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L1

## REAL STRUCTURE AND TOTAL POWDER PATTERN FITTING. PROGRAM MSTRUCT

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### Real structure and classical XRD line profile analysis

The term “real structure” is often used but not clearly defined. We have discussed this in relation to a short course on *real structure of materials* included in *Struktura 2009* in Hluboká nad Vltavou [1]. In XRD, real structure is related mainly to lattice defects in atomistic scale, and in a larger scale to size, shape and distribution (possibly preferred orientation) of grains (or crystallites – coherently diffracting domains) and also their interactions (residual stress). The fields of texture analysis and residual stress analysis have been developed and for the X-ray diffraction they consist in measurement of integrated intensities of selected diffraction peaks  $hkl$  in dependence on the angle of the corresponding lattice plane with respect to the surface and analysis of peak positions in the same dependence, respectively. The analysis of lattice defects can be done for example by careful study of diffuse scattering which is usually possible only for single crystals or the so-called XRD line profile analysis. The latter procedure was also described briefly in [1].

XRD line profile analysis can be done directly on individual well-separated diffraction peaks by determination of some relevant parameters as for example FWHM (full-width-at-half-of-maximum), integral breadth, moments – mainly the second moment *variance* and *Fourier coefficients (FC)*. These parameters can be subsequently analyzed and some physical characteristics like crystallite size and microstrain are determined. However, in this procedure, for laboratory data  $K_2$  component must be separated either before the determination of parameters or after that which was done in the past. Then it must be considered that the measured profile is convolution of physical profile with the instrumental one containing the influence of geometry and optics of the instrument and broadening of spectral lines. Therefore, some deconvolution or correction must be performed, unless the difference between the instrumental and physical broadening is large like for example in really nanocrystalline materials (with the crystallites e.g. below 10 nm). Some of the methods were described for example by Klug and Alexander [2]. For approximative method using just line widths there are a few simple methods of correction of instrumental broadening. Famous Warren-Averbach (WA) [3] analysis consists of several steps. Typically, the FC of several diffraction profiles of

the standard sample are determined as coefficients corresponding to the instrumental profile, then the *FC* for diffraction peaks of several reflection orders of analyzed sample are calculated and for example the Stokes method [see 3] (with a benefit of not necessary  $K_2$  elimination) is applied and the finally obtained *FC* of the physical profile are analyzed by the WA method. This is a several-steps procedure with some critical points, mainly the deconvolution of noisy and finite profiles.

### Rietveld analysis

In practice, we must work quite often with heavily overlapped profiles, sometimes even for one phase. In this case, peaks are usually fitted with some suitable phenomenological peak-shape functions, mainly the Pearson VII, pseudo-Voigt or Voigt functions, describing quite well profiles of individual components. Then, basically, we could proceed as in the previous case. Of course, by such fitting, some profile features can be masked. Principle difference between the so-called size and strain broadening is its different behavior in reciprocal space, the former being constant and the latter proportional to the diffraction vector magnitude, respectively. Significant anisotropy ( $hkl$  dependence) can be caused by anisotropic crystallite shape for the former effect and for example dislocation type in the latter case, respectively.

In sixties, the Rietveld method appeared [e.g. 4] which later has become extremely popular. The idea of the method is to describe whole powder diffraction pattern with a suitable function containing everything relevant in some, if possible analytical, function with free parameters to be determined. Then, in principle, all required characteristics could be get in a few iterations. Of course, it is often not so simple. The first aim was to apply the analysis for structure refinement since the integrated intensities are primarily related to the structure factors, that means also atomic positions. Peak positions are related to the lattice parameters. Quite quickly the Rietveld method was also used for the phase analysis. However, since all relevant effects must be included in the procedure also parameters related to real structure were considered, usually in some more or less phenomenological way. They described texture, size and strain line broadening in some cases also residual stress and nowadays they are including also anisotropic effects. Probably, the most popular classical



Rietveld type programs are **FULLPROF** by Juan Rodriguez-Carvajal [5] and **GSAS** by Bob von Dreele [6]. There are also others (see [7, not updated] for available Rietveld software) like **BGMN** [8] by Joerg Bergmann, **BRASS** [9] and, of course, there is also powder pattern fitting in famous **Jana2006** [10]. There are also commercial Rietveld or multiple purpose programs like TOPAS (Bruker), High-Score (Panalytical) and others.

