



Te for two, II: A neutron powder diffraction study of the structure of the "Ni₃InTe₂" solid solution

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A new phase in the Ni-In-Te ternary system that shows a gradual but systematic composition-dependent change between commensurate and incommensurate superstructures has been found. It is described in terms of a modulation of the structural motifs from the *CdI₂*, *NiAs* and *Ni₂In* structure types, all coexisting within the one compound.

1. Introduction

Many wide range non-stoichiometric $T_{1\pm x}B$ (T = a transition metal, B = a group III-VII element) solid solution phases adopt either the trigonal $P\bar{3}m1$, *CdI₂* or the hexagonal $P6_3/mmc$, *NiAs* or *Ni₂In* average structure types. All are based on a fully occupied hcp array of B atoms. The T atoms occupy equally all the octahedral sites thereof in the case of the *NiAs* or *Ni₂In* structure types while alternate octahedral T metal atom layers have different occupancies in the case of the *CdI₂* structure type. In the case of transition metal rich, $T_{1+x}B$ compositions, the T atoms also occupy an additional trigonal bipyramidal site within the hcp array of B atoms. In the Ni-In-Te ternary phase diagram we have previously found two solid solution ranges, SS1 and SS2 [1]. In this contribution, we report the refined crystal structures of three separate compositions within the *NiAs*-related, $T_{1\pm x}B$ SS2 solid solution phase and discuss the structures and crystal chemistry for these alloys.

2. Sample preparation

Three samples, Ni₃InTe₂ (A), Ni_{3.12}In_{0.86}Te_{2.14} (B) and Ni_{3.31}InTe₂ (C) were made by reacting the pure elements (4N purity or better) in evacuated silica tubes at 1000 °C for 2-3 h and then quenching in water. The ingots were then pressed to pellets which were repeatedly annealed, with intermediate grinding and re-pelleting, in evacuated silica tubes at 570 °C for periods of fourteen days each. The samples were regularly checked with X-ray powder diffraction (XRPD) and were considered at equilibrium when no significant changes in their respective parent unit cells could be seen. Neutron powder diffraction patterns were recorded at Neutronforskningslaboratoriet (NFL) in Studsvik, Sweden, while electron diffraction patterns (EDPs) were recorded in-house.

3. Results

The XRPD results as well as the EDPs showed that a commensurate superstructure was present in samples B and C, with the primary modulation wave vector $\mathbf{q}^* = \frac{2}{3} \mathbf{c}^*$, while sample A showed an incommensurate value of $\mathbf{q}^* \sim 0.71 \mathbf{c}^*$. The first order superstructure reflections were also present in the neutron powder patterns.

3.1 Samples Ni_{3.31}InTe₂ and Ni_{3.12}In_{0.86}Te₂

The refined neutron powder diffraction pattern of the 1x1x3 superstructure observed for Ni_{3.31}InTe₂ (*i.e.* sample C) is shown in Fig. 1. The refinement was done with the JANA 2000 program package.

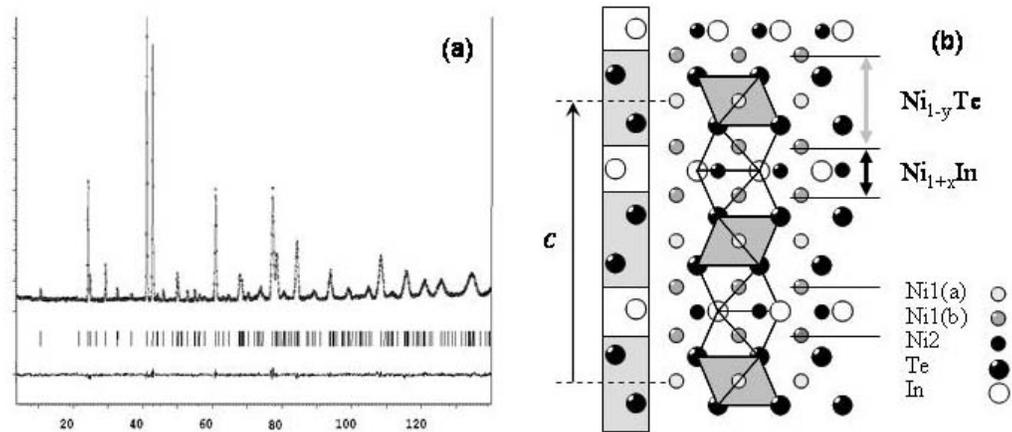


Fig. 1. (a) Refined neutron powder pattern of $\text{Ni}_{3.31}\text{InTe}_2$ (GoF 1.21) and the obtained superstructure (b) The pure anion-motif to the far left is a simplified building block used to describe the layer stacking order in the incommensurate and the commensurate structures.

The commensurate $1 \times 1 \times 3$ superstructures found for samples B and C can be illustrated as a regular ordering of anion layers with a "-Te/Te/In-" stacking sequence along the c direction tripling the parent c -axis. Nickel atoms are inserted between these layers in two octahedral sites [Ni(1a,b)] as well as in a trigonal bipyramidal position within the In-layer [Ni(2)]. The structure can be described as composed of alternating slabs of the Ni_2In (Ni_{1+x}In) and CdI_2 (Ni_{1-y}Te) structure types, the boundary between the slabs being the Ni(1b) atoms (*cf.* Fig. 1b). Note that the Ni(1a) occupancy in the Te octahedra is less than 100 % which makes this the metal-poor part of the CdI_2 structure type. The neighbouring, fully occupied octahedra is made up of three In-atoms and three Te-atoms. Because In and Te have different sizes, it is necessary to expand the size of the In-layer in order to make it fit to the size of the adjacent Te-layer. This is achieved via the introduction of Ni(2) atoms into the trigonal bipyramidal positions within the In-layers.

