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

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Abstract: This thesis presents the crystal structure analysis of several transition metal silicides. The crystal structures were studied primarily by precession electron diffraction tomography (PEDT) employing the dynamical refinement, a method recently developed for accurate crystal structure refinement of electron diffraction data. The optimal values of the parameters of the method were proposed based on the comparison between the dynamical refinement of PEDT data and a high-quality reference structure. We present the results of the comparison using a Ni_2Si nanowire with the diameter of 15 nm. The average atomic distance between the model obtained by the dynamical refinement on PEDT data and the one by single crystal X-ray diffraction was 0.006 Å. Knowing the accuracy and limitations of the method, the crystal structure of Ni_3Si_2 was redetermined on a nanowire with 35 nm of diameter. The model obtained had an average error in the atomic positions of 0.006 Å. These results show that the accuracy achieved by the dynamical refinement on PEDT data is significantly superior to that of the refinement using the kinematical approximation. With the method validated, the elucidation of the phases of the system $Cu_{3+x}Si$ were pursued. Due to the complex incommensurate modulated structures observed during our PEDT measurements, the dynamical refinement could not be used and a combination of single crystal and powder X-ray diffraction was used. Temperature dependent powder X-ray diffraction revealed a complex Cu-Si phase diagram, where six distinct phases were observed, instead of the three phases reported so far in the $Cu_{3+x}Si$ phase-field. In order of increasing temperature, the phases observed were η''', η'', η', η_3, η_2 and η_1. At least four of the six phases observed are incommensurately modulated. The crystal structures of η''' and η'' were elucidated by single crystal X-ray diffraction, while the phases η_2 and η_1 were indexed on the powder diffraction data. η' is known, and we could index only the main structure of η_3. η''' and η'' are very similar and both have a (3+2)-dimensional incommensurately modulated structure. Given the complexity of their modulation the refinement in the superspace could not be performed, and the models were described in a supercell approximation.

Keywords: Precession electron diffraction tomography, dynamical refinement, nickel and copper silicides, (3+2)D incommensurately modulated structures.