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PULSNÍ LASEROVÁ DEPOZICE $LuFeO_3$ STUDOVANÁ RTG ROZPTYLEM BĚHEM RŮSTU

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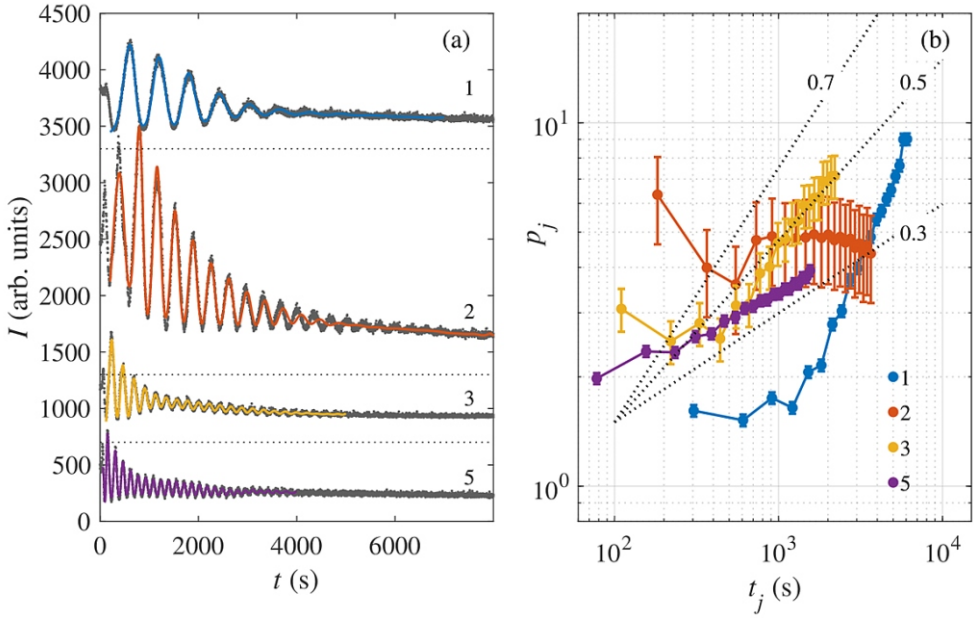
Hexagonální $LuFeO_3$ je typickým příkladem multiferoického oxidu, který vykazuje ferroelektrické a magnetické uspořádání při pokojové teplotě. Tenké vrstvy multiferoických oxidů se připravují pulsní laserovou depozicí (PLD). Ve srovnání s molekulární epitaxy (MBE) představuje metoda PLD vysoce nerovnovážný proces, a přesto umožňuje získat tenké epitaxní vrstvy s hladkým povrchem, jejichž strukturní kvalita se blíží vrstvám získaným metodou MBE. Tento experimentální fakt není dosud úplně objasněn a metoda PLD proto vyžaduje další zkoumání.

Předkládaný referát popisuje výsledky měření rtg rozptylu (rtg difrakce, metoda GISAXS a rtg relexe) během PLD depozice vrstev $LuFeO_3$ na různých substrátech (safír, safír/Pt, YSZ). Měření bylo provedeno v PLD růstové komoře umístěné na NANObeamline synchrotronu KARA (KIT Karlsruhe).

Elementární buňka hexagonálního $LuFeO_3$ je centrovaná, a tedy difrakce 000L (L je liché) je zakázaná. Toto extinkční pravidlo platí v bulkových vzorcích; v tenkých vrstvách je splněno, pokud vrstva obsahuje sudý počet monomolekulárních vrstev. Měření časového vývoje intenzity takové zakázané difrakce (0003 v našem případě) je proto důležité pro sledování kinetiky růstu vrstvy. Obrázek 1 ukazuje příklad experimentálních dat a jejich fit fenomenologickým růstovým modelem.

Pro analýzu naměřených dat jsme vyvinuli kvazi-fenomenologický růstový model založený na numerickém řešení stochastických rovnic růstu. Výsledkem simulací je časová závislost pokrytí jednotlivých monomolekulárních vrstev. Tato závislost vykazuje škálovací exponenty, jejichž hodnoty jsou charakteristické pro převažující atomistické procesy na povrchu (nukleace zárodků, desorpce molekul z povrchu, připojení molekul k monomolekulárním schodkům). Srovnáním s experimentálními daty získanými pro různé kmitočty záblesků růstového laseru a různé teploty substrátu jsme sledovali závislosti těchto atomistických procesů na parametrech depozice.



