Nanoparticles belong to modern, progressive materials with wide application potential. Its interesting properties come from the high surface to volume ratio and often differ from the properties of bulk or coarse-grained materials with the same chemical composition. Nanoparticles catalytic, magnetic, electric or optical properties are just examples. In this study we investigated niobium nanoparticles prepared by magnetron sputtering in combination with gas aggregation cluster source operated in DC mode in argon atmosphere.

Studied nanoparticles deposited on silicon substrates were characterized by combination of X-ray scattering and diffraction methods and transmission and scanning electron microscopies with energy-dispersive X-ray spectroscopy. These analytical methods provide the information about the nanoparticles sizes, shapes, their distributions, chemical composition and the real atomic structure. In order to determine the thermal evolution of nanoparticles microstructure, the in situ high temperature XRD measurement was done in ambient air atmosphere up to 800 °C. Measured SAXS data for temperatures in range between 50 °C – 800 °C are shown in Figure 1. Two main transition are observed and described.

Thin oxygen layer is present on the surface of as prepared niobium nanoparticles, which acts as a protection barrier against further corrosion. The thickness of this amorphous oxide layer, as determined by fitting the SAXS patterns, is about 0.9 nm. The nanoparticle core is formed by pure niobium bcc phase and its mean radius is 11 nm. With increasing temperature, the growth of the oxide shell layer at the expense of the size of nanoparticle metallic core occurs. Slightly above 200 °C the nanoparticles are fully

**Figure 1.** The SAXS patterns measured during annealing of nanoparticles from 50 °C to 750 °C, at ambient air atmosphere.

**Figure 2.** Temperature dependence of nanoparticle sizes, two different models were used to fit the measured data: core@shell model up to 200 °C, above 200 °C spheres model.
amorphized which is clear from XRD patterns. In this temperature range the mean nanoparticle size remains almost same. The results of SAXS measurement are plotted in Figure 2. Crystalline phase of niobium pentoxide is formed at temperature around 450 °C. Additionally, we observe one more phase transformation at 625 °C after which also pronounced increase of nanoparticles sizes starts. Based on the combination of SAXS and XRD measurement we conclude that the size of original niobium nanoparticles corresponds to the mean crystallite size, i.e. it means one nanoparticle consists of one coherently diffracting domain. At the end of the annealing process, after heating to 800 °C and formation of the orthorhombic niobium pentoxide phase, there are more crystallites in one particle.

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### STRUCTURAL ANALYSIS OF CLAY MINERALS INTERCALATED WITH DRUGS SOLVED BY CLASSICAL MOLECULAR DYNAMICS AND DFT METHODS

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We report comparison of results of computational approach to physico-chemical description of clay minerals-based drug nanocarriers. Two different types of layered clay structures were described. The first one was Mg₂Al layered double hydroxide (LDH) intercalated with three drugs – mefenamic acid, sulindac and pravastatin. These drugs have anti-inflammatory and ant nociceptive effects (anti conduction of painful stimuli) and clay drug nanocarrier promotes its stability and sustained release process. The series of models with different amount and initial arrangement of intercalated drug were built and analysed in order to compare the calculation results with experimental data published in [1-3]. The second clay mineral was Halloysite intercalated with irinotecan drug. This mineral posses spiral shape nanotube morphology with different charge distribution on inner and outer surfaces. The results for different pH conditions will be presented [4].

DFT calculations for small crystal cell were carried out in QuantumEspresso using PBE exchange-correlation functional and MD calculations in Materials Studio software package using combination of two compatible forcefields CVFF and ClayFF. Comparison of calculated XRD patterns, basal spacings, concentration profiles, free volumes and mean square displacements will be presented for LDH supercell with total surface area of 400 Å². DFT calculation were used for studying of interactions between LDH surface and drug. The whole complex structure was analysed by MD calculation on ns time scale. Results for modified forcefields in comparison with DFT substructure calculation and experimental results will be presented.

The energetically preferred bilayer or pseudo bilayer arrangement of intercalated drugs will be discussed in order to describe differences in behaviour for individual drugs and its impact on sustained release process.