Most of these programs use the so-called Cagliotti polynomial

$$FWHM(rad)^2 = U \tan^2 \theta + V \tan \theta + W \quad (1)$$

for the description of angle-dependence of instrumental XRD line broadening. In case, the corresponding profile function used is the pseudo-Voigt (weighted sum of Gauss and Cauchy functions), we can introduce also angle dependence of Cauchy-Gauss mixing parameter and possibly asymmetry  $A$  as follows

$$\eta = \eta_0 + \eta_1 2\theta \quad (rad),$$

$$A = A_0 + A_1 / \sin(2\theta) + A_2 / \sin^2(2\theta) \quad (2)$$

The parameters  $U$ ,  $V$ ,  $W$ ,  $\eta_0$ ,  $\eta_1$ ,  $A_0$ ,  $A_1$ , and  $A_2$  are determined by the fitting of standard diffraction pattern measured on the same instrumental arrangement as the one used for the measurement of the investigated samples. These relations are often extended and used also for the analysis of the physical broadening, in last versions of the above programs in very flexible and more general way.

It seems that the most comprehensive description of instrumental effects it is the so-called fundamental parameters approach consisting in calculation of all instrumental and spectral components. This was introduced mainly by R.W. Cheary and it is used in TOPAS and also in Jana now.

The use of the Voigt or more pseudo-Voigt functions is preferred now to the Pearson VII. The Cauchy (Lorentz) and Gauss functions can be expressed as follows

$$G(x) = \frac{1}{\sqrt{2\pi} \sigma} \exp\left(-\frac{x^2}{2\sigma^2}\right), \quad H_G = \sqrt{8 \ln 2} \sigma$$

$$C(x) = \frac{2}{\pi H_C} \frac{1}{1 + \frac{4}{H_C^2} x^2} \quad (3)$$

where  $H_C$  and  $H_G$  are FWHMs of the Cauchy and Gauss components, respectively.

Extension of polynomial (1) is made slightly differently in FULLPROF, GSAS and Jana. In Jana, similarly to GSAS the Gauss FWHM is written as [11]

$$H_G^2 = U \tan^2 \theta + V \tan \theta + W + \frac{P}{\cos^2 \theta} + (1 - \zeta)^2 \Gamma_A^2 \quad (4)$$

where the fourth term is the Scherrer coefficient for Gauss broadening.

The Cauchy FWM is composed of five terms

$$H_c = \frac{X + X_e \cos \varphi}{\cos \theta} + (Y + Y_e \cos \varphi) \tan \theta + \zeta \Gamma_A \quad (5)$$

The  $X$  terms accounts for Lorentzian Scherrer particle broadening and stands for isotropic and anisotropic part, respectively.  $\varphi$  is the angle between the diffraction vector and the broadening direction. The  $Y$  terms describe strain broadening. The last term stands for the Stephens's strain anisotropy, where the anisotropic strain is described by a symmetrical 4th order tensor [12] and this contribution to FWHM is:

$$\Gamma_A = \sigma(hkl) d^2 \tan \theta, \quad \sigma^2(hkl) = D^{ijmn} h_i h_j h_m h_n \quad (6)$$

GSAS [13, more recent 14] offers several functions for time-of-flight and for XRD and constant wavelength neutron diffraction and XRD. Basically, some of them are similar as the above functions used in Jana. They can include possible asymmetry, anisotropy and one of them also effect of macroscopic strain.

FULLPROF uses equations quite similar as (4-5).

$$H_G^2 = (U + (1 - \xi)^2 D_{ST}^2(\alpha_D)) \tan^2 \theta + V \tan \theta + W + \frac{P}{\cos^2 \theta} \quad (7)$$

$$H_c = \frac{X + F(\alpha_z)}{\cos \theta} + (Y + \xi D(\alpha_{ST})) \tan \theta \quad (8)$$

where  $D$  and  $F$  functions have different expressions depending on the particular model of size and strain broadening. The parameter  $\xi$  is mixing coefficient to mimic Cauchy contribution to strains. The metric parameters  $a_i$  are considered as stochastic variables with Gaussian distribution characterized by the mean value and the variance-covariance matrix [15]. The anisotropic strain broadening is modelled using a quartic form in reciprocal space. The Stephens approach can be used as well. FULLPROF offers different models for size (e.g. needle-like domains) and strain (with different symmetries of strain and lattice), and also possibility to define some reflection families (for specific  $hkl$  broadened or unbroadened) which can simulate the effect of stacking faults. The same is possible to introduce in GSAS. The anisotropic crystallite shape is modelled with a linear combination of spherical harmonic functions  $y_{lmp}$  normalized according to M. Järvinen [16]. The size contribution to integral breadth is

$$\beta_h = \frac{\lambda}{D_h \cos \theta} = \frac{\lambda}{\cos \theta} \sum_{lmp} a_{lmp} y_{lmp}(\theta_h, \phi_h) \quad (9)$$

The arguments are the polar angles of the vector  $\mathbf{h}$  with respect to the Cartesian crystallographic frame,  $D_h$  is the crystallite size.

