STRUKTURA 2024

Loučná nad Desnou, Dlouhé Stráně, 18.11.-22.11. 2024

Session I, November 18, Monday

L1

CRYSTALLOGRAPHIC ABSURDITIES EXPOSED

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The increasing volume of scientific publications leads to a rise in intriguing, yet sometimes dubious, crystallographic results being published. As reviewers cannot be experts in every field, many absurd results appear even in top-tier journals. In my slightly informal talk, I will present an overview of the most astonishing crystallographic absurdities I have encountered in recent years. Together, we will explore instances of:

- **Faked XRD data:** Do some of the peaks contradict your conclusions? Feel free to delete them!
- **Surprising duplicities:** It is more ecologically friendly to recycle your old Bragg-Brentano scans and use them in your next article about a totally new sample of different composition.
- **Interesting fits:** The fact that your calculated and observed curves do not match at all does not need to prevent you from publishing in, say, the *Journal of Molecular Structure*.
- **Weird XRD patterns:** Yeah, smoothing will always make your curves look better! It does not matter that your functions are no longer functions, Figure 1.
- **Almost poetic AI-generated article sections:** "At room temperature, when the X-ray generators were working at 40 kV and transmitting a charge of 30 mA to the target, it was considered a successful hit."- **And much more.**

My aim is not only to provide good cheer but, more importantly, to spread awareness and highlight the most common issues you might encounter while critically reviewing an article. Since people are sneaky and inventive, not all the flaws discussed will be as obvious as those listed above. I will also introduce *pubpeer.com* as an example of platforms that allow users to discuss and review scientific research after publication.

1. B. Bekele et al., *Journal of Nanomaterials*, 2021(1), 9210817.

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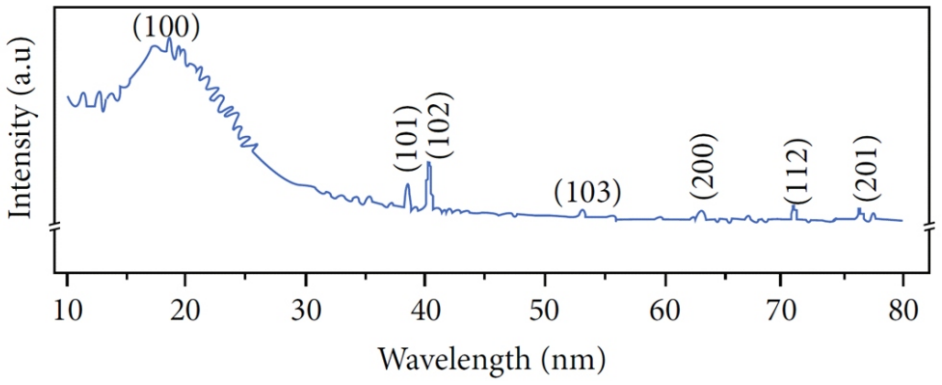

Figure 1. "XRD spectral analysis of hydrothermal synthesis of ZnO nanoparticles from $ZnSO_4.7H_2O$ zinc salt precursor." as an example of an interesting XRD pattern. Additionally, the authors have accidentally labelled "Two theta (degree)" as "Wavelength (nm)". Adapted from [1] (showing only one of the three curves from the original figure). The original content is licensed under a CC-BY-4.0 license.

L2

AZINT-PRACTICAL: SHAPING 2D SYNCHROTRON DATA FOR RIETVELD REFINEMENT

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Rietveld refinement [1] is a widely recognized method of analysis of X-ray and neutron powder diffraction data for the characterization of various aspects of crystalline materials. In case of X-rays, the powder diffraction data can be acquired using a range of instruments including dedicated industrial and laboratory diffractometers or highly optimized powder diffractometers at synchrotron beamlines. Given the valuable insights that powder X-ray diffraction can offer, this technique is frequently employed in multimodal experiments or as a supplementary method in the beamlines at accelerator-based photon sources.

The most prevalent scattering geometry at the light sources today is the transmission (Debye-Scherrer like) geometry with a flat area detector positioned in the forward direction (Fig. 1). This experimental geometry is straightforward to implement, it takes advantage of intensive X-ray diffractions at lower scattering angles, and by utilizing large, fast area detectors, it delivers sub-millisecond time resolution with robust signal strength and a decent angular resolution.

