Oral presentation

Is my crystal structure solved correctly?

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The role of the single-crystal X-ray analysis (SC-XRD) in chemistry from 1990's as a '*fast, first resort analytical tool*' [1] is even more relevant nowadays, as the structural characterization of novel compounds becomes a pre-requisite for publication in the high- level chemical journals. In this context, the problem of evaluation of crystal structure, either solved during chemical research or found in the literature, is very relevant. Many 'users of SC-XRD' rely upon the quality factors like R-values. Is that enough for the structure to be correct? Another important aspect: when we can say that we did the best with diffraction data we have and reached the optimal structural model? Our long-time experience in SC-XRD tells that good R-value can be deceiving because of many 'little things' that can be easily overlooked or done wrongly on the way from the structure solution to the final structural model.

Generally, the best strategy in evaluation of the crystal structure solution is always to start with the careful analysis of the 3D diffraction pattern (the diffraction images), if it is available [2]. At this stage a twinning, pseudo-symmetry, modulation and OD-effect (order-disorder phenomenon) can be detected. These phenomena are not as rare as one might think. Taking 270 crystal structures of boron- and silicon-containing organic compounds solved during past two years in the group of Prof. Dr. M. Wagner in our university as an example, 28 showed pseudo-merohedry twinning (Fig. 1a), in two translational pseudo-symmetry was found (Fig. 1b), two structures revealed order-disorder (OD) effect (Fig. 1d) and one compound was incommensurately modulated.

Even minor twinning still can have a significant impact on the data [3]. The OD-effect resulting from, e.g., stacking faults [4], becomes obvious from the $\Delta\rho$ map due to the presence of the 'second version' ('shadow') of the structure (Fig. 1d). At that, when this effect is about a few percent, it still can significantly influence the R-value and the validity of the structural model [5].

Structure solution first assumes the knowledge of the correct space group that ideally must fulfil the '*the highest symmetry causing the lowest disorder*' principle. Incorrect space symmetry is quite common issue [6], which can cause, e.g., a correlation between the parameters during the least-squares refinement affecting important geometrical characteristics of the structure. Then, the assignment of the atomic sorts to the electron density peaks is mutually interrelated with the understanding the crystallographic disorder. 'Decoding' of the disorder may be vital for understanding chemically essential features. For example, the compound "$C_5Me_5Tc_2O_3$" is nothing else but $C_5Me_5ReO_3$ where half-occupied positions of Re atoms were wrongly assigned to the technetium [7]. The $GeCH_3/SiCl$ positional disorder in the group IV heteroadamantanes reveals the existence of the skeletal isomers (Fig. 1c) [8]. Note that a common practice of usage of PLATON/SQUEEZE routine might result not only in the 'removal' of severely disordered solvent molecules, but also counterions leading to wrong ideas about charge balance.

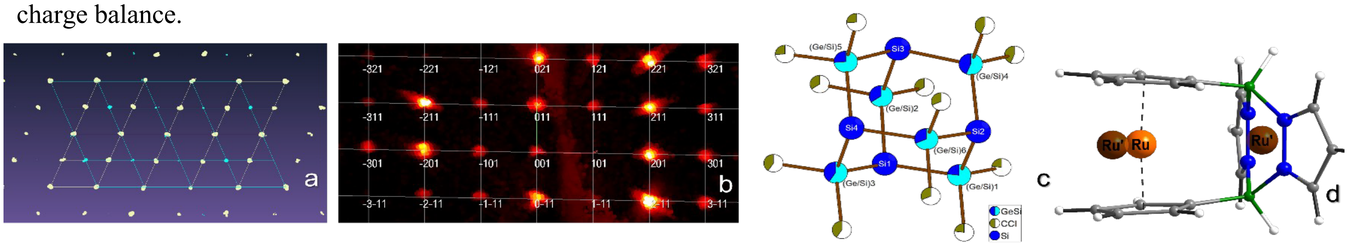

Figure 1. Examples of twinning (a), pseudo 'a/2' symmetry (b), disorder (c) and manifestation of the OD-effect (d).

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