### Total powder diffraction pattern modelling and fitting

Another way came from the groups primarily dealing with the *real structure*. The first one was Charles Houska [17, 18]. As he realized the mentioned above problems of sev-

eral-steps WA analysis, he tried to describe the whole individual profile by physical function. The profile function  $P(s = 2 \sin \quad)$  was expressed in terms of the Fourier coefficients of individual components including instrumental ones (replacing in such a way deconvolution with convolution, the way dominating nowadays). The physical FC included two parameters related to the crystallite size effect and two more or less phenomenological microstrain parameters as follows

$$\frac{I(s)}{2\langle L \rangle I_0} = \int_0^{S_c} A_L^{lc} A_L^{lg} A_L^S A_L^{dc} A_L^{dg} \cos(2\pi u_L s) du_L \quad (10)$$

where  $A^{lc}$  and  $A^{lg}$  correspond to the Cauchy and Gauss component of the Voigt function used for approximation of the instrumental profile,  $\langle L \rangle$  is mean crystallite size in the measured direction  $u_L = L/\langle L \rangle$ . Integration limit  $S_c$  is dependent on the variation coefficient of crystallite size distribution  $V_c$ ,  $S_c = 1 + 3V_c$ . The size coefficients  $A^S$  can be expressed as the third-order polynomial of  $u$ , and there are two types of strain coefficients

$$\begin{aligned} A_L^{dg} &= \exp(-2\pi^2 L^2 \langle \varepsilon_U^2 \rangle / d^2) \\ A_L^{dc} &= \exp(-2\pi^2 L \langle \varepsilon_D^2 \rangle / d^2) \end{aligned} \quad (11)$$

with the so-called uniform ( $\varepsilon_U$ ) and nonuniform strain ( $\varepsilon_D$ ) related to the mean-square strain as

$$\langle \varepsilon_L^2 \rangle = \frac{\langle \varepsilon_L^2 \rangle}{L} + \langle \varepsilon_U^2 \rangle \quad (12)$$

The relation is empiric based on many observed cases. The functions were simultaneously fitted to several reflection orders or neglecting anisotropy just to a few diffraction profiles with different  $hkl$ . The method was later extended with stacking faults. Examples are also shown in [19]. There is no software currently available for the method.

Later, Rietveld-type programs focused on real structure have been developed by Matteo Leoni and Paolo Scardi in Trento, **Pm2k** [20-23] and Gábor Ribárik in Budapest, **CMWPFIT** [24-25]. Separately, also quite well-known system **MAUD** was developed by Luca Lutterotti [26-28]. Each of the programs has some features which are common and also some which are unique. Since we have not been fully satisfied with any of these, we have been developing our own system **MSTRUCT** [29-32] written by Zdeněk Matěj as extended FOX system [33] based on Crystal Objects library. All the above programs are freely available, some of them require registration.

CMWPFIT, Pm2k and MSTRUCT are basically working with similar algorithms for the description of size and dislocation broadening

Total formula for peak profile is like this, similar as description by Houska (9)

$$\begin{aligned} I_{hkl}(\Delta s) &= \int_{-\infty}^{\infty} T_{pV}^{IP} A_{hkl}^S A_{hkl}^D [A_{hkl}^F \cos(2\pi L \Delta s) - \\ &\quad - B_{hkl}^F \sin(2\pi \Delta L)] dL \end{aligned} \quad (13)$$

with instrumental Fourier coefficients  $T$ , size, strain and stacking fault  $FT$ s  $A^S$ ,  $A^D$  and  $A^F$ , respectively.

Physical effects can be conveniently modelled in real space (Fourier coefficients). The size broadening effect is described by the model function for *log-normally distributed spherical crystallites* with two parameters to be refined—*median of crystallite size* and *variance of the distribution* or alternatively by the *distribution histogram*.

The expression for the size distribution can look as follows [e.g. 24]

$$\begin{aligned} A_L^{sph} &= \frac{m^3 \exp[(9/2)\sigma^2]}{3} \operatorname{erfc} \left[ \frac{\ln(|L|/m)}{\sqrt{2}\sigma} - \frac{3}{2}\sqrt{2}\sigma \right] - \\ &\quad - \frac{m^2 \exp[2\sigma^2]}{2} |L| \operatorname{erfc} \left[ \frac{\ln(|L|/m)}{\sqrt{2}\sigma} - \sqrt{2}\sigma \right] + \\ &\quad + \frac{|L|^3}{6} \operatorname{erfc} \left[ \frac{\ln(|L|/m)}{\sqrt{2}\sigma} \right] \end{aligned} \quad (14)$$