Furthermore, area detector data can yield additional information on the preferred orientation of crystallites (texture) in the sample. When texture information is not the primary focus, the area detector data are typically reduced to 1D diffraction patterns, which offer a standard representation of the diffraction experiment and serve as input for the Rietveld method.

There are numerous dedicated software options for azimuthal integration (AZINT) of the area detector data, including *fit2d* [2], *PyFAI* [3], *diffpy.srxplanar* [4], *Nika* [5], and *AZINT-module* [6,7]. While some of these computer programs were initially designed for small angle scattering data, they often extend their applicability to the powder diffraction modality.

Complementary to AZINT software there are multiple software options for the Rietveld refinement. A non-exhaustive list includes *FullProf* [8], *GSAS II* [9] and *EXPGUI* [10], *Maud* [11], *TOPAS* [12], *Jana2020* [13] or *MStruct* [14]. Only two of these software [9-11] provide an "all in one solution" that also covers the AZINT reduction step and detector calibration.

Beamlines at light sources often include the AZINT reduction step as part of their automated data processing workflow [6,15], so users may choose to bypass the internal AZINT step in the latter software as well. AZINT software come with numerous settings and can optionally apply several intensity corrections on data, including solid angle correction, polarization correction, air-absorption correction, sample absorption or sample scattering corrections, parallax effect correction, and detector flat-field correction. Other notable options include a "normalization

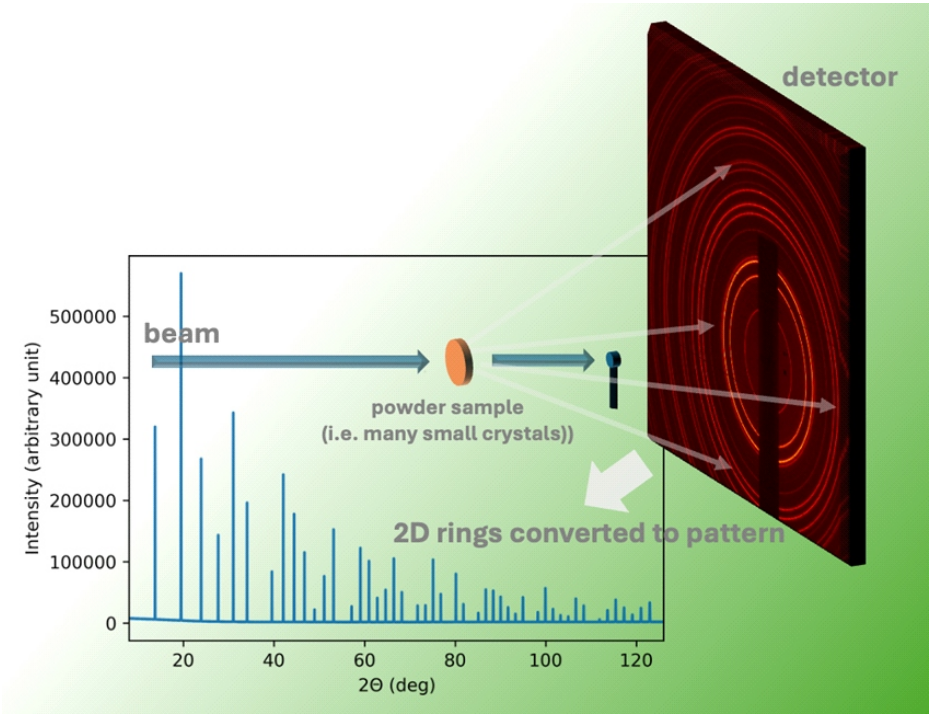

Figure 1. The transmission X-ray diffraction geometry with a flat area detector in the forward direction.

model" [3], "error propagation model" [3] or possible correlation between powder pattern points [4].

Simultaneously, all Rietveld software [8-14] have many options and can account for some of the intensity corrections mentioned above.

This contribution provides an overview of software options for AZINT and the suitable settings for some of the software implementing the Rietveld method.

