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Database of organic and organometallic structures

DATABÁZE ORGANICKÝCH A ORGANOMETALICKÝCH STRUKTUR

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The Cambridge Structural Database, C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, Acta Cryst. B72, 171-179 (2016). DOI: 10.1107/S2052520616003954

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Nové informace o CSD najdete například na adresách .. https://email.seznam.cz/#search/prefix%3Acsd/193876 https://email.seznam.cz/#inbox/194314

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LATTICE PARAMETERS FROM ELECTRON DIFFRACTION: VAIN(?) STRUGGLE AGAINST IMAGE DISTORTIONS

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Transmission electron microscope is an electron optical system. The imperfections of its elements introduce aberrations in the images obtained by the TEM. In electron diffraction experiments, the main concern is about the geometrical distortions that change the positions of the objects in the image. These geometrical distortions cause the shift of the positions of the recorded reflections, leading to problems in the analysis of the diffraction data, in particular in the determination of lattice parameters of the investigated material.

To characterize the distortions in a general manner, we expand the geometrical distortions into a series of circular harmonics. Be (x,y) the undistorted coordinates in the diffraction pattern and (x', y') the distorted coordinates (Fig.1), then we define the relationship as:

 $x' = x + (\Delta r \cos \varphi - \Delta t \sin \varphi)$ $y' = y + (\Delta r \sin \varphi - \Delta t \cos \varphi)$

where r and t are the radial and tangential components of the distortion, and are parameterized in terms of the polar coordinates r, of the point (x,y) (Fig. 1):

$$\Delta r = \sum_{n=0}^{N} \left(\cos(n(\varphi - \varphi_{r,n})) \sum_{m=1}^{M} \rho_{n,m} r^{m} \right)$$
$$\Delta t = \sum_{n=0}^{N} \left(\cos(n(\varphi - \varphi_{r,n})) \sum_{m=1}^{M} \tau_{n,m} r^{m} \right)$$

And *r*,*n*, *t*,*n*, *n*,*m* and *n*,*m* are the parameters of the distortions. Such an expansion includes naturally all commonly known geometrical distortions like the spiral,

 $\begin{array}{c}
\Delta t & \Delta r \\
\varphi \\
\varphi
\end{array}$

barrel-pincushion or elliptical distortion (Fig. 2) but it in-

Figure 1. Decomposition of the distortion vector into radial (r) and tangential (t) components.

cludes also other distortions.

Traditionally, the distortions are determined by recording a single oriented diffraction pattern of a known material and comparing the recorded reflection positions with the expectation. However, such a measurement provides only a limited amount of data and limited accuracy. Instead, we use a full 3D electron diffraction (3D ED) data set, which typically comprises over a hundred diffraction patterns recorded at a range of orientations of the crystal [2]. The refinement of distortions against such data yields an



Figure 2. Examples of the typical distortions. Each figure shows, how the distortion deforms an object composed of a square, circle and a cross. Undistorted object in blue, distorted object in orange. Label below the figure is the name usually given to this distortion. The lower line indicates, which coefficient of the general expansion are non-zero for each distortion.

Krystalografická společnost

	а	b	с				RMSD
Known and fixed lattice parameters, no distortions	8.369	10.721	5.115	90	90	90	0.0108
Unrestrained cell refinement, no distortions	8.266	10.600	5.155	89.948	90.050	89.473	0.0050
Unrestrained cell refinement, optimized distortions	8.352	10.743	5.115	90.01	90.00	89.85	0.0041

Table 1.: Lattice parameters obtained with three different approaches to the refinement. RMSD is the root mean square deviation (in reciprocal Angstroms) of the predicted and measured reflection positions.

unprecedented accuracy of the determined distortion coefficients. We can distinguish three cases:

- Known lattice parameters, unknown distortion coefficients: In such a case the distortion coefficients can be determined with very good accuracy. These coefficients can be then used in the analysis of other data sets. Refinement of the distortion coefficients also proved a better prediction of reflection positions on the diffraction images, leading to a more accurate intensity extraction.
- Unknown lattice parameters, known distortion coefficients: The lattice parameters can be refined against reflection positions corrected for the (previously determined) distortions. The accuracy of the lattice parameters is then dramatically improved (see below).
- Unknown lattice parameters, unknown distortions: This is the most complicated situation and in the most general case it is not possible to refine reliably the lattice parameters and distortion coefficients simultaneously. The correlations can partly be suppressed by using the information about lattice

symmetry (i.e. Bravais class), or by combining data from more than one crystal.

The parametrization of the distortions and the refinement of the distortion coefficients was implemented in the computer program PETS for analysis of 3D ED data [3]. As illustrated in Table 1, the use of distortions in the refinement of the lattice parameters can dramatically improve the accuracy of the lattice parameters as well as the accuracy of the prediction of the reflection positions.

To characterize the distortions in a general manner, we expand the geometrical distortions into a series of circular harmonics. Be (x,y) the undistorted coordinates in the diffraction pattern and (x', y') the distorted coordinates (Fig.1), then we define the relationship as:

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Crystal structure prediction

PREDIKOVÁNÍ KRYSTALOVÝCH STRUKTUR

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Predikování krystalových struktur látek, založené pouze na znalosti základních stavebních jednotek (atomů či molekul), bylo cílem fyziků od padesátých let. Ještě v roce 1988 popsal John Maddox, jako editor časopisu Nature, stav oboru touto výstižnou větou: "One of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of oven the simplest crystalline solids from a knowledge of their chemical composition."[1]. Jako taková se predikce krystalových struktur začíná formovat okolo přelomu tisíciletí, kdy byl také vyhlášen první "blind test" [2]. Úspěchy tohoto oboru byli podmíněny prudkým rozvojem a nyní i cenovou dostupností výpočetní techniky. Jde o hledání kompromisů mezi přesností popisu meziatomových sil a jejich výpočetní náročností. Problém nalezení globálního minima se řeší chytrými algoritmy, jako jsou evoluční algoritmy, různé metody simulovaného žíhání či relativně nové mechanizmy jako "Particle swarm optimization" (optimalizace hejnem částic) [3]. Pro porovnání energií mezi jednotlivými kandidáty se využívá nejčastěji DFT či molekulární mechanika (MM).

Významnou událostí jsou tzv. blind testy pořádané organizací CCDC. Účastníci dostanou plošný nákres několika málo organických molekul a jejich cílem je správně předpovědět krystalovou strukturu daných



Obrázek 1. Schématické znázornění procesu hledání/předpovídání krystalové struktury organické molekuly.

molekul. Tato struktura je už vyřešena pomocí klasických difrakčních dat, ale ještě nebyla veřejně publikována. První blind test běžel v roce 1999 [2] a pár let později byl zas otevřen další [4-8]. Poslední, sedmý, blind test byl spuštěn letos v říjnu [9]. Cílem této události je získat aktuální přehled o úspěšnosti a problémech daného oboru. Od šestého blind testu účastníci poslali seřazený list 100 možných předpověděných krystalových struktur pro danou molekulu, v předešlých ročnících to byli pouze 3. Pro zajímavost, v šestém blind testu jeden účastník předpověděl správnou krystalovou strukturu jedné molekuly s využitím pouze 26 procesorových hodin a naopak tým, který na danou strukturu použil 30 000 000 procesorových hodin, byl neúspěšný.

Nalezení vhodného kandidáta na pravděpodobnou krystalovou strukturu je jako hledání jehly v kupce sena. Počet možných kombinací je veliký a na cestě k úspěšnému nalezení globálního minima stojí řada lokálních minim. S úspěchem se využívají algoritmy globální optimalizace. Kromě, krystalografům dobře známých, jako je simulované žíhání či paralelní temperování, které se využívají při řešení struktury v přímém prostoru, se používá řada dalších přístupů. Některé z nich se inspirovali přírodou, jako jsou evoluční algoritmy [10], či optimalizace houfem částic [11] nebo "ant colony optimization" [12], jiné vycházejí z pravděpodobného tvaru potenciální plochy jako metadynamika [13], "basin hopping" [14], "minima hopping" [15], a další.

Z komerčních programů můžeme jmenovat například Materials studio či Grace. Pro akademické uživatele jsou zdarma dostupné například tyto programy: XtalOPt [16] – volně stažitelný, pro platformy Windows, Linux, Mac, používá evoluční algoritmus, pro vyhodnocení energií externě volá Gulp (MM), Vasp (DFT), Quantum Esspreso (DFT), Castep (DFT) nebo Siesta (DFT).