Very popular and often also realistic is log-normal size (D) distribution with two parameters and

$$g_L(D|\mu, \sigma) = \frac{1}{D \sigma \sqrt{2\pi}} \exp \left[ -\frac{(\ln D - \mu)^2}{2\sigma^2} \right] \quad (15)$$

The strain broadening can be described by the dislocation model including three parameters—*dislocation density*, *dislocation-correlation parameter*, cut-off radius, and dislocation types - *fraction of edge dislocations*. Assuming probable dislocation types the *contrast factors* can be calculated in specific cases. The strain Fourier coefficients can be written as

$$A_{hkl}^D(L) = \exp \left[ -\frac{1}{2} \pi b^2 \langle \chi_{hkl} \rangle \rho L^2 d_{hkl}^2 f^*(L/R_e) \right] \quad (16)$$

where  $b$  is the Burgers vector magnitude,  $\rho$  is the dislocation density,  $d^*$  the interplanar spacing of the first order reflection,  $R_e$  cut-off radius (dislocation-correlation parameter) and  $f^*$  complicated but known van Berkum or Wilkens function. For cubic materials, the orientation factor can be written as follows

$$\langle \chi_{hkl} \rangle = A + BH^2, \quad H^2 = \frac{h^2 k^2 + h^2 l^2 + l^2 k^2}{(h^2 + k^2 + l^2)} \quad (17)$$

with two parameters  $A$ ,  $B$  to be fitted or calculated.

CMWPFIT is focused on the analysis of some microstructural parameters for cubic or hexagonal materials. The whole measured powder diffraction pattern is fitted by the sum of a background function and ab-initio theoretical functions for size and strain broadening. In the calculation of the theoretical functions it is assumed that the crystallites have lognormal size distribution and the strain is caused by dislocations. Strain and size anisotropies are taken into account by the dislocation contrast factors and the ellipticity of crystallites. The fitting procedure provides the median and the variance of the size distribution



and the ellipticity of crystallites, and the density and arrangement of dislocations. Instrumental correction is convoluted. There are no other effects included. The program is working on-line.

*Pm2k* [23] has been designed with modularity and expansibility in mind. Three main entities can be identified in the program: kernel, plug-ins and user interface. The kernel is performing nonlinear least squares minimisation. Plug-ins are compiled independently as dynamic loading libraries and linked to the kernel at runtime. Users can easily implement their own models into the kernel. There are quite a lot of interesting features included (implemented as plug-ins)

- Instrumental broadening: Rietveld-Caglioti formula.
- Size broadening: histogram model for size distribution (sphere, cube, tetrahedron, octahedron, ellipsoid, hexagonal prism, cylinder, harmonics), analytical model for size distribution (delta, lognormal, gamma, generalised gamma, York distributions of sphere, cube, tetrahedron, octahedron, ellipsoid, hexagonal prism, cylinder, harmonics).
- Strain broadening: dislocations (fcc,bcc,hcp) using the simplified and full Wilkens models of dislocations (all symmetries) using harmonics invariant or Green function. Houska-like models (Houska, Adler-Houska, modified Houska)
- Stacking faults for fcc, bcc and hcp of correlation probability, antiphase boundaries. Grain surface relaxation effect
- Additional broadening models: grain-dependent lattice parameter variation, broadening due to stoichiometry fluctuations.

The program runs via interface but basically runs on the base of input and output file.

*MAUD* is probably the most complex program available for the analysis of real structure but it does not include dislocation models. Regular schools on the software are organized in France. There is no manual but several tutorials available. The program is written in Java and controlled by a GUI with many optimization algorithms available and can work with X-ray, synchrotron, neutron, TOF and electron diffraction data. It can simultaneously fit several different spectra, work with the data from 2D detectors, with fluorescence data. It can fit reflectivity curves and it can also make complete texture and residual stress analysis using part or full spectra. The program is well-adopted for the analysis of thin film and multilayers and of course microstructure analysis (size-strain, anisotropy, planar defects, turbostratic disorder and distributions) is included.

**MSTRUCT** program is a subject of the course at this meeting and during last years different features have been included affecting different XRD line profile parameters as described for example in [30].

**Peak positions** are determined by variable *unit-cell parameters* and *zero-shift error*. *Specimen displacement* error is not considered for the parallel-beam geometry but included for symmetrical  $-2\theta$  scans. For low angles of incidence close to the angle of total reflection, which are required for very thin films, mainly below  $1^\circ$ , *refraction correction* must be included. *Residual stress* can influence the peak positions. Peak shifts then can also be anisotropic. The effect of residual stress in the current version of

**MSTRUCT** is included for simple symmetrical biaxial stress in the plane of a sample surface and can be *hkl* dependent. X-ray elastic constants  $s_1(hkl)$ ,  $s_2(hkl)$  are calculated in two extreme models of grain interactions—Reuss and Voigt. In the case of lower symmetry, they can be conveniently calculated according to [33-35], and then two refinable parameters i.e., *residual stress* and fraction of the *Voigt-Reuss* models appear.