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L3

SIMPLE XRD LINE PROFILE FITTING. PROGRAM LIPRAS.

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The evaluation of powder diffraction patterns is nowadays often well performed by some form of the Rietveld method that is in principle the method of total powder pattern fitting. The programs like Fullprof [1], GSAS [2], Maud [3] or MSTRUCT [4, 5] and others can use full information obtained in the pattern for refinement of crystal structure, lattice parameters, for phase analysis, estimation of some parameters of real structure, certain evaluation of texture and stress. These programs consider many different parameters related to these quantities and those related to instrumental aberrations and effects. Their success depends on the relevance of the used models and functions to the structure and microstructure of examined samples.

In many cases, it can still be useful just to determine the parameters of individual diffraction profiles. Since these profiles are often overlapped, it is also necessary to decompose them by fitting of suitable functions. For this approach, commercial software can also be used but even this may appear insufficient because to control well the procedure one needs also to easily control possible constraints and bonds between the parameters and mainly to see graphically the decomposition and not only the overall fit. The fitting of peak functions and decomposition of the profiles can be done quite easily in general mathematical software, software plotting graphs like Origin but for evaluation of many experimental patterns this is not ideal either. Moreover, typical laboratory X-ray data include K doublets. Open software for fitting of particularly diffraction profiles can still be welcome.

In 1991-2 I have written an MS-DOS program Difpatan with keyboard control. By using short cuts the fits can be done very quickly but currently to run the program, MS-DOS emulation software is required. It can be run well under DOS Box but still it is not so comfortable, and the philosophy of the program may be a little outdated. The program is still available, though [6]. Fitting can also be done well by Winplotr, a part of the Fullprof package. Petr Veřtát created user-friendly program in Excel that is widely available [7]. However, with many data points it can be rather slow. After several attempts to find open simple, fast and robust such a program, I have found the free software LIPRAS (Line-Profile Analysis Software) developed in Matlab at North Carolina State University [7]. The Matlab version requires MATLAB® 2016b, or higher, with Curve Fitting ToolboxTM and GUI Layout Toolbox [8] or at GitHub. In addition to Matlab version, stand-alone version is also available. It utilizes MATLAB® runtime which is free and can be downloaded online or through the installation manager [9].