Calypso [17] – po registraci, Linux, používá optimalizaci houfem částic, externě volá Gulp (MM), Vasp (DFT), Quantum Esspreso (DFT), Castep (DFT), Siesta (DFT), nebo CP2K (DFT+MM)

Uspex [18] po registraci, Linux, používá evoluční algoritmus, ale umožňuje také optimalizaci hejnem částic, metadynamikou nebo s využitím náhodného vzorkování, externě volá Lammps (MM), Gulp (MM), Vasp (DFT), Quantum Esspreso (DFT), Castep (DFT), Siesta (DFT) nebo CP2K (DFT+MM).

Základní postup při predikování krystalové struktury je naznačen na Obr. 1. Pro látky pro jejichž popis nevyužíváme molekuly, ale jen samostatné atomy, začínáme v pravém sloupci od části "balení". Pro molekulární látky začínáme tzv. konformační analýzou, kdy se pomocí změny volných paramterů dané molekuly snažíme najít její tvar (tvary) s co nejmenší energií. Je sice pravděpodobné, že v krystalu tvar molekuly nebude úplně odpovídat tvaru molekuly s nejmenší energií ve volném prostoru, ale zároveň síly mezi molekulami nejsou v krystalických látkách veliké a dá se najít určité množství tvarů, které se od "ideálního" tvaru liší jen o určité množství energie. Pro výběr vhodných kandidátů pro krystalickou formu můžeme použít několik nástrojů. Co je pro nás důležité, je jejich výpočetní náročnost. Geometrická optimalizace je náročnější než jen výpočet energie pro daný tvar a ten může



být zase výpočetně náročnější než třeba porovnávání torzních úhlů. Řekněme, že pro naší molekulu jsme nagenerovali velký počet náhodných konformerů, jejich počet, dále můžeme zredukovat na základě podobnosti torzních úhlu. Pro tento menší počet můžeme spočítat energii pomocí MM. Pro několik konformerů s nejmenší energíí můžeme použít výpočet energie pomocí náročnějších, ale přesnějších výpočtů ("hrubé" DFT). Na základě hodnot energií získaných pomocí MM a hrubého DFT můžeme stanovit nepřesnost určení energii MM oproti hrubé DFT a stanovit okno propustnosti konformerů do dalšího kola. Tím může být jemnější (přesnější) nastavení DFT nebo se můžeme pustit do geometrické optimalizace. Ta může být opět provedena v několika kolech. Po jejím provedení můžeme opět přejít ke klastrování a spojit pod jeden konformery s velmi podobným tvarem. Opět provedeme energetické hodnocení a můžeme se pustit do umísťování nejpravděpodobnějších konformerů do krystalu.

Při umísťování konformerů do krystalu se s úspěchem využívá krystalové symetrie a je možné si vybrat jen několik nejpravděpodobnějších prostorových grup, v kterých budeme hledat. Vybrané konformery je buď možné umisťovat jako fixní nebo jim nechat nějaké stupně volnosti. Mřížkové parametry je možné v první přiblížení nastavit tak, aby byli molekuly blízko sebe, ale nepřekrývali se. Hledání krystalické formy s nejmenší energií je pak obdobné hledání vhodných konformerů. Ke klastrování se v tomto případě dá využít i třeba podobnost práškových záznamů. Pro stabilitu dané krystalické formy je podstatná Gibbsova volná energii G, která je daná součtem krystalové energie E, součinu tlaku p s objemem V a záporně vzatý součin entropie S s teplotou T, viz rovnice (1). Člen $p \cdot V$ se dá snadno spočítat, ale jeho vliv je při atmosférických tlacích malý. Výrazný problém je vyjádření entropie. Tento člen se proto často zanedbává.

G = E + pV - ST

Kromě predikování krystalových struktur ab-initio je možné využít výpočetní metody také jako doplněk k neúplným či nekvalitním difrakčním datům. Např. v práci [19] je popsáno predikování struktury s využitím neúplných difrakčních dat měřených na vzorku za vysokých tlaků v diamantové cele. V tomto případě tedy šlo o predikci s malým množstvím experimentálních dat. Prakticky tyto data nemusí být difrakční a může jít i o jiné experimentální výsledky. Pro difrakční komunitu může být energetický výpočet nápomocný např. při lokalizaci vodíkových atomů, stabilizaci zpřesňování atomových pozic, či lokalizaci dvou podobně difraktujících prvků. Energetický výpočet by také mohl urychlit konvergenci řešení struktur z práškových dat.

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SUBFAMILY D NON-MDO SIX-LAYER POLYTYPES OF CRONSTEDTITE

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Keywords: cronstedtite; 1:1 layer silicates; $6T_1$, $6T_3$, $6R_1$, $6R_2$; twinning.

 $({\rm Fe}^{2+}_{3-x})$ The layered 1:1 silicate cronstedtite Fe_{x}^{3+} (Si_{2-x} Fe_{x}^{3+})O₅(OH)₄, (0.5 < x < 0.85) belongs to the serpentine-kaoline group. It forms relatively numerous polytypes generated by stacking 1:1 structure building layers - equivalents of OD packets with the trigonal protocell a = 5.5, c = 7.1 Å. Polytypes are subdivided into four OD subfamilies, or Bailey's groups A, B, C, D according to different stacking rules. Cronstedtite occurs rarely in low temperature hydrothermal deposits [1], in certain meteorites (CM chondrites) [2], and presumably on asteroids. Synthetic micrometer-size crystals were prepared by Pignatelli and her co-workers [1,3].

The data collected by four circle single-crystal X-ray diffractometer with area detector processed by an appropriate software provide precession-like reciprocal space sections (RS sections in the following). Similar RS sections are obtained by electron diffraction tomography (EDT), for small crystals [1]. Distributions of so called subfamily reflections along the reciprocal lattice rows $[2l]^* / [11l]^* /$ $[2l]^*$ in $(l_{hex})^* / (hhl_{hex})^* / (2hl_{hex})^*$ RS planes is used for subfamily determination. Similarly, distributions of characteristic reflections along [10l]* / [01l]* / [1l]* rows in $(h0l_{hex})^* / (0kl_{hex})^* / (hl_{hex})$ planes allow determination of particular polytypes. For this purpose, graphical identification diagrams simulating distribution of reflections along named rows are used [1]. Modern diffractometers allow checking of many specimens and generation of RS section in a reasonable time.

Lot of specimens of cronstedtite from various terrestrial localities and synthetic run products were studied by the author [1, 4, 5, 6]. RS sections were recorded, and selected ones were published.

This contribution is focused on the polytypes of the OD subfamily D. Its stacking rule is characterized by alternating 180 rotations of consecutive layers, combined by $\pm b/3$ (of the orthohexagonal cell) or zero shifts. The sample studied originate from the locality Ouedi Beht, El Hammam, Morocco, about 80 km SEE from Rabat (GPS 33°33'15.19"N, 5°49'53.68"W). The most common polytypes in the occurrence however, are quite common two-layer $2H_1$ and $2H_2$, occurring either isolated or in mixed crystals. Much more rarely, six-layer polytypes were found. They usually occur in complex mixed crystals containing more polytypes, up to six! Diffraction patterns of such crystals are thus confusing. Fortunately, in many cases polytypes were isolated mechanically by cleaving crystals into smaller fragments, later studied separately. In some cases, the cleaving procedure was repeated until the fragment containing one polytype was isolated.

Hall et al. [7] theoretically derived 24 possible sequences of layer stacking for six-layer polytypes of the subfamily D serpentine minerals, valid also for cronstedtite. Their diffraction patterns were modelled by the author, identification diagrams were constructed, and compared with real RS sections obtained from the experiments. This simulation revealed, that five pairs of sequences (No. 4+6, 7+18, 8+10, 9+13, 11+12) provided identical theoretical diffraction patterns. Polytypes really found in the Ouedi Beht occurrence correspond to following sequences: 1 (Hall's $6T_1$), 5 (proposed $6T_3$), 8+10 $(6T_5)$, 11+12 (6T₄) (trigonal polytypes), 22 (Hall's 6R₁), 23 (Hall's $6R_2$) (rhombohedral polytypes). The sequence 24 was declared by Hall et all. [7] as rhombohedral $(6R_3)$. Modelling of the structure, however, excluded the rhombohedral cell, thus the real symmetry is also trigonal and proposed symbol is $6T_6$. This polytype was also discovered in the occurrence.

The hexagonal polytype $6H_2$ corresponding to the sequence 14 was found, too. However, the identical diffraction pattern can be produced by the obverse-reverse twin of the rhombohedral polytype $6R_2$ (sequence 23).

With exception of $6R_1$, all six-layer polytypes mentioned above are so-called non-MDO (Maximum Degree of Order), or non-standard ones. In these polytypes, all triples, quadruples,*n*-tuples of consecutive layers are not equivalent.