**Peak intensities** are calculated by the ObjCryst library from a known crystal structure. The *structural parameters* can be varied when necessary. However, they are used as constraints for the peak positions and intensities. The effects of *absorption* and *texture correction* in a thin film can be included. In general, the texture correction can be obtained from a known model of the ODF after appropriate integration over all crystallites with diffracting (hkl) planes perpendicular to the direction of the measured diffraction vectors both for asymmetric and symmetric scans. In principle any type of the ODF function can be supplied to the algorithm and used for texture correction, but only a simple model using the Gaussian distribution of crystallites and possible inclinations of texture with respect to the sample normal is included.

**Peak profiles** are given by numerical convolution of a known instrumental function and physical profiles including several refinable parameters. Size and dislocation-induced strain broadening are described above. For some cases, phenomenological microstrain broadening can be useful. For this case, the peak broadening is modeled by the pV function and its FWHM angular dependence is given by the Cagliotti polynomial containing only the quadratic term  $U$ . This means that the FWHM in reciprocal space units is linearly increasing with the diffraction vector magnitude. The shape factor of the pV function common for all *hkl* diffraction peaks can also be refined. Then relations for microstrain  $e$  can be used.

$$\beta(2\theta) = 4e \tan \theta, \quad 4e = \left( \frac{1-\eta}{\Phi_G} + \frac{\eta}{\Phi_C} \right) \sqrt{U} \quad (18)$$

where  $\Phi_G = 2(\ln(2)/\pi)^{1/2}$  and  $\Phi_C = 2/\pi$  are the Gauss and Cauchy shape parameters, respectively.

Anisotropic size broadening model was introduced in **MSTRUCT**. A model of rods and platelets like crystallites were also complemented with quite common model of ellipsoidal shape.

If appropriate specific model is unknown a possibility of arbitrary *hkl* dependent multiplication factors for peak intensities and also peak shifts can be introduced.

New non-standard models in **MSTRUCT** were described in a lecture at Struktura 2017. These are for example: stacking faults on prismatic planes in WC, Warren-Bodenstein model for turbostratic nanoparticles, configuration model for description of bimodal microstructure, unconventional analysis of nanocrystalline and amorphous like materials [36].

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L2

### FitExc - program for fitting of diffraction lines in MS Excel

## FitExc - PROGRAM PRO FITOVÁNÍ DIFRAKČNÍCH LINIÍ V MS EXCEL

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Základním krokem při studiu materiálů metodami rentgenové, neutronové či elektronové difrakce je pečlivá a korektní analýza jednotlivých naměřených difrakčních maxim, získaných často ve formě jednodimenzionálních závislostí  $I(2\theta)$ . Pro mnohé aplikace, jako je například přesné určení mřížkových parametrů, stanovení koeficientů teplotní roztažnosti či měření zbytkových napětí, je pak analýza několika málo reflexí naprosto dostačující. V moderních komplexních programech je však tato snadná úloha pro nepřívětivost a přehnanou robustnost uživatelsky často v krátkém čase a při větším množství dat obtížně proveditelná. Nemalou roli rovněž mnohdy hraje nezanedbatelná cena licencí specializovaných programů.

Z těchto důvodů jsme vyvinuli vlastní vyhodnocovací program umožňující přesnou analýzu jednotlivých difrakčních profilů. Tento je vytvořen v prostředí MS Excel za užití maker v jazyce VBA. Je tedy spustitelný prakticky na jakémkoliv počítači vybaveném standardním balíčkem MS Office a díky svému uživatelsky přívětivému rozhraní je ihned připravený k analýze difrakčních dat.

V současné době umožňuje program načtení několika nejčastěji užívaných typů souborů s naměřenými difrakčními  $I(2\theta)$  záznamy (.xrdml, .xy, .xye) a jejich rychlé fitování běžně užívanými analytickými funkcemi (Cauchy, Gauss, Pearson VII, pseudo-Voigt) na základě přednastavených či uživatelsky definovaných charakteristických spekter užitého záření. Samozřejmostí pak je přehledné grafické znázornění naměřených dat i fitu, fitování pozadí, fixování libovolných parametrů, vykreslení rozdílové křivky či výpočet krystalografických faktorů shody. Program umožňuje fitování až tří profilů najednou, tudíž je možné jej s výhodou použít k rozlišení překrývajících se reflexí a stanovení poměru jejich intenzit.