Obrázek 1. (a) Časový vývoj intenzity zakázané difrakce 0003 během PLD růstu, parametr křivek je kmitočet laserových záblesků v Hz. Tečky jsou naměřená data, barevné křivky jsou výsledky fitu růstovým modelem. (b) Šířky časových profilů pokrytí jednotlivých monovrstev.

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MODULATED STRUCTURES AND TWINS – A NIGHTMARE FOR CRYSTALLOGRAPHERS?

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Most standard structures can be solved using "modern programs for solution and refinement of crystal structures" in minutes without understanding what the programs do. Therefore, one may get the impression that structural crystallography is a closed field and that the crystallographers involved in the methods have long since done their job. The crystallographer's task is to measure and identify structures with automatic tools, check the chemistry, prepare figures, describe weak interactions and explain or avoid PLATON alerts.

From time to time, however, problems do occur, and standard programs fail. Apart from poor data and very large structures, the most common cause of such failures is that the structure is modulated or the crystal is affected by twinning. These can create nightmares for busy "structural crystallographers", who are expected to solve several structures daily and not waste time with one structure many days. How, then, explain to the chemists who prepared the crystal that their crystal is not standard?

While crystals affected by twinning require solving a geometric puzzle about how the crystal domains coexist in bulk, modulations in a crystal imply a fundamental change in the understanding of crystal symmetry. The diffraction pattern of modulated structures differs significantly from that of unmodulated structures. For standard structures, all diffraction spots can be indexed using three reciprocal lattice vectors. Modulation in the crystal creates additional satellite spots. So-called modulation vectors must be introduced to index them. Then each diffraction spot is described by (3+d) diffraction indices. This implies that the translational symmetry of the crystal is broken, however, regularly.

Satellite diffraction spots are usually much less intense, and their possible neglection leads to an average structure, which in many cases sufficiently proves the chemical structure of the substance under study. On the other hand, there are also cases when modulations fundamentally affect the physical properties. Then, the information about the actual structure and its change with temperature, pressure, or detailed composition is essential, and the complete solution of modulated structure cannot be avoided.

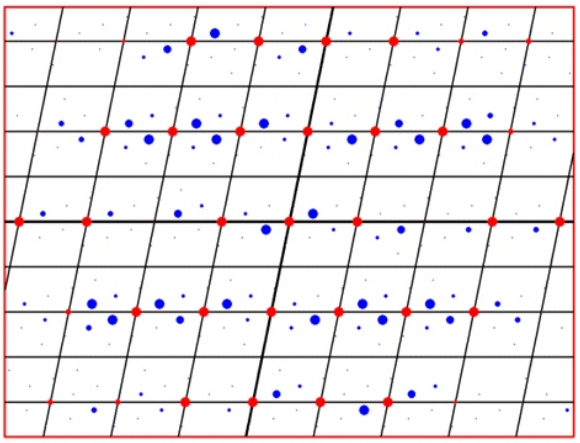

Figure 1. Simulated diffraction pattern of Na_2CO_3 [1]. The main reflections are red, and the satellites are blue.

Measurement, solving and refining modulated structures are analogous to procedures known for ordinary structures. Most modern diffractometers allow multiple indices when integrating diffraction spot intensities. Since the beginning of the 1980s, the possibility of refining modulated structures based on the use of the superspace approach [2] has gradually been included in some programs (REMOS [3], MSR [4], JANA [5]). The program Superflip [6], developed much later, allows for the direct solution of modulated structures without the intermediate step of solving the average structure. All steps of structural analysis are included in Jana2006 [7] or Jana2020 [8] program systems, which try to be user-friendly and reach the situation described at the beginning of this contribution as "the crystallographers involved in the methods have long since done their job". Still, a much deeper knowledge of the fundamentals of modern structural crystallography is required to understand the meaningfulness of results and their interpretation.