3.2 Sample Ni_3InTe_2

In the incommensurately modulated Ni_3InTe_2 , or sample A, the primary modulation wave vector \mathbf{q}^* is $\sim 0.71\mathbf{c}^*$ (see Fig. 2a).

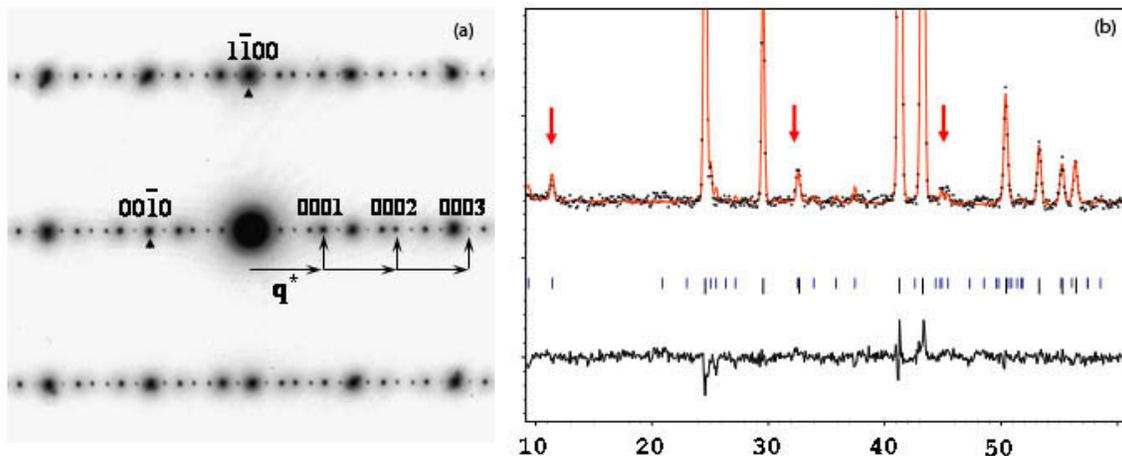


Fig. 2: $\langle 110 \rangle_p$ zone axis EDP of Ni_3InTe_2 (a) and the Rietveld refinement using a crenel-function to describe the incommensurate modulation (b)



Satellite reflections of up to third order are clearly visible in the pattern, pointing to a ‘block-like’ modulation of the parent structure in real space, best described using a crenel-type modulation function [2]. In the corresponding neutron powder diffraction pattern, however, only first order harmonic satellite reflections are observed, suggesting that the modulation would be best described using a sinus function. One explanation for this apparent contradiction is that microstructural stacking faulting is present in the material, also known as “*phason wobble*”. The effect of such stacking faulting is to wipe out the higher order harmonic satellite reflections in the neutron powder pattern.

The stacking sequence of the Te-rich and In-rich layers is directly related to the length of the modulation wave vector q^* .

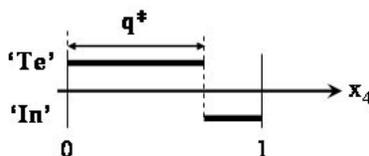


Fig. 3: An occupational crenel function drawn in hyper-space *i.e.* as a function of $x_4=q^* \cdot (r+t)$. The width of the ‘Te’ occupancy domain given by $q^* \sim 0.71$ and the length of the ‘In’ occupancy domain by $1-q^*$.

In real space the repeat distance of this modulation is $q (= 1/q^*) \sim 1.408 c_p$. The relative lengths of the ‘Te’ and ‘In’ parts of this repeat distance are $0.71 \times 1.408 c_p = 1 c_p$ and $0.29 \times 1.408 c_p = 0.408 c_p$, respectively. In the diagram below the position of the atomic layers of the parent structure is given by vertical lines, black (**thick**) for the unit cell repeat and grey (thin dashed) for the intermediate layer (*cf* Fig. 1). The “type of layer” in the stacking sequence is given by the crenel function (illustrated in grey). If a ‘Te’ part crosses the “layer position line” that layer is of the Te-rich CdI_2 -type layers while a ‘In’ part means a layer of Ni_2In -type (*cf* Fig. 1b and Fig. 4).

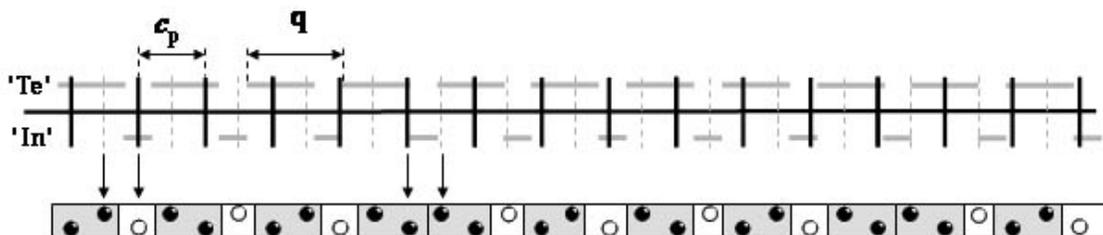


Fig. 4: As can be seen, double layers of CdI_2 -type now periodically appear which did not occur in the case of the $1 \times 1 \times 3$ superstructure (*cf* Fig. 1b).

The result is a structure with the possibility of continuously changing the ratio of the CdI_2/Ni_2In structural components in response to the relative composition of Ni, In and Te.

References

- [1] L. Norén, R.L. Withers and F.J. Brink, *J. Alloys and Comp.* **353**, 133 (2003).
- [2] V. Petříček, A. van der Lee and M. Evain, *Acta Cryst. A* **51**, 529(1995).