The study presents a nice example, how different diffraction patterns can be produced by cleaved fragments of one complex crystal.

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Session II, Use of synchrotron radiation, Wednesday, November 25

L5

X-RAY DIFFRACTION STRUCTURAL BIOLOGY USING SYNCHROTRON RADIATION

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Over the past decades, X-ray diffraction of biological samples, also called macromolecular crystallography (MX) has been developed to the most powerful method to gain insights into the 3D structural space of biological macromolecules, like protein, protein-protein and other complexes. One key for these advances is the use of highly brilliant X-rays produced by electron storage rings to investigate crystals of large unit cells or micrometer sized crystals.

Within this presentation, an overview of this technique and its current applications are provided.

L6

A SHORT OVERVIEW OF TOMOGRAPHIC IMAGING CAPABILITIES AT SYNCHROTRONS IN EUROPE AND ELSEWHERE

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Tomographic imaging aims to map the 3D electron density in a non-destructive manner. The method is relevant to study materials of almost all types including biological systems. State-of-the-art X-ray imaging instruments are used to create virtual representations of materials down to tens of nanometre spatial resolution. Perhaps the biggest asset of synchrotron imaging instruments is their excellent temporal resolution at this length scale [1]. The limits in the temporal domain are mainly set by the detector and the mechanics. For the spatial resolution the biggest concern is the radiation dose resulting from the interaction of X-ray radiation with the studied matter. I will give an overview of recent achievements in micro- and nano-scale tomographic imaging with emphasis on the specific capabilities of imaging beamlines in Europe.

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L7

APPLICATION OF PAIR DISTRIBUTION FUNCTION FOR STUDY OF HIGHLY-DISOREDRED COMPOUNDS

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Compared with crystalline counterparts, metallic glasses (MGs) have some superior properties, such as high yield strength, hardness, large elastic limit, high fracture toughness and corrosion resistance, and hence are considered as promising engineering materials. Fe- and Co-based amorphous alloys have been the subject of considerable research interest and activities for the last decades due to applications related to their outstanding soft magnetic properties. Structurally, metallic glasses can be classified as disordered materials. X-ray diffraction (XRD) using high-energy photons has proven to be well suited for describing the structure of highly disordered systems such as MGs.

Time-resolved in situ XRD experiments may nowadays be performed at high-brilliance synchrotron radiation sources for a variety of conditions which help to elucidate the structure-property relations.

In this contribution structural changes occurring in an $Fe_{72.5}Cu_1Nb_2Mo_2Si_{15.5}B_7$ alloy during a combination of constant rate heating (20 K/min) and isothermal holding at 500 and 520 C will be investigated using in situ high-energy X-ray diffraction. It was found that the ferromagnetic-to-paramagnetic transition of the amorphous phase is revealed as a change in the slope of the thermal expansion curve when heating a sample at a constant rate up to 520



C. Real space analysis by means of the atomic pair distribution function (PDF) demonstrated that the rate and extent of the thermal expansion strongly depend on the interatomic separation. The PDF proved to be a reliable method for the description of crystallization kinetics. Further it allows determination of sizes of ultrafine nanocrystals with grain sizes well below 8 nm and thus makes

L8

observation of early stages of nanocrystallization possible. This contribution presents results showing how pair distribution function can be successfully used for tracking the ferromagnetic-to-paramagnetic transition of amorphous phase in the vicinity of the Curie point.

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IN-SITU X-RAY SCATTERING STUDY OF PULSED-LASER DEPOSITION OF LuFeO₃/Pt SYSTEMS

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Growth of multiferroic epitaxial layers of hexagonal LuFeO₃ has been studied by X-ray scattering in-situ during pulsed-laser deposition (PLD). For this purpose we used a unique PLD chamber attached to the NANO-beamline of the Institute of Photon Science and Synchrotron Radiation (IPS) attached to the KARA storage ring (Karlsruhe, Germany). The LuFeO₃ layers have been deposited on single-crystalline sapphire substrates, in some samples we also deposited thin Pt interlayers prior to the LuFeO₃ growth. In the first part of the talk I report on grazing-incidence small-angle scattering (GISAXS) measured in-situ during the Pt deposition. From the data we determined the Pt growth kinetics, in particular we study the dependence on the island-to-layer percolation threshold on the substrate temperature [1]. In the second part I discuss the parameters of the LuFeO3 thin layers and their development during deposition [2]. The layers are mosaic and we studied the angular mosaic spread and mean size of the mosaic blocks as functions of the substrate deposition temperature and of the Pt thickness underneath. The final part of the talk is devoted to the study of growth oscillations during the LuFeO₃ deposition; the oscillations were recorded by measuring the time dependence of the intensity of the quasi-forbidden reflex (0003) of LuFeO₃. From the data we determined the growth rate and the height of the Ehrlich-Schwöbel diffusion barrier as functions of the laser repetition frequency [3].

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L9

FUTURE DATA ANALYSIS SERVICES AT EUROPEAN AND NATIONAL PHOTON AND NEUTRON FACILITIES

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The most powerful X-ray laser facilities as well as multiple 4th generation synchrotron light sources are in user operation across the Europe. Preparation for the European spallation source is ramping up, more photon and neutron (PaN) facilities are planning upgrades. With the excellent brightness, larger and faster detectors enormous volumes of scientific data are produced. The variety of experiments as well as PaN user communities are broadening, publish-



ing practices and academic institutions requirements for scientific data management, including interest in open-data, are increasing. In late 2018, within the European Open Science Cloud (EOSC) initiative, several major European PaN facilities started a project called PaNOSC [1], which was complemented by ExPaNDS [2] project at the national research PaN institutes a one year later. Both projects aim for expanding scientific data catalogues and analysis services in order to make scientific data at PaN facilities comply with the FAIR data principles. This includes adjustments to scientific data policies, extension of scientific data retention period, tools to search for datasets of possible scientific or scholar interest, improvements of data accessibility, data formats and metadata catalogues and finally a possibility to reproduce the scientific results by means of remote data analysis services. Within the wide scope of the projects several application use cases have been chosen to prototype all the services including data analysis. The selected scientific use cases cover multiple methods including crystallography, for the ExPaNDS project in particular serial crystallography [3], CryoEM and powder diffraction [4], but also other techniques as small angle scattering, reflectometry or ptychographic X-ray computed tomography [5]. The use cases represent several types of PaN sciences analysis workflows including Python Jupyter notebooks, conventional high-performance distributed computing, cloud-like containerization for data-science and remote desktops for visualization. The idea is to match the environments to run scientific software with archived datasets and records in metadata catalogues. The projects outcomes include definition of application interfaces and a functional protype that can be deployed at research facilities, can be interconnected with other tools, developed and extended in a sustainable way, allowing to bridge more scientific data into EOSC.

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L10

PHASE TRANSFORMATIONS IN Ti-15Mo SINGLE CRYSTAL INVESTIGATED BY SYNCHROTRON X-RAY DIFFRACTION

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In metastable titanium alloys, the transformation from the high-temperature phase (bcc) to the low-temperature phase (hcp) can be suppressed upon quenching to room temperature [1]. Due to the thermodynamically metastable nature of the phase, particles of the so-called phase form in the material by a diffusionless shuffle mechanism already during quenching. The crystallographic structure of phase is either trigonal or hexagonal, depending on the completeness of the transformation, and there are four crystallographic orientations (variants) of the phase particles are coherent with the parent phase, their [2] size ranges from a few nanometres [3] to a few tens of nanometres and they were found to be spatially weakly ordered in a cubic array [4]. With increasing temperature, particles evolve and grow by a diffusion-assisted process until they reach a stability limit at which the precipitation of phase becomes the dominant transformation.

The main goal of this research is to investigate the sequence of transitions occurring in single-crystals of Ti-15Mo (in wt.%) alloy during linear heating by synchrotron X-ray diffraction. For this purpose, a single crystal was prepared using the floating zone method [5], solution treated above the -transus temperature and quenched to water to produce a well-defined starting condition for the heating experiments. X-ray diffraction was measured at the high-energy beamline ID11 at ESRF, Grenoble. The photon energy was 60 keV and the primary beam was parallel to [100] direction in the studied crystal. The heating was performed in a dedicated furnace equipped with a quartz chamber, allowing to reach high vacuum (approx. 10^{-6} mbar). The diffracted signal was collected in situ during linear heating with the rate of 5°C/min. An example of a measured diffraction pattern together with calculated pattern explaining the origin of individual peaks is displayed in Fig. 1.