In a twinned crystal, each independently diffracting part provides the same diffraction pattern, the position of which is determined by the respective twinning operations. In general, this means that 3n reciprocal vectors must be used to describe the diffraction image of a twin consisting

of n independent domains. However, these vectors need not be integer independent, which allows us to distinguish two extreme cases, the fully overlapped and the fully separated twins. The condition for full overlaps means that all twinning matrices reproduce the reciprocal lattice; therefore, their elements are integers, and there are only three integer-independent vectors.

The observed intensity of the diffraction spots is then the sum of the intensities of the individual domains

$$\mathscr{F}^2(\vec{h}) = \sum_{i=1}^{n} \nu_i F^2(\vec{h}\vec{T}_i) \qquad \sum_{i=1}^{n} \nu_i = 1 \tag{1}$$

where F is the structure factor, ν_i is the volume fraction of the i^{th} twin domain and $\mathscr{F}^2$ is a square of the resulting structure factor related to the measured intensities.

The above-mentioned condition for complete overlap of diffraction spots of individual domains induces the relation between the lattice and structure point groups. The latter must be a subgroup of the former. The cases with full overlaps are classified as sygnonic and metric merohedry. Determining the point and space group by directly analysing the measured intensities is difficult [9]. Indeed, in the case where the domains are uniformly occupied, the apparent point group is identical to the lattice point group. For non-uniformly occupied domains, the apparent point group is lower than the lattice point group but not necessarily equal to the point group of the crystal structure. On the other hand, in these cases, there is no problem in determining the unit cell.

However, in cases where the number of integer-independent vectors is lower than for completely separated domains but higher than for completely overlapped domains, there is also a problem in determining the proper unit cell of the crystal under study. The twinning matrices are composed of rational numbers, and such twinning is called reticular merohedry. Two cases are presented in fig 2 and 3. No problem can be detected in the first, while in the second, it is evident that the smallest possible cell in the reciprocal space is not the correct choice.

Most conclusions resulting from the analysis of the measured data for twins are more like warnings of potential issues, and it is up to the user to decide how to use such information. The recent version of Jana2020 [8] includes procedures to identify problems that may arise when studying modulated and twin-affected crystals. During the talk, these tools will be presented as examples.

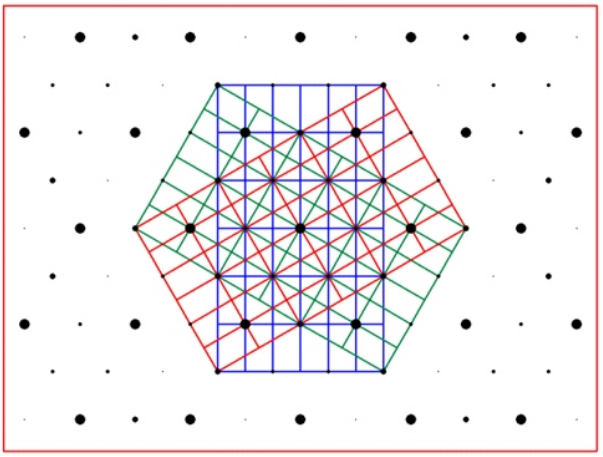

Figure 2. Orthorhombic unit cells in three twin domains of $CsLiSO_4$.

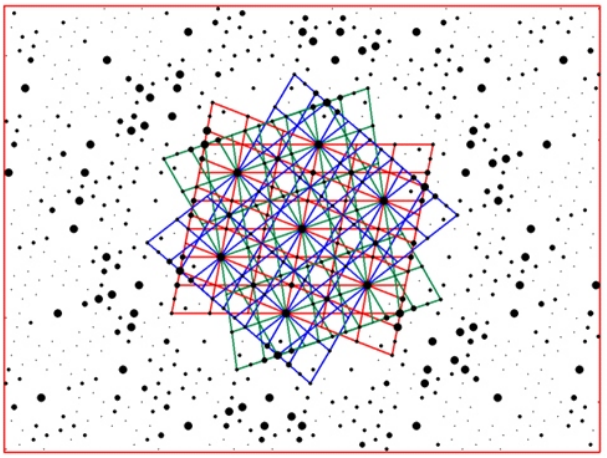

Figure 3. Diffraction pattern of the six-fold twinned structure of -$Ca_{11}B_2Si_4O_{22}$ (lattice symmetry 6/*mmm*, point group 2/*m*) published in [10] . The first triplet (blue, green and red) shows the unit cells of three twin domains related by the three-fold axis. The second triplet arises from the first one by applying one of the remaining operations of the original hexagonal lattice point group.