STUDY OF ARRANGEMENT OF INTERCALATED ORGANIC SPECIES WITHIN LAYERED MATERIALS BY MOLECULAR SIMULATION METHODS

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We used classical molecular simulations to study the arrangements of various intercalated organic species (i) optically active 4,4'-dipyridylamine derivatives [1] within the layers of zirconium 4-sulfophenylphosphonates (ZrSPhP) and (ii) molecules of anti-inflammatory drugs within the layers of Mg-Al layered double hydroxides (LDH). We present the arrangement of the intercalated molecules of 3-methoxy-N-(pyridin-4-yl)pyridin-4-amine (moAPY2, see Fig. 1) between the layers of ZrSPhP and mefenamic acid (see Fig. 2) intercalated within the layers of LDH. Their mutual positions and various orientations were calculated by the molecular simulation methods with the respect to the lowest value of the total potential energy.

Figure 1. Molecule of 3-methoxy-N-(pyridin-4-yl)pyridin-4-amine (moAPY2).

Figure 2. Molecule of mefenamic acid.

For the case of ZrSPhP, the simulations revealed that the alternating orientation of the intercalated moAPY2 molecules is preferred. The best calculated model is shown in the Fig. 3. The intercalate is characterized by disordered arrangement where at several places the intercalated mole-
lated molecules are stacked together in the optimized arrangement by the interactions between the pyridine rings.

Regarding the intercalation of LDH, molecules of mefenamic acid as drug with anti-inflammatory effect were inserted between the layers of Mg$_2$Al LDH together with chlorine anions, in accordance to the chemical analysis [2]. From different types of arrangement of the intercalated molecules, the lowest value of potential energy and the best agreement with experimental XRD pattern [2] was reached for the bilayer arrangement, shown in Fig. 4. Due to the electrostatic interactions, the chlorine anions are closely attached to the layers of positively charged hydroxides and the COO$^-$ functional groups of mefenamic acid molecules are turned to the LDH layers.


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BOUND STATE OF CRYSTAL ELECTRIC FIELD EXCITATION AND A PHONON IN CePd$_2$Al$_2$

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The existence of a bound state (vibron state) between 4f electrons and phonons is closely associated with CeAl$_2$ [1] compound. The magnetic excitations observed by neutron scattering were not possible to be described by standard crystal electric field theory using cubic symmetry for Ce surrounding. Also local static distortion on Ce site was excluded. The observed magnetic excitation was finally described by the Thalmeier-Fulde model of vibron state [2]. This model explains the observed magnetic excitations and also gives a prediction which phonon mode should be involved in the bound state (in case of CeAl$_2$ it is $\Gamma_{15}$). This phonon mode is then influenced by the vibron state – the phonon mode softens and broadens [1].

For a long time CeAl$_2$ was a unique compound in which this enhanced interaction was observed. The increasing interest in recent time is motivated by new tetragonal materials which exhibit similar behaviour of magnetic excitations: CePd$_2$Al$_2$ [3], CeCuAl$_2$ [4] and CeAuAl$_3$ [5]. But the study of phonon dispersion curves and the influence of the vibron state is still missing.

Our interest is focused on CePd$_2$Al$_2$ and non-magnetic analogue LaPd$_2$Al$_2$ which crystalize in tetragonal CeBe$_5$Ge$_2$ structure type and undergo a structural phase transition decreasing their symmetry in the basal plane. The resulting structure can be then described within the orthorhombic Cmme space group. We succeeded with preparation of single crystalline (Ce,La)Pd$_2$Al$_2$ samples.

Figure 1. Comparison of A$_{1g}$ phonon mode of CePd$_2$Al$_2$ and LaPd$_2$Al$_2$ at 1.5 K.
and investigated their phonon dispersion curves, mainly the temperature dependence of $A_{1g}$ phonon mode, see Fig. 1. The results will be discussed in terms of enhanced magneto-elastic interaction which is responsible for formation of the vibron state.