The set of measured data allowed us to determine the sequence of phase transformations by following the evolution in regions around selected diffraction spots during linear heating, see Fig. 2. The intensity in these regions first decreases with increasing temperature, but the reflections do not disappear completely. On the contrary, around 673 K (400 °C), the peaks sharpen and their intensity increases – this is most visible in Fig. 2 c) which shows an spot closest to the Ewald sphere (Figs. 2 a) and b) display peaks further from the Ewald sphere, so the intensity increase is not readily apparent due to their sharpening). At 833 K (560 °C, denoted by a black vertical line in Fig. 2), all reflections disappear, suggesting a complete dissolution of the phase. The intensity observed at the highest measured temperatures corresponds to phase diffraction spots which lie close to the original reflections.



Figure 1. a) Measured diffraction pattern at room temperature and b) calculated pattern showing the positions of observed and diffraction spots (square and ellipse symbols, respectively).

Numerical fitting of measured diffraction peaks allowed us to estimate the temperature dependence of phase fraction (red points in Fig. 3) and interface area matrix and particles (blue points in between the Fig. 3). Both quantities depend linearly on the number of irradiated particles; the steeper decrease of S/S_0 above 523 K (250 °C) suggests that while particles grow, their number decreases (a process similar to Ostwald ripening). The increasing trend observed in Fig. 3 is caused by progressive coarsening of particles. As the temperature nears the stability limit of the phase at 833 K (560 °C), both the phase fraction and the interface area decrease rapidly. More information on this topic and a comparison with complementary data from electrical resistivity measurements can be found in [6].

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Figure 3. Evolution of phase fraction of the phase (red points) and the interface area (blue points).



TEMPERATURE INDUCED STRUCTURAL EVOLUTION OF POROUS IMIDAZOLATE COMPOUNDS VIA SYNCHROTRON XRPD

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Zeolitic imidazolate frameworks (ZIFs) are an interesting class of metal-organic frameworks, structured by tetrahedrally configured transition metal cations bridged by imidazolate (Im). ZIFs are able to reproduce the zeolitic topology but also incorporate the electronic properties of the transition metal ions.[1]

In this research, novel high-temperature polymorph of sodium imidazolate, HT-NaIm was discovered. Solid-state NMR was used for initial elucidation of structural features, the crystal structure was determined by single-crystal X-ray diffraction, while the *in-situ* HT-XRPD experiments utilizing synchrotron radiation have been performed in order to gain the insight into the structural evolution and thermal stability which was additionally analized by differential thermal analysis and hot stage microscopy measurements. HT-NaIm exhibits pores of 50 Å³ that suggest possible application for gas sorption/separation. Once formed, high-temperature polymorph of NaIm retains its structure and remains stable at room temperature, what is important application-wise.

Additionally, new family of mixed bimetallic imidazolates $AMIm_3$ (A = Na, K; M = Mg, Mn) has been

synthesized and crystal structures were determined from powder X-ray diffraction data. Temperature aided decomposition during *in-situ* SR HT-XRPD experiments gave the information about structural changes ad thermal stability of the prepared samples. All compounds have the imidazolate ligand connected to four metal cations forming a complex 3D network with channels running along the *c*-direction, thus showing the similar sorption potential because of the empty volume of around 30 C³ incorporated inside the channels (Figure 1).[2]

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Figure 1. Extended crystal packing of KMgIm₃ showing channels along the *c*-direction.

Krystalografická společnost



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The European Synchrotron Radiation Facility (ESRF) is the most powerful synchrotron source in Europe. The ESRF is one of the world's largest synchrotron science centres. Every year, 9000 scientists from 22 partner countries and from around the world travel to Grenoble to use its extremely brilliant X-rays for leading-edge research. The ESRF Upgrade Programme 2009-2018 maintains the world-leading role through a continuous quest for higher performance figures, meeting the needs of returning users, and attracting scientists from new disciplines [1]. ESRF–EBS (Extremely Brilliant Source) is the ESRF's 150M€ facility upgrade, over 2015-2022, bringing its scientific users a first-of-a-kind, low-emittance, high-energy synchrotron light source and new, cutting-edge beamlines. With a revolutionary new storage ring concept that increases the brilliance and coherence of the X-ray beams produced by a factor of 100 compared to present-day light sources, ESRF–EBS represents a new generation of synchrotron and an extraordinary new tool for scientists to study the heart of matter.

The Czech republic is a member state of the ESRF, enabling Czech scientist to apply for beamtime. Our membership is financed through the MŠMT program Inter-Excellence and is secured for the period between 2018-2022.

1. www.esrf.eu



Session III, Thursday, November 26

L13

JANA2020, A NEW VERSION OF THE CRYSTALLOGRAPHIC COMPUTING SYSTEM

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Program Jana [1] si během svého více než třicetiletého vývoje vydobyl světové renomé jako krystalografický systém pro řešení komplikovaných struktur. Zpočátku byl úzce zaměřen na problematiku modulovaných struktur řešených z monokrystalových dat, později propojil řešení standardních a modulovaných struktur v jednom systému, od roku 2006 bylo možné program použít i na prášková data [2] a od roku 2010 se intenzivně rozvíjely moduly pro řešení magnetických struktur [3]. Program Jana je propojen s programy Superflip [4] pro řešení fázového problému v libovolné dimenzi, s programem Dyngo [5] pro upřesňováni struktur z elektronové difrakce za využití dynamické teorie, s programem MCE [6] pro vizualizaci elektronové hustoty, s internetovým nástrojem ISO-DISTORT [7] pro analýzu representací a s několika dalšími programy. Ačkoli program Jana nikdy nedosáhl rozšíření srovnatelného s programem SHELX, v některých oblastech je dominantním nástrojem a roční počet citací stabilně dosahuje několika set.

S narůstající komplexností programu vyvstal problém, jak jej uživatelsky zjednodušit. Cílem našeho snažení bylo

vytvořit program, kde jednoduché úlohy půjde vyřešit zcela intuitivně, zatímco pro složité krystalografické úlohy, kde se předpokládají nadstandartní znalosti uživatele, budou intuitivní alespoň základní společné postupy. Pro tento cíl bylo nutné vytvořit kreslící program, který jednak v reálném čase ukazuje změny struktury během upřesňování, ale současně umožní i editaci strukturních parametrů jednotlivých atomů nebo jejich skupin. Za tímto účelem bylo zcela přepsáno grafické rozhraní programu Jana2006, aby bylo možné využít knihovny OpenGL, čímž vzniknul nový program Jana2020, jehož beta verzi zde představujeme.

Program Jana2020 obsahuje všechny dosavadní možnosti programu Jana2006, ale má zcela jiné ovládání. Uživatel má k dispozici rozvinovací lištu s jednotlivými nástroji a dále přepínač (Obr. 1), kterým si volí, co by měl program vizualizovat. Momentálně lze volit buď obrázek struktury, nebo práškový profil, a v obou případech lze pozorovat probíhající změny v důsledku upřesňování anebo editace strukturních nebo profilových parametrů. V dalších verzích bude nabídka vizualizace rozšiřována,



Obrázek 1. Část okna programu Jana2020. Pomocí vyznačené velké ikony vlevo nahoře je jako cíl vizualizace nastavený obrázek struktury. V rozvinovacích nástrojích vlevo je vybrané upřesňování struktury. Po spuštění upřesňování struktury (Run refinement) bude obrázek aktualizován po každém upřesňovacím cyklu.

Krystalografická společnost

například o mapu elektronové hustoty. Prostřednictvím obrázku struktury lze editovat strukturní parametry atomů, spojovat atomy do pevných těles a přidávat další polohy těchto těles. Ve vývoji je propojení obrázku s mapou elektronové struktury a mnoho dalších možností, které se nabízejí díky existenci kreslícího nástroje.

Program Jana2020 bude začátkem prosince 2020 k dispozici na stránkách <u>http://jana.fzu.cz</u>

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Examples of applications of program CRYSTALCMP for comparison of packing of molecular crystals

UKÁZKY POUŽITÍ PROGRAMU CRYSTALCMP PRO POROVNÁVÁNÍ PAKOVÁNÍ MOLEKULÁRNÍCH KRYSTALŮ

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Pravděpodobně každý krystalograf se dostal jednou do situace, kdy potřeboval porovnat dvě nebo více krystalových struktur organických nebo organokovových látek a hledal způsob a nástroj, jak to provést, aniž by nad tím zbytečně strávil čas navíc. Všechen ten čas uplynulý před monitorem, kdy se krystalografové pomocí ručního otáčení modelů krystalových struktur snažili mezi nimi najít podobnost, je němým svědkem toho, že nějaký nástroj pro tento účel je vhodné si osvojit.