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PIXEL CORRECTIONS FOR THICK SENSOR DETECTORS

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Flat hybrid pixel detectors present the most common instruments for recording photon counts in crystallographic experiments at accelerator-based light sources as well as in X-ray laboratories. To optimize efficiency of the detection process the ratio of detector sensor thickness and pixel face size is commonly set quite high. A narrow X-ray beam entering such a detector at an oblique angle is absorbed in multiple consecutive pixels. This is causing an effective shift of the detected signal known as the "parallax" effect. The absorption of X-rays in the detector sensor is also more complete. The latter is called an "oblique incidence effect". These effects can cause a characteristic blur of diffraction spots depending on the detector incidence angle. Appropriate corrections are well established in software for single crystal diffraction data processing [1] and known in software for azimuthal integration of diffraction patterns from X-ray area detectors [2]. A framework [3] was created to simulate the parallax and oblique incidence effects by means of point spread function (PSF) using a simple raytracing of the interaction of X-rays with the detector and assuming a point X-ray source. The model can describe realistic detector cases including gaps between detector submodules knows as "wide pixels" (Figure 1). Detector PSF is represented by a sparse matrix and so the calculation of the blurred image for any type of ideal simulated signal is very effective. More complex is the deconvolution of known simulated PSF from a measured images that should result in position and intensity corrected diffraction images and optimally also sharpen diffraction spots. Several methods (Richardson-Lucy, Deep learning, and Direct inversion) are presented and compared. Their applications for diffraction data processing are briefly discussed.

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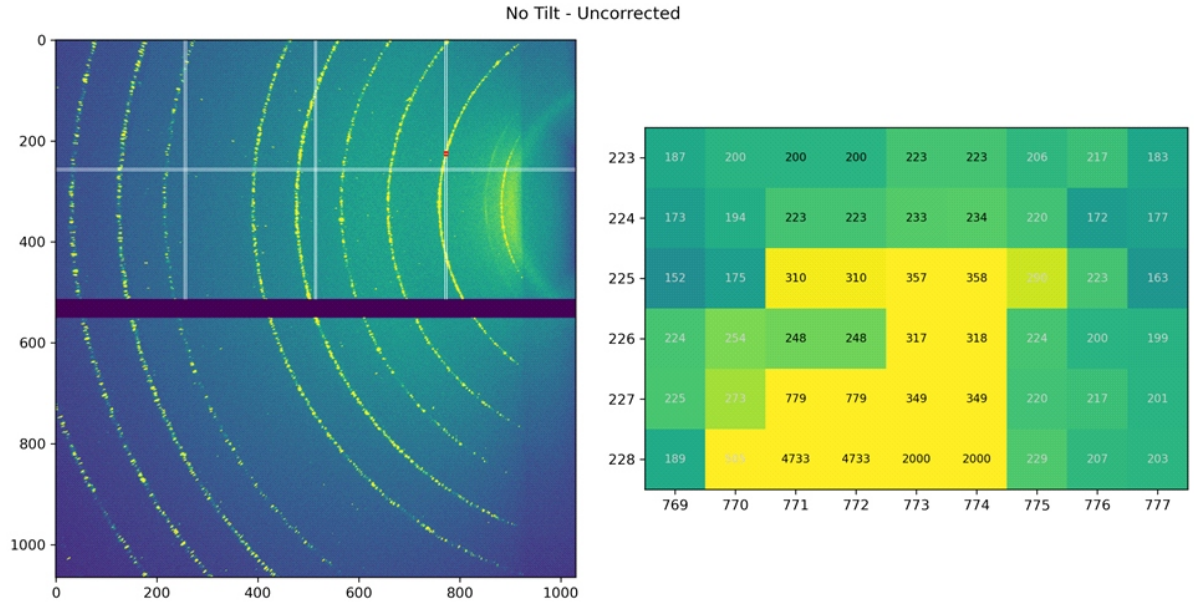

Figure 1. Detector submodules are shown in the upper left part. "Wide-pixels" are visible in the enlarged image area on the right.