspoks, A. Kalinko, P. Kulis, A. Kuzmin, B. Polakov, J. Timoshenko, EXAFS spectroscopy of the local environment in PbS quantum dots, First Baltic School on Application of Neutron and Synchrotron Radiation in Solid State Physics and Material Science (BSANS-2012), October 1-4, 2012, Riga, Latvia.

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