V minulosti bylo publikováno několik metod pro porovnávání krystalových struktur [1-7]. Mezi uživatelsky přívětivé nástroje bych zařadil funkci Crystal Packing Similarity v programu Mercury [7], a programy COMPSTRU [8], xPac [9] a CrystalCMP [10]. Nástroj Crystal Packing Similarity je zpřístupněn uživateli jen v placené verzi programu Mercury. Program COMPSTRU je vytvořen jako online nástroj na stránkách Bilbao Crystallographic Server a programy xPac a CrystalCMP lze volně stáhnout.

Nástroje Crystal Packing Similarity, xPac a CrystalCMP používají podobný přístup pro porovnání pakování molekul v krystalových strukturách. Programy vyberou u každé porovnávané struktury reprezentativní molekulární klastr, kde je možné zvolit např. jen jeden typ molekuly (obvykle té největší ve struktuře). Následně provedou porovnání na základě rozdílů pozic molekul v obou klastrech. Jednotlivé implementace se liší ve způsobu porovnání obou klastrů a v rychlosti porovnání. Metoda porovnání použitá programem COMPSTRU se od zbylých třech metod výrazně liší. Její přístup bych nazval jako více krystalografický. Program najde nejlepší transformaci základních buněk porovnávaných struktur a pak provede porovnání pozic atomů v základní buňce. Uvedené nástroje určené pro porovnávání krystalových struktur se mezi sebou liší použitou metodou, uživatelským rozhraním a dostupností. Je tedy jen na uživateli, který z nich si nakonec vybere.

Jak už bylo zmíněno, metoda programu CrystalCMP je založena na porovnávání reprezentativního molekulárního klastru, do kterého je možné zahrnout jeden typ molekuly, obvykle té největší. Během porovnávání dojde k překrytí vygenerovaných molekulárních klastrů jednotlivých krystalových struktur a podobnost je spočítána jako odchylka středů překrývajících se molekul a úhlů natočení molekul od sebe. Výsledná podobnost (v tomto případě spíš rozdílnost) je dána vztahem:

$$Ps_{a,b} = D_c + wA_d$$

kde D_c je průměrná vzdálenost (v Å) středů překrývajících se molekul a A_d reprezentuje odchylku natočení překrývajících se molekul v prostoru. Hodnota w je volena uživatelem a reprezentuje váhu mezi D_c a A_d .

Větší váha je ve výchozím nastavení programu kladena na rozdíl natočení molekul v prostoru. Je to z toho důvodu, že stejné pakování není ani tak podmíněno stejnou pozicí molekul v prostoru, jako spíš jejich stejným natočením. Pomocí takto definované funkce $Ps_{a,b}$ je umožněno porovnávání molekulárních struktur, které byly změřeny za různých teplot. Objemová změna struktury má totiž na změnu $Ps_{a,b}$ funkce malý vliv. Lze tedy porovnávat pakování molekul ve strukturách, jejichž expanze je způsobena např. přítomností molekul solventů či koformerů různých velikostí, jako je tomu např. v tzv. solvatomorfních řadách. Výsledkem porovnání programem CrystalCMP je podobnostní matice a z ní vypočtený dendrogram, který seskupuje jednotlivé látky podle podobnosti v čitelné podobě. Samotné porovnání krystalových struktur je provedeno buď automaticky, nebo za interakce uživatele. Porovnání dvou krystalových struktur je v průměru provedeno během 0.5 s, což umožňuje během několika minut porovnat desítky krystalových struktur mezi sebou.

Program je napsán v jazyce C/C++, využívá knihovny OpenBabel pro generování SMILES definic a pro grafické rozhraní používá wxWidgets a OpenGL. Program je volně ke stažení na

adrese <u>http://sourceforge.net/projects/crystalcmp/</u>, kde lze také nalézt jeho zdrojový kód.

Tento příspěvek byl financován projektem LO1603 v rámci Národního programu udržitelnosti Ministerstva školství, mládeže a tělovýchovy České republiky,

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Session IV, Thursday, November 26

L15

TEACHING CRYSTALLOGRAPHY ONLINE WITH MS TEAMS – COMMENTS, EXAMPLES

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A few months of this crazy year brought high concentration on online teaching in basically all levels of education. Of course, the least problematic is such teaching in universities where many things can be transferred to online form without significant losses and in certain cases even with some benefits. So, the only part that cannot be done online is practical work, in particular the work that should teach students some skills. Otherwise, there are no limits for interactive communication during the online teaching. However, it may be easier for the teachers rather than for students. It can be more difficult and/or unpleasant to sit at the computer several hours a day.

Universities are supporting different platforms for online teaching e.g. [1]. While for organizing of meetings I prefer to use Zoom [2, 3], for teaching I have decided to prepare everything in MS Teams [4] in the form developed by the Charles University [5] where it is easy to create a team for subject and assign there students from the list of students of the University and/or invited guests by e-mail or code.

In addition to common meetings, as e.g. in Zoom etc., there is a common space

Our faculty requires that all the presentations be recorded, and the records are available, in addition to presentations (ppt, pdf), to all relevant students till the end of semester. Both are saved in folder Files of MS Teams. This folder can also contain some other shared files e.g. of Office like Excel or Word files.

Probably the most useful part is Notebook that can contain different folders owned by teacher only, shared for all and owned by each individual student. In the shared folder anybody can write formatted text, draw, insert pictures, tables directly in Teams or in One Note application with a few more advanced features.

Students cannot see folders and pages of other students while the teacher can see everything. So, the teacher can easily click on the corresponding page of any student and see up-to-date information where the student is during his/her task. Teacher can also write directly to their document. Usually, it is working quite quickly if the Internet is not too slow. In Figure 1, there is a screen copy from the online course where the students (left column) got different symmetrical patterns (right), should draw elementary cell and corresponding symmetry elements, and determined the plane group from the list. In order, to make their life easier,



Figure 1. Copy of MS Teams screen during the task of determination of plane groups for different symmetrical patterns.

Krystalografická společnost

they could use a portfolio of all symbols and it was then sufficient to move specific symbols to relevant positions. A similar way was used for space groups (complete diagrams of general positions with symmetry elements or vice versa complete diagrams of symmetry elements with general positions, determination or estimation of the space group)

A little more complicated was preparation of *online practical course*. This is the basic problem of powder diffraction – determination of lattice parameter of unknown cubic phase and then also phase analysis of mixture of 3-6 phases. Since, the task consists mainly in evaluation, it was decided to adopt this also to online form. This practical part always begins with a short excursion in X-ray laboratory showing them a few instruments, description of powder diffractometer, preparation of different samples, specimen alignment and automatic measurement in symmetrical scan. So, everything was recorded to video and what was only missing for students was their own specimen preparation. This is followed by demonstration of fast evaluation

of powder pattern and generation of a file with peak parameters. Students used this output (each with different parameters) to index peaks according to procedure described on web link and determined the lattice parameter considering the instrumental aberrations. The first part is closed by looking into the Powder Diffraction File in order to find the phase. However, usually it is not found because the lattice parameter deviates from the database value from some reason. This reason is discussed.

In the second part, the pattern was evaluated in different software, the list of peaks was generated (2 , d, I) and the students obtained scanned education edition of Hanawalt index and made the search. Finally, for homework, the students should download 30-days trial of program Match and use it for the phase analysis of the mixture. Each of the students received different dataset.

Finally, I think that such tools can be well used for teaching even if, hopefully, we will come back to more or less normal time.

Session V, Friday, November 27

L16

BASHELIXIR HAS NEW FEATURES AND NEW GUI P. Kolenko^{1,2}, J. Stránský², M. Malý^{1,2}, T. Kovaľ², J. Dohnálek²

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Many computational tools to perform experimental phasing have been developed. Most of them are concentrated in the *CCP4* [1] and *PHENIX* [2] program packages. Recently, the command-line tool *baSHELiXir* [3] has been published to provide fast and efficient phasing protocols linked to the application of the *SHELX C/D/E* [4,5] program package. The program independently enables searches for the correct space group, screening of the solvent content parameter and high- and low-resolution diffraction limits. In *baSHELiXir*, *SHELXE* processes are parallelized to reduce the computational time and provide a thorough analysis of the computational results based on provided data.

Several cases have been selected to demonstrate the full applicability and capacity of *baSHELiXir*. They cover single-wavelength anomalous dispersion, multiple-wavelength anomalous dispersion with two to five datasets collected at different wavelengths, single isomorphous replacement with anomalous scattering and radiation-damage-induced phasing protocols.

baSHELiXir is a powerful tool for a thorough analysis of experimental phasing information contained in crystal-lographic data. It is simple to use from the command line.

Moreover, a graphical user interface has been developed for easier launching of the analysis.

