Review of the thesis

Structure analysis of some transition metal silicides using X-ray diffraction and dynamical refinement against electron diffraction data

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The thesis is focused to two main problems. The first one is more methodological but very important. This is the application of precession electron diffraction and electron diffraction tomography for structure determination of crystals, in particular nanocrystals the structure of which cannot be determined by single crystal X-ray diffraction (SCXRD) or it is more difficult. The main advantage of the precession electron diffraction consists in the suppression of the effects of multiple scattering – dynamic diffraction. This was the goal of the method developed in nineties and supported by corresponding instrumentation (precession electron diffraction - PED). However, the advisor of the PhD student – Lukáš Palatinus has shown that the dynamical effects cannot be neglected and should be taken into account and if they are included in the calculations, significantly more precise results are obtained. Therefore the task of the work was verification of the dynamical refinement by comparisn of the structural parameters determined with those obtained by single crystal X-ray diffraction. For this task, materials with known structures were used, nanowire of which were measured by PED and bulk samples by SCXRD. The second and longer part was an application of dynamical refinement to unknown structure. For these experiments, transition metal silicides were selected as materials of high practical interest in nanotechnology – nanoscale electronics and photovoltaic devices.

The thesis is divided into four chapters. After a short introduction (8 pages) showing also the above objectives of the work, the first brief but compact and informative chapter describes application of electron diffraction to the structure determination including precession electron diffraction tomography and evolution of dynamical refinements. More details on it can be found in the second part that is on the implementation of the method into famous Jana program including the considerations on the crystal shape related to the shape of nanocrystals studied by this method. It would be interesting to know, if the author also contributed to this methodological part before testing measurements. In this chapter, the above mentioned first aim of the thesis is included on 17 pages. The structure tested belongs to one of the first structures determined in Czechoslovakia by XRD - Ni_2Si. Two kinds of samples were used – nanowires and bulk samples. Comparison of the results were made by using the residue values and average distance to reference atoms (ADRA) and the behavior of the values of main optimized parameters is analyzed, i.e. the excitation error S_g and the ratio of the excitation error without precession and the maximum excitation error reached by the precession circuit R_{Sg} and other three parameters. Illustrative examples of meaning of the parameters would be welcome during the defense. The conclusions of these first measurements indicate that the above two parameters have the strongest influence on the results and that the full dynamic approach gives clearly better results than both kinematic approach and dynamic two beam calculations. Are there significant differences in computing time and complications for these dynamical methods and can the above conclusions based on this single studies be taken as general?

Next testing study was performed on Ni_3Si_2 and it was shown by both PEDT and SCXRD single crystal diffraction that previous determination of the space group $Cmc2_1$ found in the literature was incorrect and the correct group should be *Cmcm*. Trial of symmetry reduction did not improved

the fits, hence then the more symmetrical group was taken as the correct one. The comparison of kinematical and dynamical calculations gave similar conclusions as in the previous case.

The rest of the thesis (36) is devoted to the structure determination of new modulated structures $Cu_{3+x}Si$. Unfortunately, this is quite complicated structure and dynamical calculations would be very cumbersome or impossible at all. Therefore SCXRD was used and for phase analysis also powder diffraction was applied. In both cases, evolution of the system with temperature was studied. Copper silicides are used e.g. as contacts between copper conductors and silicon and therefore are of practical importance. In the beginning of the chapter the way of description of modulated structure is introduced and then Cu-Si phase diagram indicating several superstructures and modulated structures is shown and the results found in the literature are discussed. Then the experimental part is given including energy dispersive X-ray spectroscopy (EDS) and high-temperature single crystal and powder diffractometry. I did not find any explicit results obtained EDS. I guess that the compositions given came from the structure refinement not from EDS. Two incommensurately modulated structures η'' and η''' with similar averages structures were solved and showed strong modulation with large anisotropic atomic displacements. Because of complexity, the structure was described as commensurate one in superspace and also because of lack or reflections the calculations required smart procedures. In chapter 3.4.5 there is a detailed discussion on chemical crystal structure of both phases studied. In some places of the text and figures notation η^2 is used in other places η_2. I think, these quantities should be identical. In part 3.4.3, the calculations with „free“ and „fixed“ models are compared and it is concluded that the fixed one gives more realistic results. What could be the reason? The refinements of the „free“ model seems to be significantly better.

In the last chapter, the main results of the thesis are well described. They are methodological – with dynamical refinement of PED data the precision can achieve values of standard XRD single crystal structure determination – and practical – detailed study of the $Cu_{3+x}Si$ system with modulated structures. Both parts bring new results. The Cu-Si system appeared to be more complex than expected and requires further studies that are indicated as well. There are several phase transitions and quite many phases appear. How this and also chemical composition is related to above mentioned practical applications of the material? Is it of great importance or not? The text of this part contains quite many numbers and it is less readable. The concentration of the data in a table may help.

There is no doubt about the quality and novelty of the thesis as well as about significant contribution of the student to most individual parts of the research mentioned in the thesis. The thesis is well organized and written without significant mistakes. I know the student from several seminars and should mention that she received a diploma for the second place in the Czech and Slovak student symposium and competition at the conference Struktura 2015 in Luhačovice. The thesis is well supported by five publications, for three of which the student is the first author. I recommend the acceptance of the doctoral thesis of Cinthia Antunes Corrêa, if successfully defended.

In Prague 20. 8. 2017

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