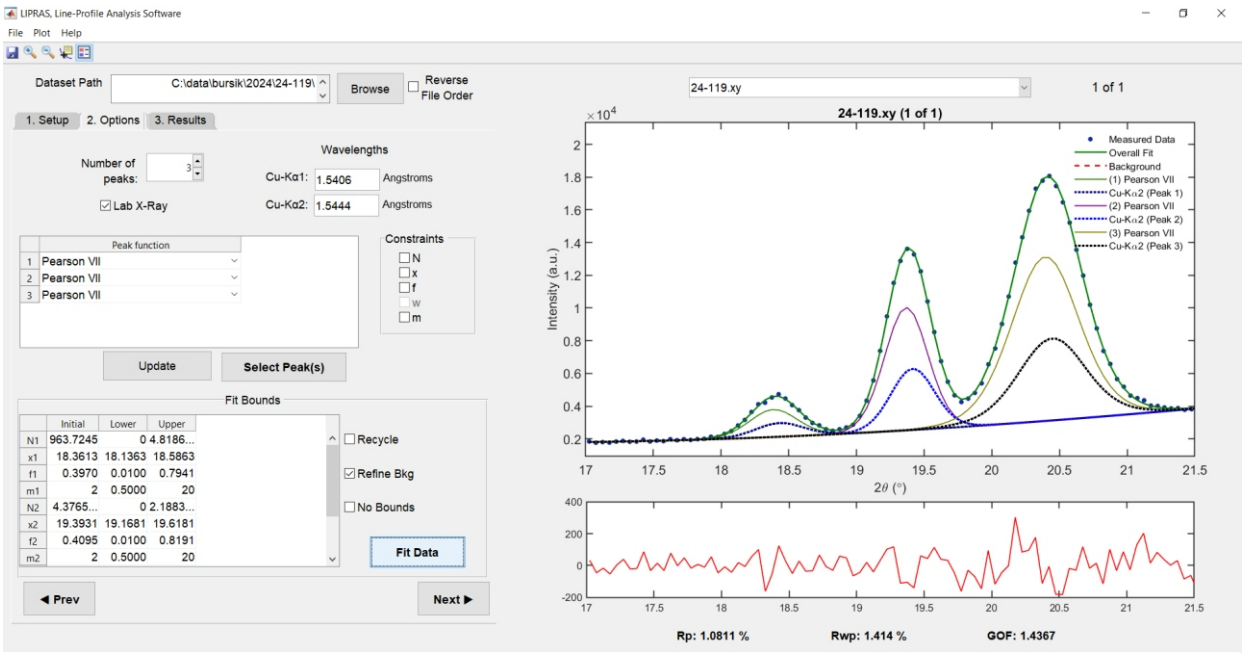

Figure 1. Example of main fitting window with three peaks and Pearson VII function.

I have found the software useful, simple to use, robust for fitting of even complicated overlapped diffraction peaks. The fitting is simple. Several different file formats can be used including, of course, two column ASCII data. After opening the file, it is possible to define range of interest, select polynomial for background fitting and click background points. The next window is the main one. There, single wavelength data or XRD lab data ($K_{1,2}$ doublets) should be selected, number of peaks, the used function for each of them and click approximately their positions as initial values for non-linear optimization algorithm. Constraints on fitted parameters can be put, if necessary, and then the fitting can be performed either with or without background refinement. In last window, fitted parameters can be read.

The features of the program are shown in download pages

- Quickly extract relevant peak information about the position, full width at half maximum (FWHM), and intensity
- Conduct Bayesian inference on least-squares results using a Markov Chain Monte Carlo algorithm
- Customize the background fit by either treating it separately (Polynomial or Spline) or including it in the least-squares routine (Polynomial only)
- Can analyzes files with a different number of data points and/or X-values, however, check fitting range before attempting
- Fit up to 20 peaks in the current profile region
- Choose from 5 peak-shape functions: Gaussian, Lorentzian, Pseudo-Voigt, and Pearson VII, and Asymmetric Pearson VII
- Peak-shape functions can be constrained in terms of intensity, peak position, FWHM, and mixing coefficient
- Automatically calculate Cu-Kalpha2 peaks when working with laboratory X-ray data
- Change any of the starting fit values and instantly view a sample plot of the fit, before conducting a fit
- Visualize results with a plot of the resulting peak fit and residual plot
- Parameters files are written to recreate fits and detail what fit parameters and profile shape functions were used
- Accepts the following file types: .xy, .xye, .xls, .xlsx, .fxye, .xrdml, .chi, .csv (Windows Only)
- Resulting coefficients values can be viewed with file number
- For multiple diffraction patterns, results from previous fit are subsequent starting parameters for next fit

The last items allows easy and quick fitting of multiple files. Typically, for example, sets measured with changing temperature when only diffraction parameters of the peaks are smoothly changing and then plot of the parameters vs. file number that can easily be changed to the temperature, for example.

