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Unit cell refinement of nano-sized Ni_4Ti_3 precipitates by quantitative electron diffraction

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One of the major benefits of gathering diffraction data by using the electron beam in a TEM is that the probe diameter can be very small, down to a few nm if needed, and the beam might be positioned accurately in the area of interest. Furthermore by a using CCD camera or imaging plates the reflection intensities can be measured in an accurate way, needed for quantitative analyses. This asset is of great benefit when refinement needs to be done of nano-sized particles or areas for which traditional neutron or X-ray crystallography might not be of usage. An example of this are the Ni_4Ti_3 precipitates occurring in NiTi shape memory alloys; they only exist as a solid solution in the NiTi matrix and have sizes of a few nm up to a few microns. Moreover, these precipitates are a superstructure of the B2 NiTi matrix and the unit cell is rhombohedral having space-group R-3 resulting in 8 orientation variants. Up to now the atomic coordinates were only roughly estimated by Tadaki et al. [1] based on traditional electron diffraction techniques. In this work quantitative electron diffraction is used to refine the atomic coordinates of the Ni_4Ti_3 unit cell. Since the diffraction data obtained in this way is dynamical in nature (multiple scattering) this needs to be incorporated in the refinement procedure and in order to do so the MSLS (Multi Slice Least Squares) method, developed by J. Jansen [2], was used. Similar to what is used in other refinement methods, the R-factor is defined as a goodness of fit indicator and is minimized by the procedure. The diffraction data was obtained with a CM30 microscope with an accelerating voltage of 300kV and recordings made on a 1K CCD camera. Two zone orientations in reference to the rhombic unit cell were used, namely the <100> and <111>. For each zone several patterns were taken from areas with different thicknesses resulting in a final set of 651 reflections used in the refinement procedure. A good starting structure was needed, in order not to refine to a local minimum of R resulting in a wrong structure; for this reason a density functional calculation was used starting from the atom positions of the known structure. This structure was then further refined by the MSLS method and resulted in a final one with R-factor 8.2% which is an improvement compared to the R-factor of 12.5% obtained for the original structure. During refinement the rhombohedral unit cell was maintained, as well as the R-3 space-group symmetry and composition. An evaluation of the newly refined coordinates points out that the shrinking of the unit cell compared to the matrix is explained in a better way and that a DFT calculation of the structures total energy shows a decrease of 0.063eV/atom compared to the original one.

[1] Tadaki, T., Nakata, Y., Shimizu, K., Otsuka, K. (1986). *JIM 27.* 731-740.
[2] Jansen, J., Tang, D., Zandbergen, H. W., Schenk, H. (1998). *Acta Cryst.* A54. 91-101.

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Structure determination of the hexagonal λ'-$(Al,Si)_4Cr$ by the strong reflections approach

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By means of transmission electron microscopy (TEM), a new hexagonal quasicrystal approximant of λ'-$(Al,Si)_4Cr$ (a = 2.01 and c =1.24 nm) often found coexisting with the hexagonal λ-$(Al,Si)_4Cr$ (a = 1.998 and c = 2.4673 nm, isostructural with (-Al_4Mn) and also with the hexagonal λ-$(Al,Si)_4Cr$ (a = 2.839 and c = 1.239 nm, isostructural with λ-Al_4Mn) and Al-Cr-Si decagonal quasicrystal. It is evident from their electron diffraction patterns that the structures of these phases are related. The strong reflections in λ' and λ are distributed in a similar way. They all exhibit a pseudo icosahedral symmetry. The structure factor amplitudes and phases for the strong reflections of the λ' phase could therefore be adopted from those of the λ phase, according to the strong reflections approach. A structure model of the λ' phase is thus deduced from the known λ-Al_4Mn. λ' consists of chains of 3+3 or 4+2 interpenetrated icosahedra along the <100> directions. Similar to the λ phase, there are two flat layer (F) and four puckered layers (P) in each unit cell of λ', stacked along the ***c***-axis in a sequence of PFP(PFP)' where the (PFP)' block is related to the PFP block by a 6_3 screw.