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THE CRYSTAL STRUCTURE OF THE FIRST HALOALKANE DEHALOGENASE TETRAMER

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Haloalkane dehalogenases (EC 3.8.1.5) are microbial enzymes that catalyze the breakdown of halogenated compounds resulting in a halide ion, proton and alcohol. These enzymes are applied in industrial catalysis, bioremediation and biosensing of environmental pollutants. Novel haloalkane dehalogenase DpaA that belongs to the superfamily of / hydrolases was isolated from a psychrophilic and halophilic bacterium Paraglaciecola agarilytica NO2 found in marine sediment collected from the East Sea, Korea. Here, we report its crystallization and X-ray diffraction data analysis. DpaA was crystallized using the sitting drop vapor diffusion method. Two independent crystallization and data collection experiments resulted in several data sets with the resolution ranging from 2.2 to 3.0 Å and from 2.5 to 3.17 Å, respectively. During structure solution DpaA shows interesting structural properties of its tetramer conformation and its interactions between individual chains.

The difficulties during initial data processing and the right space group determination reveal the presence of pseudotranslation at every collected data set, which required further investigation and improvements of the existing model. Finally, merohedral twinning and subsequent structure modeling and refinement resulted in a tetrameric model of DpaA, highlighting an uncommon multimeric nature for a protein belonging to the HLD-I subfamily.

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L18

ADVANCED BIOLOGICAL APPLICATIONS OF SAXS IN-HOUSE J. Stránský¹, A. Keilbach², J. Dohnálek¹

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Small angle X-ray scattering (SAXS) serves as one of the complementary methods of structural biology. SAXS allows both characterization and low resolution structural studies of macromolecules, with advantage of liquid samples. Several such complementary methods can be directly coupled with SAXS. Thanks to the high flux X-ray sources like MetalJet (Excillum), these applications are now possible not only at sunchrotrons, but also in-house. Here, in situ UV-Vis absorbtion spectroscopy and size exclusion liquid chromatography coupled with SAXS, as available in Centre of Molecular Structure, will be presented.

Centre of Molecular Structure is equipped with SAXSPoint 2.0 (Anton Paar) instrument with MetalJet C2+ X-ray source and Eiger 2M detector. Samples can be

loaded to variety of the capillaries using an autosampler. The set of temperature controlled sample stages include low noise cell and capillary capable of in situ UV/Vis absorption spectrometry. Recently, a dedicated liquid chromatography system AktaGo (GE Healthcare) was introduced.

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Session V, Friday, November 27



INTRODUCTION TO NANOTOXICOLOGY

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The nanoparticles are widely used not only in laboratories but also in our households. They are just everywhere we look. We add them to the food, medical products, cosmetics etc. We are actually making so much nanoparticles that they become significant pollutant of our natural environment. This stands in contrast with nature made nanoparticles - their quantity is 9x higher but they are natural part of environment and are not causing significant problems.

In this talk I would like to concentrate on the tools and methods of studying the nanotoxicity of nanomaterials and interaction of nanomaterials with the biological environment. Especially I would like to speak about protein corona formation and its influence on the nanoparticle destiny in



the biological environment. I would like to address the key properties of nanoparticles which are influencing their toxicity. For example: size, shape, surface charge, surface groups and composition.

L20

STRUCTURE AND MICROSTRUCTURE OF ROTARY-SWAGED W-Ni-Co PSEUDOALLOY STUDIED BY NEUTRON DIFFRACTION

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Tungsten heavy alloys (THAs) are two-phase composites consisting of tungsten particles/agglomerates surrounded by a ductile matrix [1]. Due to their superb mechanical properties and high specific mass, tungsten heavy alloys are used in demanding applications, such as kinetic penetrators, gyroscope rotors, or radiation shielding. Effective structure refinement can be introduced via methods of severe plastic deformation. However, their structure, consisting of hard tungsten particles embedded in a soft matrix, makes the deformation processing a challenging task.

This study focused on the characterization of deformation behaviour during thermomechanical processing of a W-Ni-Co tungsten heavy alloy (THA) via the method of rotary swaging at various temperatures. Rotary swaging is an intensive plastic deformation method advantageously used in the industry to gradually reduce cross-sections and increase lengths of axisymmetric workpieces [2].

The primary aim was to determine microstrain and characterize the dislocations and active slip system in the original sintered THA as well as in the rotary swaged bars, in order to characterize the effects of thermomechanical treatment on the microstructure. Emphasis was given on

the investigation by neutron diffraction. Characterization of advanced materials by neutron powder diffraction provides information not accessible by other techniques. Thanks to the low absorption of neutrons, the bulk of the material and large-grain samples can be investigated, moreover - in many cases - in situ at elevated temperatures.

The sintered bars were processed by rotary swaging either at room temperature or at 900 °C into circular swaged bars with a diameter of 10 mm. The neutron diffraction patterns for structure and microstrain determination were collected at ambient temperature on the MEREDIT diffractometer of CANAM infrastructure at NPI Řež near Prague [3].

Two phases were identified in all samples of W-Ni-Co alloy. The main phase (denoted W-B2) had -W (B2) structure and was formed by the original tungsten powder grains. The second phase (denoted NiCo₂W in what follows) with a weight fraction of 6%-7% and Ni-like structure (fcc) was present as well.

The analysis [4, 5] showed that the grains of the NiCo₂W matrix refined significantly after the deformation treatments. The microstrain was higher in the cold swaged sample (44.2 × 10⁻⁴) than in the hot swaged sample (41.2 × 10⁻⁴). The evaluation of the modified Williamson-Hall plots showed that both the samples swaged at 20°C and 900 C exhibited the activation of edge dislocations with o {110} or n {111} slip systems, and/or screw dislocations with n slip system in the NiCo₂W matrix.

Dislocation densities in NiCo₂W phase were estimated from the diffraction peaks broadening. It was seen that the dislocation densities increased approximately 5 times after rotary swaging, and that it is 15 % higher for the sample swaged at room temperature than for the sample deformed at 900°C. It was concluded from the comparison with the stress-strain test that the increased dislocation density due to swaging is responsible for the observed substantial mechanical strengthening (larger for the cold swaged bar).

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The study was supported by the Czech Science Foundation (project no. 19-15479S). Measurements were carried out at the CANAM infrastructure of the NPI CAS Řež, and at the infrastructure Reactors LVR-15 and LR-0.

ON OPTIMIZATION OF MAGNETIC NANOPARTICLES ARRANGEMENT IN PS-b-P4VP BLOCK COPOLYMER THIN FILMS

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The arrangement of inorganic nanoparticles in a polymer matrix or domains in block copolymer thin films has attached much attention due to their potential applications in diverse fields such as block copolymer lithography, nanostructured solar cells or advanced catalysts [1]. The key issue in all of these systems, which is to precisely control the spatial distribution of the nanoparticles, maintaining the thin film characteristics and polymeric domain's parameters, still remains a significant challenge [2].

In this work we demonstrate the effect of incorporating magnetite nanoparticles into polystyrene-poly-4-vinyl-pyridine (PS-*b*-P4VP) block copolymer thin films. The synthesized nanoparticles had a Fe₃O₄ core diameter of 7.2 nm and were coated by polyacrylic acid to improve affinity to P4VP block, giving overall hydrodynamic radius of 23 nm as measured by DLS. Solutions of the PS-*b*-P4VP were prepared in THF or THF/methanol mixture, where 2 wt. % of nanoparticles were mixed in. The films were prepared by dip-coating method with withdrawal speed varied in the range of 2 to 100 mm/min. The properties of the obtained films were characterized by the means of X-Ray Reflectivity, Grazing Incidence Small Angle X-ray Scattering, Atomic Force Microscopy and Transmission Electron Microscopy.

Thin films with thicknesses 9-70 nm were obtained. The V-shaped thickness dependence on withdrawal speed was validated for each system. For the films obtained from solvents mixture we have observed curve shift to lower dip-coating rates, but leading to possibility to achieve lower film thicknesses. Additionally, much better domain organization was obtained in the case of the films prepared from solvent mixture, especially in the capillarity regime (slow withdrawal speeds), while films prepared from THF



Figure 1. Film thickness as a function of the dip-coating rate. Red curve corresponds to the films, prepared from THF/methanol mix-ture; blue curve corresponds to the films, prepared from THF.

solution showed an occurrence of particles aggregates on the surface. The addition of Fe_3O_4 @PAA nanoparticles has been shown to induce the orientation of P4VP cylindrical nanodomains perpendicular to the surface. Domains of size in the range of 15 to 32 nm and spacing from 45 to 105 nm were obtained depending on the withdrawal speed. The optimal processing conditions have been found to fabricate long-range ordered hybrid organic-inorganic material without the need for further annealing or post-processing.

