

Session V, Thursday, September 12

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**Use of Computational Methods for Study of Structure
VYUŽITÍ VÝPOČETNÍCH METOD PŘI STUDIU STRUKTURY****J. Drahoukoupil***Institute of Physics AS CR, Na Slovance 2, Prague 8, 182 21, Czech Republic
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Počítačové simulace v pevných látkách dosahují v posledních letech velký rozmach. Jejich aplikace umožňuje dobrou pomoc při řešení struktury pevných látek v případech, kdy nejsou k dispozici dostatečně dobrá difrakční data. Podíváme se na dva přístupy: i) časově náročnější výpočty s využitím ab-initio DFT (Density Function Theory), ii) rychlejší výpočty s využitím molekulové mechaniky.

DFT

Základním kamenem pro teorii DFT je teorém Hohenbergera a Kohna [1], později zobecněný Levym [2], který tvrdí, že všechny vlastnosti v základním stavu jsou funkcí nábojové hustoty. Konkrétně energie může být napsána jako:

$$E[\rho] = T[\rho] + U[\rho] + E_{xc}[\rho] \quad (1)$$

kde $T[\rho]$ je kinetická energie systému neinteragujících částic s hustotou ρ , $U[\rho]$ je klasická elektrostatická energie Coulombových interakcí a $E_{xc}[\rho]$ zahrnuje všechny mnohočásticové příspěvky k totální energii (výměnou a korelační energii). Pro vyjádření posledního členu, použijeme tzv. Local Density Aproximacion (LDA), která je založena na známé E_{xc} pro jednoelektronový plyn [3]. LDA předpokládá, že nábojová hustota se na atomové úrovni jen pozvolna mění.

Pomocí DFT lze vypočítat řadu vlastností pevných látek, pro nás nejzajímavější jsou parametry základní buňky a souřadnice atomů. Na rozdíl od difrakce není možné uvažovat částečné zastoupení dané pozice atomem. Atom buď na dané pozici je nebo není. Pro popsání substitučních pozic či vakancí je nutné příslušně zvětšit základní buňku. Další nevýhodou je že se počítá tzv. základní stav tedy pozice a mřížka odpovídající 0° K. Přes tyto nevýhody dosahuje přesnost výpočtů v porovnání s experimentálními hodnotami shody několika málo procent.

Molekulová dynamika

Na rozdíl od DFT, která vychází z kvantové teorie, vycházejí modely molekulové mechaniky z klasické fyziky. Vzájemné působení atomů je popsáno pomocí silových konstant. Celková potenciální energie systému je vyjádřena jako součet vazebných a nevazebných interakcí, jejich funkce a parametry jsou shrnuty v takzvaném silovém poli (forcefield). Parametry silových polí lze získat buď výpočtem pomocí kvantové mechaniky či

porovnáním výsledků z experimentálních hodnot (difrakce, NMR, rotační a vibrační spektroskopie, elastické konstanty,...). Tento jednodušší formalismus umožňuje řešit podstatně větší problémy, už se nemusíme omezovat na jednotky či desítky atomů, ale jdou řešit problematiky obsahující stovky či tisíce atomů. Vhodný náhled do dané problematiky lze nalézt zde [4].

Unikátní spojení molekulové mechaniky a difrakce je zavedení faktoru shody R_{comb} kombinující difrakční (např. R_{wp}) a energetický faktor R_E .

$$R_{comb} = (1 - w)R_{wp} + wR_E \quad (2)$$

Optimální hodnotu váhového faktoru w je pak možné volit na základě tzv. Pareto optimalizace, kde se napočtou a porovnají hodnoty parametrů shody. Na osu x se obvykle vynáší R_{wp} faktor, který ukazuje shodu s difrakčními daty a na osu y hodnota $E - E_{min}$, viz obr. 1.

