odleštěn. Obrázek 2 ukazuje žíhání leštěného vzorku na hodnotu povrchové mikrodeformace. Měření bylo prováděno in-situ v teplotní komoře HTK 2000. Po době cca 150 minut byla teplota 2x zvýšena z 300°C na 400°C a po té z 400°C na 500°C.

Je patrné, že objemová mikrostruktura titanových vzorků připravených z komerčně dostupných tyčí titanu označovaných „Grade 2" se liší od hodnot na povrchu po přípravě povrchu leštěním. K dosažení mikrostruktury na povrchu srovnatelné s objemovými vlastnostmi jsme zkoušeli elektrolytické leštění, které nemodifikuje objemové vlastnosti, ale bohužel způsobuje nechtěný reliéf na povrchu vzorku. Na druhou stranu žíhání celého ve vakuu zachovává povrch hladký a rovný, ale na druhou stranu ovlivňuje objemové vlastnosti vzorku.

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L15

NEUTRON SCATTERING AND ITS COMPLEMENTARITY WITH X-RAY TECHNIQUES

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The unique blend of particle and wave properties - large rest mass, zero electric charge, magnetic dipole moment, isotope-specific scattering in combination with Å-scale wavelengths - makes of neutrons a very attractive and efficient tool for investigation of structure and dynamics of condensed matter. Since several decades elastic and inelastic neutron scattering became a standard experimental tool in a variety of condensed matter research domains, complementing the much more current X-ray scattering. Determination of magnetic structures, mapping the momentum and energy of structural and magnetic excitations and investigations of soft matter and biologic systems with the use of the isotopic hydrogen-deuterium contrast variation are just a few most significant examples. Thanks to the construction of dedicated national and international high-flux neutron sources this technique, originally reserved to a small number of highly specialized teams, became accessible to a broad scientific community. This trend is ongoing with the construction of next generation spallation sources like the SNS in the USA and ESS in Europe.

In this lecture we will concentrate on the fundamentals of neutron scattering techniques and on application examples of contemporary studies of functional materials related to spintronics, energy storage and molecular biology.

L16

VALIDATION OF POWDER DIFFRACTION BASED STRUCTURE DETERMINATION RESULTS BY DFT-D QUANTUM MECHANIC CALCULATIONS

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Introduction

Due to the loss of information related to measurement principle, results of crystal structure determination based on powder diffraction data are often not 100% reliable. Additional techniques like solid-state NMR, geometry check against common molecular parameters from databases or energy calculation should be used to verify the crystal structure and molecular geometry as well. The suggested methodology is described in details in article [1]. The mentioned article describes QM minimization of 225 molecular crystal structures determined by powder diffraction from witch 8.8% was found to be incorrectly solved. The aim of our work was to test whatever we can apply similar check to our results.

Methods

We did not have available VASP software nor the special force field method developed for dispersion correction implemented in GRACE software as used in the mentioned article [1]. Our calculations were done in CASTEP software as implemented in Material Studio [2] software package. We had used geometry optimization approach consisting of two steps as suggested in [1]: firstly, the cell was fixed during the geometry optimization, and secondly, cell parameters together with molecular geometry were optimized.

Table 1. RMSCD values for 6 tested structure

| CSD code	RMSCD for non H atoms (Å), cell fixed	RMSCD for all atoms (Å), cell fixed	RMSCD for non H atoms (Å), cell refined	RMSCD for all atoms (Å), cell refined
BOVDUM	0.2652	0.3762	0.2931	0.4024
SORLOC	0.1093	0.2026	0.1073	0.213
TISCAB	0.0932	0.3145	0.0937	0.3146
WAFLIA	0.0947	0.2542	0.0947	0.2542
XOGLOW	0.1346	0.2044	0.1367	0.2091
XOGLUC	0.1069	0.1668	0.1107	0.1747

Details of Computation

For the system electron shield description, the GGA-PBE functional was used. The calculation setup was corresponding to "Fine" preset: 340 eV energy cut-off, convergence criteria - 10^{-5} eV/atom energy, 0.03 eV/Å maximal force, 0.001 Å maximal atom displacements. The Tkatchenko-Scheffler scheme was used for the dispersion correction.

The original powder based data were compared with the geometrically optimized data by the Cartesian displacement RMS (RMSCD) to be able to compare atomic positions in different unit cells. The Cartesian displacement for an atom in two crystal structures (1) and (2) is described by eq. (1).

$$|G_1 \ r_2 \quad G_1 \ r_2| \ |G_2 \ r_1 \quad G_2 \ r_1| \ / 2 \qquad (1)$$

The r_i are the fractional coordinates of atoms in crystal structure i and G_i is the transformation matrix from fractional to Cartesian coordinates for structure i. The RMSCD calculation was implemented in CrystalCMP software [3].

Results

The obtained results are summarized in Tab. 1.

Discussion

According to the [1], structures with RMSCD > 0.25 Å for non H-atoms should be considered as suspicious and checked. The BOVDUM structure falls in such category. The issue can be related to disorder - for the QM calculation only one part of the disorder, which was observed in the crystal structure, was used. However, it sounds like the explanation is different. This crystal structure (capacitabine) was later re-determined by other group from single crystal [4] data and it is presented in CSD with code BOVDUM01. The structure redetermination had observed an incorrect placement of H-atom in our original powder study, see Fig. 1.