V případě zájmu o kopii programu k využití pro svůj výzkum může čtenář získat další informace na <http://people.fjfi.cvut.cz/vertapet/> či kontaktovat autora.

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L3

### Universal system for administration of samples: Development of extended web application from the developer's point of view

## UNIVERSÁLNÍ SYSTÉM PRO SPRÁVU VZORKŮ: VÝVOJ ROZSÁHLÉ WEBOVÉ APLIKACE Z HLEDISKA VÝVOJÁŘE

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Tato přednáška bude především o systému pro správu vzorků, který je využíván Fyzikálním ústavem Akademie věd ČR. A to vše očima vývojáře, studenta VUT, kluka z Valašska. Začátek tohoto systému je datován někde v září roku 2014, kdy jsem ještě jako středoškolský kluk seděl v lavicích a sotva jsem začínal s tvorbou webů. Někdy v létě 2014 jsem na na dnes již upadajícím fóru JakPsatWeb.cz dával inzerát, ve kterém bylo, že jako student nabízím tvorbu webových stránek a jednodušších webových systémů. Několik měsíců na inzerát moc lidí nereagovalo, až v září se ozval pan Michal Dušek s otázkou, zda-li ještě stále nabízím tvorbu webových stránek. Hned na první pohled mě hodně udivilo, že na takový inzerát úplně

neprověřeného kluka zareguje tak kompetentní osoba ve svém oboru s prosbou o vytvoření komplexního webového systému, který dnes celému oddělení FZU ušetří mnoho práce.

“Dobrý den, pořád ještě nabízíte tvorbu webu? Mám takový poněkud speciální požadavek týkající se provozu laboratoře.“

Přesně touhle větou vývoj začal. Během následujících týdnů jsme formovali myšlenku celého systému, jak jej udělat, co bude umět a hlavně, jak to celé zrealizovat. Jelikož jsem jednoduché weby s lehkou administrací již předtím dělal, utvrzovalo mě to v tom, že tento job není až zas tak z mého pohledu šílená věc, jak se na první pohled

zdálo. Z předchozích zkušeností jsem docela dobře uměl jazyk PHP. Bylo tedy jasné, na čem začnu stavět. Jenže jazyk jsem ovládal na potřeby přihlášení, páru URL adres a nějaká ta jednoduchá správa zpráv a uživatelů. Ovšem pro první požadavky ze strany pana Duška to stačilo, takže jsme se pustili do práce.

Po několika měsících jsme měli první verzi, kterou jsem psal na vlastním nabastleném kódu bez použití jakéhokoliv frameworku, které běží na PHP, což byla asi největší chyba a stálo mě to ve výsledku hodně práce. Kdybych to měl přiblížit, jak velký omyl to byl, tak bych to přirovnal asi k motoru dvoutaktní pŕlkubíkové motorky. Pokud bych si chtěl takový motor vyrobit, trvalo by to zcela jistě hodně týdnů. Po těch týdnech usilovné práce bych si řekl - "Ano, povedlo se mi to, ale tady to má mouchy, tady vlastně taky a nakonec to přece jen není tak dobré, jak jsem čekal". A potom by přišel kamarád s tím, že si podobný motor lepší funkčností sehnal za pár kaček u Číňana za rohem v sousední vesnici.

Systém jsme tedy měli, základní funkčnost byla a vše odpovídalo zadání. Jako u všech systémů se ale hlavní nedostatky projeví až po praktickém použití. Něco bylo špatně navrženo, něco mělo být zase jinak, něco naopak vůbec nemělo být. V tu chvíli se kód začínal šmodrchat jak Boloňské špagety při pokusu o namotání na přístroj. Ještě nějakou dobu to takhle pokračovalo, až jsme se dopracovali ke stavu, kdy jsem usoudil, že to tak dál nelze. Bylo přede mnou těžké rozhodnutí - zkusit celý kód refaktorovat

a nebo ho napsat úplně jinak. Těžká rozhodnutí bývají mnohdy na delší časový úsek, ale v mém případě to bylo po pomýšlení, jak jsem některé části "velice úhledně a čistě" napsal, zcela jasné.

Do hry s tedy dostal další zcela nečekaný faktor - framework. Což je laicky řešeno taková souprava komponent, které se nemusí vymýšlet od začátku, ale již jsou naprogramované a hodně sofistikovaným způsobem se skládají do sebe a tím vytvářejí nějakou logickou část. Samozřejmě to zní jednoduše, bohužel tomu tak zcela není. Astra v tu chvíli byla už poměrně rozsáhlý systém, který zahrnoval mnoho funkcionalit a nabalování dalších už ho potápělo jak ve stránce výkonu, tak i přehlednosti a chybovosti.