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SPUTTERING ONTO LIQUIDS: THE BEHAVIOUR OF NANOPARTICLES UNDER THERMAL ANNEALING

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Metal nanoparticles (NPs) are extensively studied due to their unique physical and chemical properties rising from their high surface area and nanoscale size. NPs are suitable candidates for various fields, including catalysis, imaging, medicine, energy production and storage, and environmental applications [1].

The synthesis of metal NPs is divided into two main groups, i.e., physical and chemical. Each of these methods has pros and cons; the physical approach allows the production of pure NPs while the chemical one allows the fine control of the size, dispersion, and shape [2]. In order to improve the synthesis of NPs, the combination of methods is of interest. The sputtering onto liquid is an approach combining both the physical and chemical ways. In this approach, the solid substrate conventionally used during the sputter deposition of a thin film is replaced by a liquid withstanding low pressure. Thus, the metallic target is sputtered in a vacuum chamber. The sputtered elements reach the surface of the liquid. Then, the nucleation and the coalescence of the species occur, and ultimately, NPs are formed [3].

Since the first reported use of this approach in 1974, more than 125 scientific papers have been published based on this process. Most of them highlight the sputtering of monometallic NPs and the influence of parameters on the resulting morphology of the NPs. One of the most used liquid host for sputtering process are ionic liquids due to the higher control of the NPs size and dispersion compared to oil. Moreover, ionic liquid interacts weakly with the sputtered species, so the purity of the obtained NPs is very high. However, ionic liquids are quite expensive and often hygroscopic. Thus, the replacement of ionic liquids by stable organic oils is favourable. The use of such oils raises interrogation concerning the interaction between the metal surfaces of NPs and the oil molecules.

In this context, we report on the synthesis of monometallic NPs (Cu and Au) and alloy NPs (Au/Cu) onto an organic oil, pentaerythritol ethoxylate (PEEL). Moreover, we reveal the behaviour of these NPs under thermal annealing. The synthesis of NPs has been performed by magnetron co-sputtering of a copper and a gold target onto PEEL; these two targets can be simultaneously sputtered to synthesize alloy NPs. Five samples were synthesized: one using only the copper target, one with only the gold target, and three samples with both targets while varying the sputter power on the gold target to achieve different gold concentrations within each sample. The resulting dispersions of NPs in PEEL were analysed using UV-vis spectroscopy, Transmission Electron Microscopy (TEM), and Small Angle X-ray scattering (SAXS). The hypotheses drawn during this study were supported by quantum chemistry-based calculations carried out at the DFT level [4].

The study reveals the successful synthesis of Au/Cu alloy NPs when using both targets. Moreover, the oxidation of the Cu NPs, obtained by sputtering only the Cu target, is reported. As highlighted in previous work [5], the mean diameters of alloy NPs appear to be smaller than the one of the monometallic NPs, i.e., 2 nm for Au/Cu NPs against 6 and 4 nm for Au and Cu NPs, respectively. We explain this behaviour by the interaction energy between each metal (and alloy) with the PEEL molecules.

Following the synthesis of the NPs by magnetron sputtering, solutions containing the NPs were further annealed at 200 °C for 5h with aim to increase the mean NP size. By selecting different intermediate annealing temperatures, we were able to follow the behaviour of each metal and alloy NPs during the thermal treatment in PEEL solutions. First, the gold NPs, which are initially 6 nm-in-diameter spherical NPs evolve to an interconnected ligament structure with a ligament size around 140 nm. Then, for NPs obtained by sputtering a copper target, the diameter evolves from 4 to 80 nm with almost no change in shape. Finally, the diameter of the spherical Au/Cu NPs grows, without change of shape, from 2 to 16 nm. Moreover, the alloy NPs are still composed of homogeneous Au/Cu alloy after annealing.

This study provides an essential insight into the sputtering onto liquids process to synthesize NPs and their development. One of the main issues raised here is the significant growth of the NPs when dispersed in PEEL and further annealed. However, the difference in affinity between the crystallographic facets of a metal NP leads to non-spherical structures after heating treatments.

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MICROSTRUCTURE ANALYSIS IN AIMnCu SAMPLES E. de Prado¹, O. Molnárová¹, S. Habr¹, P. Málek², P. Lejček¹

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Due to the versatility, easy processing, and the multitude of applications of metals, an important number of research centres join their efforts seeking to improve the properties of this type of materials. Among the different mechanisms for improving mechanical properties, grain refinement achieved using severe plastic deformation (SPD) methods has been shown to be effective in increasing simultaneously the strength and toughness of the materials. A new method capable to produce ultra-fine grained tubular samples from bulk billets in one single step [1] has been employed to produce $Al_{0.98}(Cu, Mn)_{0.02}$ cylinders.

X-Ray measurements were performed on the lateral surface of the cylinder (see Fig.1a) carried out using Co K radiation with a point focus and Bragg-Brentano (theta/2theta) geometry. Following Rietveld refinement analysis was made providing a mean volume-weighted crystallite size Lvol-IB=248 nm with a microstrain of about 2%.

Then the sample was cut in order to make residual stress measurements on both outer and inner surfaces of the cylinder (see Fig. 1b). The \sin^2 plot method has been used to evaluate the macroscopic residual strain of the sample which value is proportional to the observed slope. The



Figure 1. Setup for the X-ray measurements with the employed nomenclature .

Parallel 0.9291 γ<0 Linear fit 0.9290 d (A) 0.9289 intercept: 0.929050 ± 1.2E-5 slope: -2.277840E-4 ± 2E-5 R²=0.9194 0 9288 0.0 0.2 0.4 0.6 0.8 1.0 $\sin^2(\chi)$

Figure 2.: \sin^2 plot for the interplanar distance of planes (133).

measurements have been taken using Co K radiation and a graded multilayer mirror (Göbel mirror). The reflection from the plane (133) found at 2theta=148.65 degrees was



Figure 3. \sin^2 plot for the interplanar distance of planes (133) measured in all the 3 different conditions.

selected for this study. The measurements have been performed using a geometry in pseudo inclination mode (measuring at different angles) at two different phi positions: with the diffraction plane placed along the axis of the cylinder (Fig 1a) and perpendicular to it. The measured diffraction peaks were fitted with asymmetric pseudo-Voigth functions in order to determine the position of the intensity maximum. In Fig.2 is shown one of the sin² plot used in this study where can be appreciated the small slope from which a compressive stress in the order of tens of MPa has been calculated. This is a small value compared with other metals as steals which have values one order of magnitude higher.

Figure 3 shows the results obtained from the 3 different measurement conditions considered in this study.

It is noticeable that the cutting induce some relaxation of the residual stress while very small difference was observed between the outer and inner surfaces being the stress slightly smaller in the inner part. Further investigations will be performed in order to determine the stress gradient along the wall of the cylinder.

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L24

X-RAY DIFFRACTION STUDY OF THE PREFERRED ORIENTATION OF SINANODONTA WOODIANA SHELLS

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Bivalve mollusks shells are of interest to leading experts in many areas of human activity, such as ecology, biology, paleontology, but also materials engineering. In recent years, much attention has been paid to studying the preferred orientation of biological tissues such as mollusks shells [1-4]. These polycrystalline materials are characterized by anisotropy of physical and mechanical properties, which are closely related to the preferred orientation (texture) of their grains. The above biological objects can serve as a bioinspiration for material scientists, because nature itself can create entities that are characterized by incredible mechanical properties using relatively small amounts of material. Therefore, the characterization of texture and its correlation with the above-mentioned properties is a cornerstone for understanding the properties of biological polycrystalline materials.

Preferred orientation and exact phase composition of two samples of freshwater shells of the species Sinanodonta woodiana collected from Czech freshwater steams were measured – (i) an adult shell and (ii) a young individual.

Pole figures were measured for planes (111), (021), (002), (211), (220) and (221). Texture data processing was done by MTEX (Matlab) [5]. All diffraction experiments were performed on the SmartLab Rigaku X-ray diffractometer (Cu K). Complete pole figures were calculated for planes (100), (010), (001), (101) and (110).

From the phase analysis it is clear that the Sinanodonta woodiana shells consist only of the aragonite phase. The c-axis of aragonite is perpendicular to the inner surface of the shell and crystallographic texture in all studied shells is strongly uniaxial. The sharpness of the texture is higher for young shells.