Example of main fitting window is on Fig. 1

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L4

X-ray radiography and computed tomography on a small table-top diffractometer

RENTGENOVÁ RADIOGRAFIE A VÝPOČETNÍ TOMOGRAFIE NA MALÉM STOLNÍM DIFRAKTOMETRU

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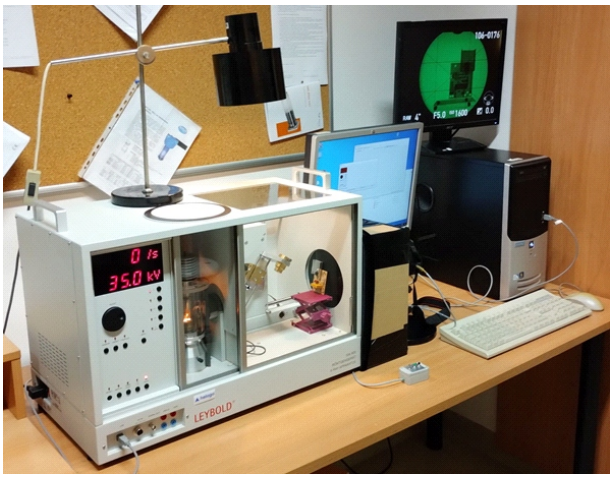
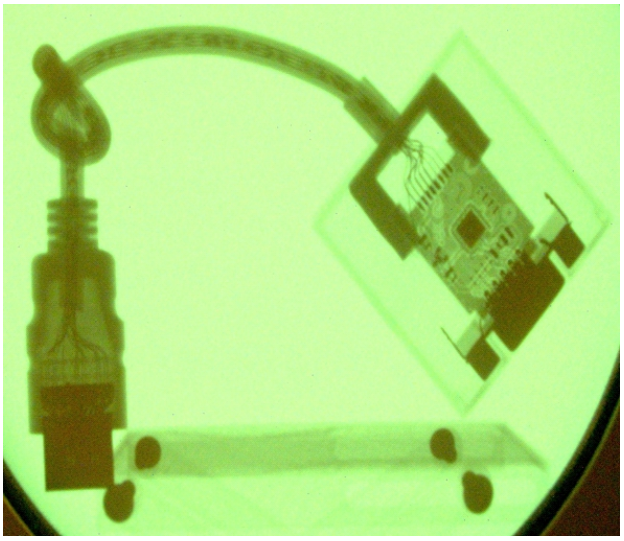
Rentgenová radiografie patří mezi nejstarší techniky pro zobrazování vnitřní struktury objektů neprůhledných ve viditelném světle. Zřejmě největší uplatnění metod rtg radiografie je v medicíně, kdy je možné pomocí rtg paprsků získávat obraz rozložení kostí a vnitřních orgánů v těle pacienta. Dále se v praxi tato metoda využívá při nedestruktivním zobrazování materiálů, součástek a dalších objektů, například ve strojírenství. Až do 80. let 20. století byly radiografické snímky výhradně zaznamenávány na fotografický film a teprve s příchodem moderní elektroniky nové digitální technologie vytlačují původní styl záznamu na filmy. Největší pokrok v zobrazovacích metodách pomocí rentgenového záření tkví v posledních letech zejména v pokročilých možnostech detekce rentgenových paprsků 2D plošnými detektory s přímou digitalizací do počítače. To vedlo k velkému rozvoji metod výpočetní tomografie (CT), kdy je ze série nasnímaných projekčních obrazů rekonstruováno rozložení absorbce v ozářeném objemu vzorku.

Zobrazovací rentgeny a tomografy jsou dnes dostupnou součástí lékařských zařízení, laboratoří či průmyslových center. Zařízení jsou obvykle velmi drahá, zobrazené výsledky jsou však precizní a dodávaný vizualizační software dokáže spoustu pokročilých možností ve 3D zobrazování.

Naším cílem mnoha posledních let je zpřístupnit studentům metody radiografie a CT s digitalizací obrazu při použití malého školního stolního difraktometru se vzduchem chlazenou rentgenkou, který je v současné době k dispozici od firem Phywe a Leybold. Finančně nákladnou částí u komerčních zařízení je 2D detektor, což jsme vyřešili několika podstatně levnějšími způsoby – jednak díky široce dostupným zubařským detektorům (dříve pamě•ové fólie s vyčítacím zařízením, nyní digitální detektory přímo připojitelné k počítači), či fotografováním radiogramu zobrazeném na scintilačním stínítku pomocí kvalitní digitální zrcadlovky, viz obr. 1. Profesionální rotační stolky, které dosahují vysoké stability nutné pro mikro-CT, lze pro nižší rozlišení nahradit rotačním stolkem vytištěným na 3D tiskárně a řízeným Arduinem. V našem příspěvku ukážeme některá konkrétní uspořádání a výsledky získané na některých zajímavých biologických vzorcích či elektronických součástkách, viz obr. 2.



Obrázek 1. Sestava pro radiografii či CT – rentgenový difraktometr Leybold s vytištěným stolkem pro vzorek a snímáním obrazu digitální zrcadlovkou Pentax.



Obrázek 2. Radiogram kabelu VGA-HDMI.