Nastala tedy asi nejdůležitější fáze - přepis na nový framework Laravel. S výběrem jsem dlouho neváhal, tento framework nabízel veškeré funkcionality, co byly třeba. Naprosto každá věc byla nově většinou i koncepčně zcela jinak, než původně. Asi nejvíce to pomohlo šablonovacímu systému a systému přiřazování URL adres. Díky tomu jsme mohli vypisovat složitější tabulky, dělat složitější propočty a mnoho výkonu jsme přenesli na stranu klienta, což systému v mnohém pomohlo. Výborná věc byl taky způsob emailingu a automatických vychytávek, jako je třeba automatická kontrola vzorků, půlnoční emaily a jiné.

O postupu a programování systému se mnohdy špatně píše, tento případ bude ukázkový. Věřím, že v živém přednesu to dokážu i se špetkou humoru shrnout ještě lépe.

L4

## SUBSTITUTION LIMITS IN NEW MINERAL STAROČESKÉITE



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A new mineral, staročeskéite, a sulfide of Ag, Pb, Bi and Sb, was found in Kutná Hora ore district, Czech Republic, chemical composition established, structure solved, proposal for a new mineral submitted to the Commission for new Mineral of the International Mineralogical Association and mineral approved. The simplified empirical formula based on electron probe microanalysis is  $\text{Ag}_{0.70}\text{Pb}_{1.60}(\text{Bi}_{1.35}\text{Sb}_{1.35})_{2.70}\text{S}_6$ . The mineral belongs to the family of lillianite homologous series with  $N = 4$ , with a general formula  $\text{Ag}^+_X\text{Pb}^{2+}_{3-2X}\text{Bi}^{3+}_Y\text{S}_6$ . The  $N$  value represents a number of octahedra in two neighbouring blocks in the structure (sites  $M1$  and  $M2$ , Fig 1), where two main substitutions take place: 1.  $\text{Ag}^+ + \text{Bi}^{3+}, \text{Sb}^{3+} \rightarrow 2\text{Pb}^{2+}$  and 2.  $\text{Bi}^{3+} \rightarrow \text{Sb}^{3+}$ .

Staročeskéite is orthorhombic, space group  $Cmcm$ , with  $a = 4.2539(8)$ ,  $b = 13.3094(8)$ ,  $c = 19.625(1)$  Å,  $V = 1111.1(2)$  Å<sup>3</sup>,  $Z = 4$ . The structure of staročeskéite contains four sulfur sites and three metal sites: one pure Pb site  $M3$  in trigonal prismatic coordination and two mixed octahedral sites - each with three atom species:  $M1$  ( $0.52\text{Bi} + 0.356\text{Ag} + 0.124\text{Sb}$ ) and  $M2$  ( $0.601\text{Sb} + 0.259\text{Pb} + 0.14\text{Bi}$ ). The found mineral is characterized by Bi:Sb ratio 1:1

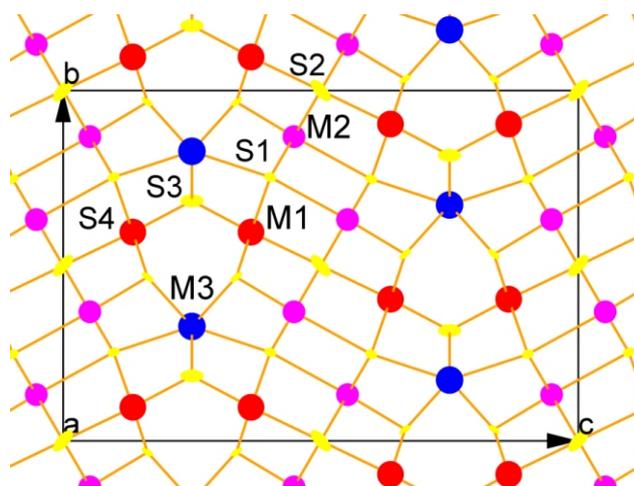
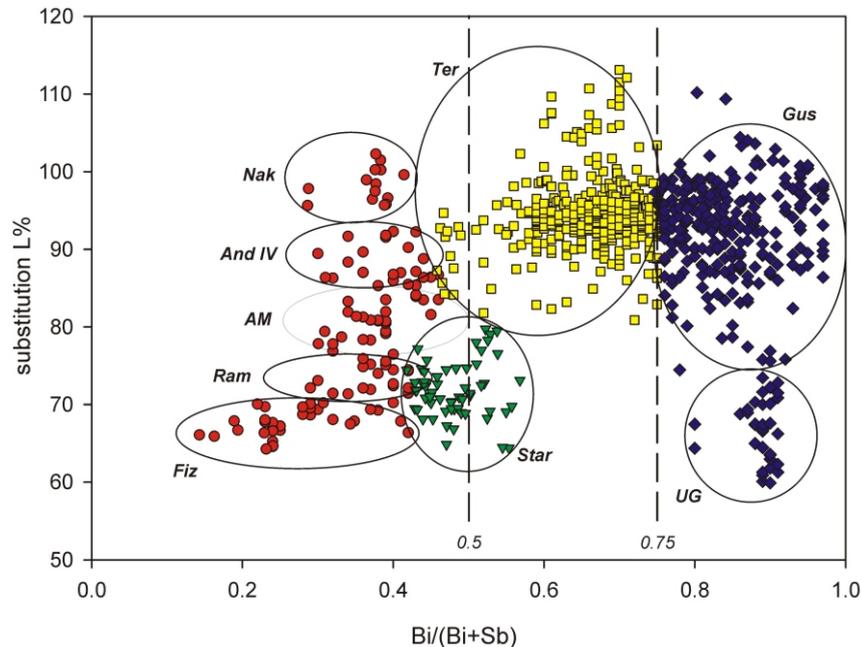