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Structure of aluminothermy reduced deep-sea nodules

STRUKTURA HLUBOKOMOŘSKÝCH KONKRECÍ ZPRACOVANÝCH ALUMINOTERMICKOU REDUKCÍ

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Hlubokomořské konkrece se zdají být zajímavým zdrojem barevných kovů, jejichž konvenční těžba je závadná nebo probíhá v nedostupných teritoriích. Novou myšlenkou je příprava přímo "přírodní slitiny", nikoliv redukce konkrecí na čisté kovy. Konkrece ze zóny Clarion-Clipperton (Tichý oceán) byly aluminotermicky redukovány s 0, 10 a 20 %







Obrázek 2. Slitina bez přebytku hliníku mapovaná metodou EBSD, a) barevná orientační mapa (IPF) proložená černobílým signálem image quality (IQ); b) barevná fázová mapa proložená černobílým signálem confidence index (CI); barevná orientační škála pro jednotlivé fáze (IPF) je zobrazena v c) – e); f) barevné kódování fází a obsah.

Krystalografická společnost

přebytku hliníku. Struktura takto získaných slitin byla následně studována kombinací XRD a SEM.

Struktura takto získaných slitin je složitá, pozorované fáze jsou nestechiometrické, případně jsou prvky ve strukturách substituovány. Slitina bez přebytku hliníku při aluminotermii obsahuje majoritní fázi - Mn_{0.66}Ni_{0.2}Si_{0.16} a tři minoritní fáze; slitina s 10 % přebytku obsahuje sedm fází, z nichž tři mají přes 10 hm. %; slitina s 10 % přebytku obsahuje 9 fází, z nichž pět je minoritních. Je zajímavé, že

majoritní fáze ve všech vzorcích je odlišná. Odhad fázového složení byl proveden pomocí XRD a následně jsme se snažili fáze potvrdit pozorován Kikuchiho obrazců metodou EBSD a zjistit jejich prvkové složení. Separace krystalograficky podobných nebo shodných fází byla možná jen kombinovaným měřením EDS/EBSD. Zcela minoritní fáze, např. MnS, byly pozorovány pouze pomocí EBSD.

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L26

COUPLING BETWEEN MAGNETISM AND CRYSTAL STRUCTURE IN THE ANTIFERROMAGNETIC UO₂

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Uranium dioxide is a major nuclear fuel and is an antiferromagnet with the Néel temperature T_N of 30.8 K [1]. The transition at T_N is accompanied by a static Jahn-Teller distortion of the oxygen cage, and strong magnetoelastic interactions that emerge from the face-centered cubic (fcc) structure. Very recent high field magnetostriction measurements showed that UO_2 is a piezomagnet and exhibits the abrupt appearance of positive linear magnetostriction, leading to a trigonal distortion [2]. In this work we observe peculiar behavior of sound velocity variation along the crystallographic axes of UO_2 at various temperatures. We employ first-principles calculations to prove a strong coupling between magnetism and crystal structure variations in UO_2 . The results are compared with

the thin films study where induce a tetragonal distortion in UO_2 by using different substrates [3].

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L27

XRD STUDY OF STRONGLY ORIENTED THIN FILMS OF HEXAGONAL FERRITES WITH POTENTIAL MAGNETOELECTRIC EFFECT

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X-ray diffraction and reflectivity techniques for analysis of thin polycrystalline thin films have been well-developed and they are routinely used when often low-angle incidence setup is applied instead or in addition to symmetrical

scan. However, for strongly oriented films more different asymmetric scans and/or reciprocal space mapping are required. During study of nanocrystalline ZnO films [1] we have applied a combination of different scans to characterize both the so-called out-of-plane orientation and in-plane orientation. Strong out-of-plane orientations were found, and only basal (001) reflections were available in symmetric scans. Therefore, the lattice parameters, profile analysis (crystallite size and strains) and residual stresses were studied by combination of several asymmetric reflections scanned at specific suitable angles of inclinations and (i.e. on the axis perpendicular to the film surface and axis perpendicular to the goniometer axis, respectively). For comparison of measured lattice parameters there was often a problem of either no data in the PDF-4+ database for specific phase or multiple but different data.

The methods were also used in later extensive study of M, Y, Z and W hexagonal ferrites with a potential of magnetoelectric effect. The films were prepared by chemical solution deposition (CSD) method and metalorganic precursor solutions prepared using the modified Pechini method. Number of processing parameters were tested and optimized with the aim to minimize the amount of impurities that could spoil the magnetic properties of final material. For preparation of highly oriented ferrite films, several substrates were used, and different substrate/seeding layer/ferrite layer architectures were proposed. From seven M phases with different chemical composition, magnetic character and lattice misfit values investigated in their use as template and buffer layers for Y ferrite growth, the best results were achieved when the misfit values between seed layer and substrate, and between seed layer and top Y-layer are approximately equal and when the surface of seed layers are formed by hexagons for which the surface area formed by top surface of hexagons is much larger than surface area formed by side walls of hexagons [2, 3].

New *Y*-ferrite phases were prepared with the composition BaSrZnCoFe₁₁(Me)O₂₂ (Me = Al, Ga, In, Sc). and it was found that for Me = Al, Ga the magnetic structure is of non-colinear ferrimagnetic type with unspecified helical magnetic structure. For Me = Ga this is a new system with potential ME effect. Moreover, these films could be prepared as well-oriented both out-of-plane and in-plane on STO - SrTiO₃(111) substrates directly without any seeding layers.

ME *Z*-type ferrite Sr₃Co₂Fe₂₄O₄₁ and

 $Ba_xSr_{3-x}Co_2Fe_{24}O_{41}$ thin films were prepared and characterized for the first time [4]. According to the XRD texture analysis the orientation relationship between Z ferrite and substrate can be expressed as (001)Z || (111)STO || and Z || STO. However, in these films the analysis was complicated by the presence of M and S (spinel) phases that were also oriented (aligned with the substrate) and therefore also many asymmetric reflections were overlapped and many of them were weak. Therefore, a careful selection of reflections suitable for the analysis had to be made.

Composition series of *W-type* $SrCo_{2-x}Zn_xFe_{16}O_{27}$ hexaferrite thin films and powders were also successfully synthetized by CSD method. For successful growth of W hexaferrite films on $SrTiO_3(111)$ substrate, annealing temperature and time falls into a very narrow interval of 1225 to 1250°C and 60 to 120 minutes, respectively, depending on the amount of substituting Zn^{2+} ion. The strong anisotropy of magnetic properties was confirmed. Currently, oriented *Y-Z* composites are studied that is another challenge for the analysis.

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L28

TEXTURE ANALYSIS OF STRONGLY ORIENTED LAYERS UTILIZING FAST RECIPROCAL SPACE MAPPING

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Polycrystalline layers of organic perovskites such as CH₃NH₃PbI₃ (MAPbI₃) are intensively studied in order to achieve high performance of solar cells. The final efficiency correlates with the defect density, size and morphology of the crystallites. These materials exhibit tendency to form strongly oriented layers with sharp fibre multi-component texture. In order to correlate the relevant physical properties of the layers with their crystallographic orientation, it is highly desirable to easily measure and describe the present texture.

As a classical and well-established approach, one can use pole figure measurement to fully determine the texture of the layers, however here the task is complicated by the fact that the low-symmetry unit cell of such materials is rather large. Consequently, the number of observable peaks is quite high and their diffraction angles are partially overlapping. Therefore it is necessary to increase the resolution in diffraction angle in order to discriminate different diffraction maxima during the pole figure measurement. As usual, it is at the expense of the collected signal making the pole figure measurement to be a time consuming. Another specific problem can be a presence of some strain influencing the peak positions.

Fortunately, fast 2D detectors are more and more available also in standard laboratory diffractometers that makes it possible to measure reciprocal-space maps very quickly. In this presentation, the measurements with 2D detector placed closely behind the sample are presented. Using the shorter sample-detector distance, the resolution is partially sacrificed while the reciprocal space area observed by the



Figure 1. Wide Reciprocal Space Maps for the MAPbI3 thin layers grown with the presence of MACl additive. The concentration of MACl during the growth determines the final texture of the layer. A low concentration results in a multi-component texture whereas a high concentration enhances just one preferential orientation. Transparent spots represent simulated peak positions for the same MAPbI3 structure, the texture components are resolved by different colours.

detector is dramatically extended. In this configuration, the continuous theta-2theta scan fully probes a long stripe in a reciprocal space. By measuring several such stripes, it is easy to reveal the full planar cut of the reciprocal space, and surprisingly the total acquisition time can be only tens of minutes for strongly oriented layers. Moreover, such measurement can be performed for different sample azimuth in order to obtain different planar cuts. This is desirable for single-crystal substrates, for which the surface symmetry can be followed. The obvious advantage of this approach is a possibility to quickly visualise the intensity in reciprocal space and to compare the obtained images with the simulations based on some expected phase/texture model giving semi-quantitative results. Therefore it is very suitable for the first-try characterization of the unknown samples.

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