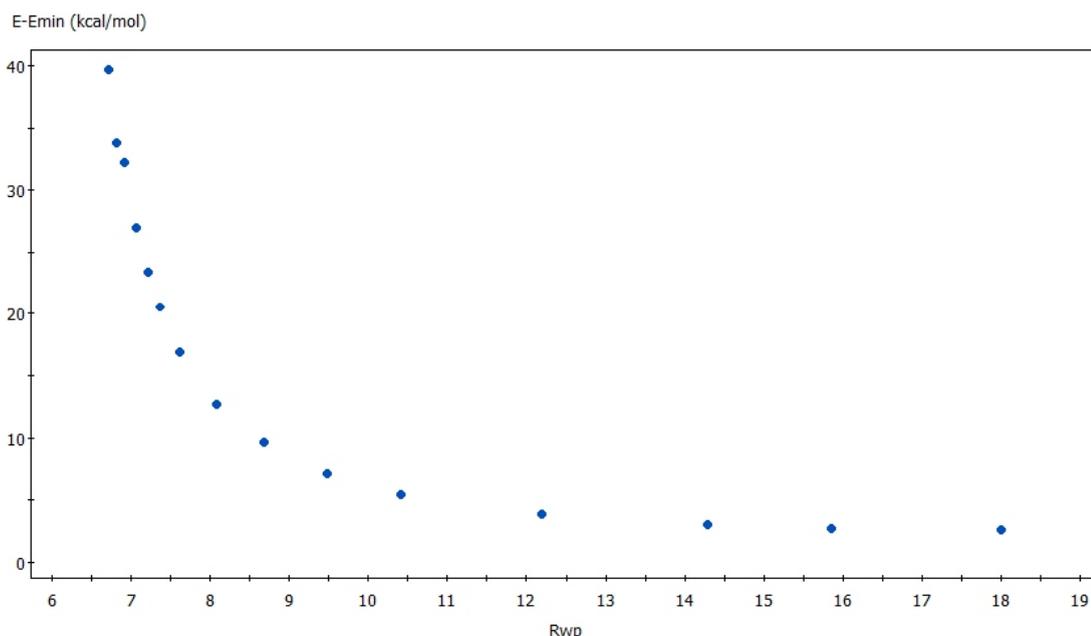
V přednášce budou předvedeny konkrétní výpočty v programovém balíku Material Studio [5] s využitím modulů Castep (DFT), Forcite (molekulová mechanika) a Reflex (prášková difrakce). Poslední zde uvedený modul umožňuje navíc kombinovat právě prášková rentgenová difrakční data spolu s výpočty pomocí molekulové mechaniky.

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Obrázek 1. Pareto optimalizace umožňuje vybrat optimální váhový faktor mezi energetickým a difrakčním příspěvkem do společného faktoru shody R_{comb} . Jednotlivé body v tomto konkrétním grafu odpovídají zleva doprava postupnému nárůstu váhového faktoru w .

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STRUCTURE REFINEMENT BY TOTAL ENERGY MINIMIZATION

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A restricted amount of structural information extractable from X-ray or CW neutron powder diffraction patterns seriously limits the accuracy of the structural data resulting from Rietveld refinement, which, as a rule, follows a structure solution step. If the information content of a powder pattern is insufficient and we are, in spite of this fact still interested in accurate structure, it is time to turn our attention to other methods of refinement. Basically, there are two possible routes. The first one in fact just modifies standard Rietveld method by introducing various improvements (and also “improvements”), which in many cases just mercifully mask the main drawback of the method, a low number of accurate structure factors confronted to a large number of refined atomic parameters.

Rietveld refinement relies on the idea that the parameters of a (probability) function approximating diffraction profiles can be refined by a non-linear weighted least-squares procedure simultaneously with the atomic parameters. Due to the surviving and perhaps unsolvable problems with accurate description of powder diffraction profiles and in particular with a small number of structure factors compared to the number of refined atomic parameters, the accuracy of the resulting structures is, more often than not, well-below to that typical for the current single crystal standards. Although several modifications of this procedure have been already proposed - restrained or rigid body

refinements, (e.g. [1-2] just among the others) the crucial problem, i.e. low number of inaccurate structure factors remains. As a result, accuracy of the structural parameters obtained in any powder refinement is lower than (or at maximum identical to) accuracy of a single crystal refinement based on the same numbers of independently collected structure factors and refined parameters. Unfortunately, in a common practice the latter case is the ideal point hardly reachable, as the accuracy of structure factors from a powder pattern is always noticeably lower, especially due to overlap of the individual diffractions caused by collapse of 3D diffraction pattern to 1D, not to speak of various sample effects.

