Evaluation report on doctoral thesis

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

I Topicality of the subject, scientific and practical importance

Structure and properties of transition metal silicides, especially those containing copper, are extensively investigated nowadays due to the significant influence on properties of silicon based devices, such as microelectronic chips or solar collectors. In spite of several decades of research effort, there is still serious uncertainty about the exact atomic order of complex crystalline phases of silicides appearing at different temperature ranges, composition ratios and crystalline grain sizes.

The thesis deals with structure analysis of silicides of two different chemical compositions, Ni_xSi_y and $Cu_{3+x}Si$, performed on three different types of specimens: nano-sized single crystals, micro-sized single crystals and polycrystalline powders.

The subject is of a high scientific value, timeliness, and remarkable practical importance.

II Goals of the thesis and applied methods

As mentioned in the "Introduction" section, the original objectives of the thesis involved verification of the parameters used in dynamical refinement of electron diffraction data (by testing the on several samples with already well characterized structure) followed by application of such optimized procedure to structure analysis of unknown Cu-...Si compounds. However, due to the complexity of the structures, an alternative approach had to be later adopted combining single crystal and powder X-ray diffraction methods and providing an easier way for refinement of the observed modulated structures. Thus, the applied experimental methods and refinement procedures involve precession electron diffraction tomography (data evaluated with aid of general dynamic electron scattering theory) and temperature dependent single crystal and powder X-ray diffraction accompanied by evaluation of the observed modulated structures in frame of the kinematic approximation.

The stated goals are ambitious and scientifically relevant. The applied experimental and theoretical procedures are on the cutting edge of the recent methods used in the field of crystal structure analysis.

III Obtained results

According to the given references, the results presented in the thesis have been published in five original articles contained in Thompson-Reuters indexed, peer reviewed journals. At three of them, the applicant is the first author. Thus, the scientific quality of the results has been independently proofed.

Two groups of results are obtained. The first group, summarized in the paragraph 2.4, is directed towards experimental methodology and deals with tests and optimization of parameters used in the dynamical refinement of electron diffraction (ED) data. Set of nickel silicide samples with various stoichiometry is used in place of the testing structures. Comparison of the structural models based on ED data with the models obtained from single crystal X-ray diffraction and the already published structures allows to characterize behavior and influence of the parameters and define the recommended optimal values. The optimized parameters are then successfully applied in re-determination of ε-Ni_2Si phase structure of a single nanowire with the diameter of 35nm.

The methodical contribution paves the way to the structure analysis of nano-scale crystalline objects that is of great practical importance.

The second group of results involves characterization and refinement of the modulated crystalline structures of copper silicides performed by means of single crystal and powder X-ray diffraction within a wide interval of temperatures from RT to 720° C. Three samples with the composition in the middle and close to the opposite boundaries of the η-phase stability field were used in the investigations. The obtained results revealed a complex system of at least six distinguished phases partially overlapped in the temperature domain, four of them being incommensurately modulated. The complexity of the phase composition did not allowed, however, for a definite revision of the phase diagram due to the found conflict with the Gibbs phase rule; further investigations performed on series of samples with finer composition difference are needed in order to understand the phase evolution.

In spite of the still opened problems, the obtained results provide undoubtedly a novel, original and very valuable contribution to the common knowledge concerning the structural order and phase behavior in copper silicides.

IV Organization of contents, formal level and language quality

The text of the thesis contains 100 numbered pages. The first two chapters are dealing with methodology and theoretical backgrounds of electron diffraction and its recent sophisticated variants, precession electron diffraction and precession electron diffraction tomography, and the dynamic theory of diffraction required in structure refinement from electron diffraction data. The description is based on the dynamical refinement procedures implemented in the SW tool Jana2006, further applied in evaluation of obtained experimental data. The last paragraph of the second chapter is devoted to the analysis and optimization of the values of key parameters scaling the dynamical refinement procedure. The third chapter provides, in its first part, the classification of modulated structures and grounds of the theoretical approaches used in their analysis followed in the second part by a detailed and extensive description of the experimental results obtained on samples of $Cu_{3-x}Si$ showing incommensurately modulated structures. The main achieved results and plans for further research are summarized in the fourth part "Conclusions a future work". The content is completed by bibliography (including the author's contributions), list of figures, tables and abbreviations. (Taking in account the large extend of used symbols and some ambiguity in their usage (e.g. the symbol "**g**" is used to mark a reciprocal lattice vector as well as the scattering vector), inclusion of a list of symbols would definitely improve the text's clarity.)

Text of the thesis is well organized and carefully written, on a good language level, with a low level of typographic errors and misspellings. The text satisfies all the requirements laid on ordinary doctoral thesis.

V Comments and questions

- Relation (1.5): Is the minus sign in the exponent correct?
- Figure 2.7: What can be the reason for the observed non-monotonous evolution of the parameter ADRA with the value of R_{Sg}?
- In the relation (2.19) for the excitation error S_g, there is a vector quantity "**K**" in the denominator. Is that correct?
- Figure 2.8: Usage of larger symbols (e.g. similar to these used in Figure 2.9) would be desirable in order to clearly distinguish between the indicated options.
- Caption to Figure 3.3: Is the mentioned period „A_1*"correct?
- Figure 3.11 and the related text: The observed second order satellites are apparently stronger for the η''' phase than for the η'' phase. Is it possible to explain the structural reason for such difference? Did you tried to test the possible influence of the second order satellites on the resulting structure? I.e., in other words, are the second order satellites compatible with the fit obtained using the first order satellites only?
- For the investigated copper silicides samples, there is a significant discrepancy in the phase transition temperatures observed by the two X-ray diffraction methods used. What is the reason for such discrepancy?

VI Evaluation summary

The content of the submitted dissertation and the results contained therein clearly demonstrate the author's scientific skills and prerequisites for independent creative scientific work.

I recommend the thesis for the defense and, in case of successful answers to all the questions and comments, I propose to award author with the Ph.D. degree.

Prague, August 8, 2017

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