Figure 1. Crystal structure of staročeskéite

( $\text{Bi}/(\text{Bi} + \text{Sb}) = 0.50$ ) and the  $\text{Ag}^+ + \text{Bi}^{3+}, \text{Sb}^{3+} \rightarrow 2\text{Pb}^{2+}$  substitution ( $L\%$ ) equal to 70 %.

Because there are several minerals of a similar and very close composition in the lillianite series of sulfosalts (Fig



**Figure 2.** Diversity of mineral species from the series of lillianite homologues with  $N = 4$ : Star - staročeskéite, Gus - gustavite, UN - undersubstituted gustavite, Ter - terrywallaceite, Fiz – fizelyite, Ram – ramdohrite, And IV – andorite IV, Nak – nakaseite (Cu-rich andorite VI).

2), it is necessary to determine the ranges of substitution (substitution limits) within which the mineral is defined. Empirically it was determined that the name staročeskéite would be valid for a lillianite structure with composition  $\text{Ag}_x\text{Pb}_{3-2x}\text{Bi}_y\text{Sb}_{2+x-y}\text{S}_6$  with the boundaries  $\frac{1}{2}x \leq 0.8$ , and  $1 - \frac{1}{2}x \leq y \leq 2$ , where the parameter  $x = \text{Ag content} = L\%$  and  $y = \text{total Bi content}$ . Thus we concluded that for staročeskéite to exist, there must be between 20 to 50 % occupation of  $M2$  site by Pb, apart from fully occupied  $M3$  site.

Other Pb concentrations in  $M2$  site lead to different minerals.

1. R. Pažout, M. Dušek (2010) Crystal structure of natural orthorhombic  $\text{Ag}_{0.71}\text{Pb}_{1.52}\text{Bi}_{1.32}\text{Sb}_{1.45}\text{S}_6$ , a lillianite homologue with  $N = 4$ ; comparison with gustavite. *European Journal of Mineralogy*, 22,741-750.
2. R. Pažout, J. Sejkora J (2018) Staročeskéite,  $\text{Ag}_{0.70}\text{Pb}_{1.60}(\text{Bi}_{1.35}\text{Sb}_{1.35})_{2.70}\text{S}_6$ , from Kutná Hora, Czech Republic, a new member of lillianite homologous series. *Mineralogical Magazine*, 1-26. doi:10.1180/minmag.2017.

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L5

### COMPARISON OF RESIDUAL STRESSES DETERMINED USING DIFFERENT METHODS

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The majority of hitherto practically used diffraction measurements methods and algorithms for residual stresses calculation assume case of isotropic (non-textured) polycrystalline material. Due to the comparatively frequent existence of preferred orientation (texture), not only in metals, it is more than desirable to have at disposal a method, procedure and even a computation algorithm for proper and correct residual stresses determination. For this purpose, a new method was used for determination of residual stresses without neglecting the texture.

For determination of residual stresses, three methods were used: standard  $\sin^2$  method, method of harmonic function [1] and new method based on a model by Dölle [2, 3]. Contrary to Dölle method, the new method determines anisotropic elastic constants as a weighted average between single-crystal and X-ray elastic constants with weighting being done according to the relative intensities in the measured directions.

The tested samples of plate shape were made of AISI 420 (ferritic), AISI 304 (austenitic) and AISI 316LN (du-