The second approach, on the other hand, totally abandons the idea of repairing of irreparable and benefits from symbiosis of powder diffraction with theoretical calculations, in this case with structure optimization by energy minimization in the solid state. If we restrict ourselves only to the solid-state DFT methods we realize, that the size of problems tractable by a laboratory computer nowadays reaches thousands of atoms per unit cell, of course in dependence on the level of approximations used by the computational method. This number largely exceeds all widely accepted limits for powder refinements, which frequently fail in providing accurate results even for the structures containing much, much smaller numbers of atoms. More-

over, since theoretical calculations are frequently done in the $P1$ space group, simultaneous optimization of the geometries of possibly symmetrically equivalent units within a unit cell provides a good measure of internal consistency of structure optimization and/or solution. The main “crystallographic” advantage of this approach is that all the atoms in a structure are treated on equal footing, i.e. not weighted by their scattering abilities. For organic structures (in fact, not only for them) this approach provides direct access to accurate geometry of hydrogen bonds, whose knowledge is in good deal of cases essential for understanding of physicochemical properties of a compound. Secondly, several “well-known” shapes or fragments (molecules or polyhedrons in inorganic structures) are further optimized under the constraints imposed by a crystal field. Last but not least, by exploiting the resulting wavefunction several interesting quantities like electronic or vibrational densities of states, distribution of the electron density in a crystal, stress tensors, etc., are easily accessible. The approach to handling of the lattice parameters is twofold. Either they are refined in advance from powder diffraction data and then kept fixed in the course of optimization of the atomic coordinates, or their values are optimized along with the atomic coordinates. Validity of both these approaches has been a subject of irrational and useless discussions with many pros and cons. In short, the main argument of the pros group is that without optimization of the cell parameters “the optimized structure is not in the minimum” (...of total energy), while the cons group proclaims that accuracy of the lattice parameters obtained from a crystallographic experiment is as a rule much higher than that of those obtained by energy minimization and there is hence no need to make it worse. (The author of this contribution pragmatically agrees with both these groups knowing that one should always use the optimal method ...)

Such a combined approach to powder structure solution and refinement was to our best knowledge pioneered by Dinnebier with co-workers [3] in their study of a rigid ferrocene-based macrocycle, $C_{48}H_{44}B_4Fe_2N_8O_4$, crystallizing in a relatively large monoclinic ($C2/c$) cell ($V = 4152.8 \text{ \AA}^3$). The initial structure models were generated by Monte Carlo method using the synchrotron data and the atomic coordinates were subsequently refined by energy minimization in the solid state. Refined structures were put to Rietveld refinement and the profile parameters were improved, while keeping the atomic coordinates fixed. The study was soon followed by the structure solution combined with the refinement by crystal energy minimization of the red polymorph of tetrahexylsexitiophene [4]. The powder pattern was collected with a laboratory diffractometer and the structure solved by Monte Carlo technique. Nearly identical solution in the space groups $C2/m$, $C2$ and $P-1$ were found, of which the first was at last chosen.

Since then, two different attitudes to co-existence of classic Rietveld refinement and refinement by total energy minimization have developed. The first and (unfortunately ...) the more frequently used, gives more weight to standard Rietveld refinement and uses theoretical calculation only to refine positions of hydrogen atoms (if any) and/or for “validation” of a refined structure (see for example

[8-13]). Regrettably, in many cases “validation” means that the authors just try to convince themselves that their Rietveld effort was not a pure waste of time. The second approach, on the contrary, is based on the presumption that it is unlikely that Rietveld refinement with all atoms relaxed can provide sufficiently accurate structural data for the structures built from more than few atoms. Rietveld refinement is therefore used only for estimation of isotropic displacement parameters (required by many journals as if they could have any reasonable meaning, neutron TOF data being an exception) and/or of selected profile parameters, like preferred orientation correction. Like the first approach, also the second has been successfully applied to both organic, metal-organic and inorganic compounds [14, 15-23]. Note, however, that the lists of the papers belonging to any of these groups are not *claimed* to be *complete* and the author apologizes for unavoidable omissions.