The TISCAB structure shows low value of RMSCD for non-H atoms, but much higher value for all atoms including hydrogen atoms (RMSCD >0.3!). The QM structure
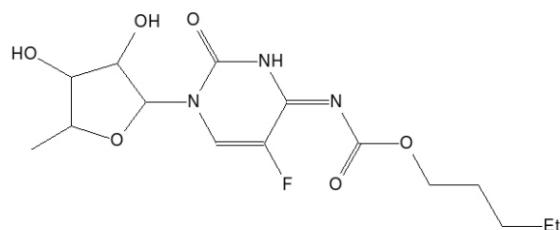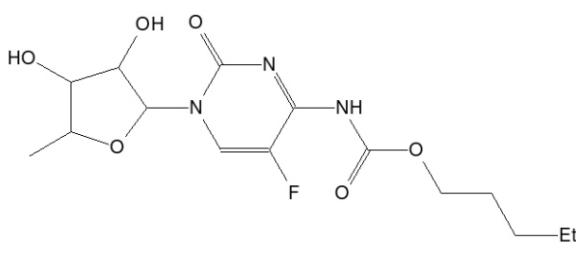
Figure 1. Comparison of incorrect (top) and correct (bottom) BOVDUM (capecitabine) formula in crystalline state.
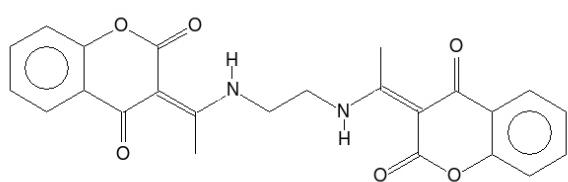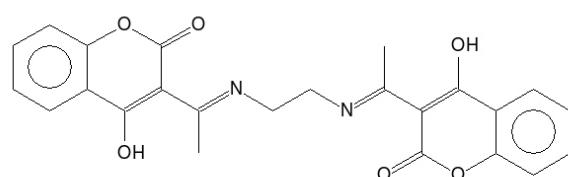
Figure 2. Comparison of incorrect (top) and correct (bottom) TISCAB formula in crystalline state.

suggests a different H atom position and bond order as described on Fig. 2.The original article [5] suggests the formula based on liquid NMR data only. In solid state, the formula can be different. A search in CSD did not find any similar crystal structure with the same order of hydrogen atoms as in [5], but it had found about 30 structures with hydrogen atoms in positions suggested by the QM.

Conclusions

In two from six our powder studies, the DFT-D calculation had found troubles mainly with positioning of hydrogen atoms. It is even worse than the 19/215 issues as found in [1] but the total number of structure checked is too low to make a reasonable statistics and conclusions. It is probably clear anyway that any molecular crystal structure solved from

powder should be checked by DFT-D geometry calculation before publications to detect possible issues.

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2.   http://accelrys.com/.

3.   https://sourceforge.net/projects/crystalcmp/.

4.   M. Malinska, P. Krzeczyński, E. Czerniec-Michalik, K. Trzcińska, P. Cmoch, A. Kutner, K. Woźniak, *J. Pharm. Sci.,* **103**,(2014), 587.

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SL5

CRYSTAL STRUCTURE OF 3-AMINO-5-(AMINOCARBONYL)-2,4,6-TRIIODO-BENZOIC ACID METHANOL ($C_8H_5I_3N_2O_3$.CH_3OH) FROM LABORATORY POWDER DATA

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X-ray powder diffraction data, unit-cell parameters, space group and 3D crystal structure for 3-amino-5-(aminocarbonyl)-2,4,6-triiodo-benzoic acid methanol, $C_8H_5I_3N_2O_3$. CH_3OH, are reported [a = 17.0017 (10) Å, b = 13.8959 (8) Å, c = 12.5964 (8) Å, unit-cell volume V = 2976(1) Å^3, MW = 589.89,   = 2.641 g/cm^{-3}, Z = 8, space group *Pbca*]. The experimental powder diffraction pattern was indexed by DICVOL04 [1], solved in direct space and

refined in DASH[2]. The results of X-ray powder diffraction structure determination will be presented.

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L17

POUŽITÍ INFRAČERVENÉ A RAMANOVY SPEKTROSKOPIE PRO UPŘESNĚNÍ KRYSTALOVÝCH STRUKTUR

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Pomocí faktor-grupové analýzy krystalové struktury je možné určit výberová pravidla pro aktivaci fononu v infračervených a Ramanových spektrech [1]. Obecně platí, že v materiálech s krystalovým centrem symetrie jsou infračervené aktivní fonony ramanovsky neaktivní a naopak. Toto názorně předvedeme na některých materiálech s perovskitovou krystalovou strukturou jako jsou $SrTiO_3$, $PbTiO_3$ a $BiFeO_3$. Naopak v materiálech s narušeným centrem symetrie jsou infračervené aktivní fonony též ramanovsky aktivní. Tohoto faktu se výhodně využívá při studiu strukturních a feroelektrických fázových přechodů. Feroelektrické materiály totiž nemají centrum

symetrie a kombinace obou spektroskopií tak umožňuje ověřit tento fakt mnohem citlivěji než difrakční metody, protože ty nejsou dost citlivé na rozlišení centrovaných a necentrovaných krystalových struktur. V infračervených spektrech se také výhodně rozliší strukturní fázové přechody s násobením primitivní buňky – bude demonstrováno na antiferoelektrickém $PbZrO_3$ s osminásobením primitivní bunky.

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