The requirements for successful application of energy minimization in structure refinement are however stricter than those typical for standard Rietveld refinement. First of all, the model must be complete, i.e. no dangling bonds resulting from intentional or accidental omission of atoms are allowed. Partial occupancies of atomic positions are not possible and must be modeled by a supercell simulating distribution of atoms or vacancies. A good beginner’s guide to the art of solid state calculations is provided in the review paper by Gillan [24] or Hafner [25].

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EXTENDING THE SAXS CAPABILITIES OF THE MULTI-PURPOSE EMPYREAN X-RAY DIFFRACTION PLATFORM

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Ever increasing demands are being made of standard X-ray diffraction platforms for the analysis of materials, particularly those that are not suitable for analysis by traditional Bragg diffraction. However with increased detector size and sensitivity and improved other components the capabilities of the Empyrean multi-purpose diffraction system has been extended to allow scattering measurements. The new ScatterX78 SAXS/WAXS sample platform was re-

cently added to the Empyrean diffraction system, enabling fast SAXS and WAXS measurements of highly diluted samples as well as measurements of weakly scattering materials under the vacuum. Combined with PIXcel3D 2x2 detector, the Empyrean system allows rapid collection of high quality 2D SAXS data. The data collected from various materials will be shown and discussed.

Session VI, Thursday, September 12

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CRYSTALLOGRAPHIC STUDY OF THE TERNARY SYSTEM PD-AG-TE

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During the experimental study of phase relations on the Pd-Ag-Te system, the synthetic analogues of the mineral sopcheite $\text{Ag}_4\text{Pd}_3\text{Te}_4$ and a new phase $\text{Ag}_2\text{Pd}_{14}\text{Te}_9$ (also termed as Pd_6AgTe_4) were synthesised and structurally characterized. The mineral sopcheite was found in the Cu-Ni sulphide ores of the Sopcha massif, Kola peninsula, Russia by [1], where it occurs as veins with size not exceeding of 0.02 mm included in chalcopyrite. The $\text{Ag}_2\text{Pd}_{14}\text{Te}_9$ phase was described as small anhedral grains (<0.1 mm) by [2] from the Nadezhda deposit in Karelia, Russia. In order to understand the behaviour of these phases in the natural conditions and to clarify mechanisms of various chemical substitutions, the crystal structures of both phases have been determined.

Because of extremely low amount of natural samples and difficulties connected with their isolation, both phases

were synthesized from elements by conventional solid-state reactions. Stoichiometric amounts of individual elements were sealed in silica glass tubes and resultant mixtures were heated at 350°C. After long-term annealing, the samples were quenched in a cold-water bath. The crystal structure of synthetic analogue of sopcheite $\text{Ag}_4\text{Pd}_3\text{Te}_4$ was solved from single-crystal X-ray diffraction data, whereas structure of $\text{Ag}_2\text{Pd}_{14}\text{Te}_9$ was solved from powder X-ray diffraction data.

$\text{Ag}_4\text{Pd}_3\text{Te}_4$: Space group *Cmca*, $a = 12.22 \text{ \AA}$, $b = 6.14 \text{ \AA}$, $c = 12.23 \text{ \AA}$, $V = 918 \text{ \AA}^3$ and $Z = 4$. In the layered structure of $\text{Ag}_4\text{Pd}_3\text{Te}_4$, the Pd atoms show a square planar coordination by the four Te atoms. The $[\text{PdTe}_4]$ squares share two opposite Te-Te edges with adjacent $[\text{PdTe}_4]$ squares forming layers parallel to (100). In addition, each Pd atom has four short contacts with the Ag atoms. The layers of