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$Ni_{5-\delta}Sn_4Zn$ ($\delta \sim 0.25$) from single-crystal data[1]

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Work on the ternary Ni–Sn–Zn phase diagram revealed the existence of the title compound pentanickel tetratin zinc, $Ni_{3.17}Sn_{2.67}Zn_{0.67}$ [Schmetterer *et al.* (2012). *Intermetallics*, doi:10.1016/j.intermet.2011.05.025]. It crystallizes in the $Ni_5Ga_3Ge_2$ structure type (orthorhombic, *Cmcm*) and is related to the $InNi_2$ type (hexagonal, $P6_3/mmc$) of the neighbouring Ni_3Sn_2 high-temperature (HT) phase, but is not a superstructure. The crystal structure was determined using single-crystal X-ray diffraction. Its homogeneity range was characterized using electron microprobe analysis. Phase analysis at various temperatures indicated that the phase decomposes between 1073 and 1173 K, where a more extended ternary solid solution of the Ni_3Sn_2 HT phase was found instead.

Comment

The title compound, shown in Fig. 1, crystallizes in a prototype crystal structure originally reported by Bhargava & Schubert (1974) as Ni_2GaGe. This compound was first mentioned by Panday & Schubert (1969) as an NiAs-like phase in Ni–Ga–Ge mixtures. The structure was finally reported by Bhargava & Schubert (1974), where the authors compared this structure to other Ni–Ga–Ge phases but did not discuss the relationship with the NiAs structure.

We prefer to call this structure type $Ni_5Ga_3Ge_2$ since this new designation better fits the stoichiometry and facilitates comparison of the structure of the prototype phase with the $Ni_{5-\delta}Sn_4Zn$ ($\delta \sim 0.25$) phase. The slice parallel to the *bc* plane of the crystal structure shown in Fig. 2 is in the same direction as the projection chosen by Bhargava & Schubert (1974) in their structure representation.

Seven crystallographically different atomic positions exist in the original $Ni_5Ga_3Ge_2$-type structure: two eightfold Ni positions (8*f*), one fourfold Ni (4*c*), one eightfold (8*f*) and one fourfold Ga (4*b*) and two fourfold Ge positions (4*c*). As the structure is fully ordered, there are no mixed occupations.

In $Ni_{5-\delta}Sn_4Zn$ ($\delta \sim 0.25$), the atomic arrangement is slightly modified to fit the different stoichiometry, *viz.* three Ni positions, three Sn positions and one Zn position. The Zn atoms can be found on 4*a*, equivalent to Ga2* (the asterisk * denotes atom positions in the prototype structure), while the Ga1* position (8*f*) is occupied by Sn3 atoms. Sn1 and Sn2 can be found on the Ge1* and Ge2* positions. The three Ni atoms are fully equivalent, with the only difference being the occupation of 0.85 at the Ni2 position found in the investigated crystal. As expected for atoms with neighbouring atom numbers and the use of conventional X-ray sources, a (partial) mixed occupation (Ni,Zn) cannot be ruled out with certainty. Different models with a variable Ni:Zn ratio or fixed anisotropic displacement parameters but variable occupation factors were refined, but the final allocation of Ni and Zn was performed by crystal chemical considerations in consistency with electron microprobe analyses.

The $Ni_{5-\delta}Sn_4Zn$ ($\delta \sim 0.25$) structure can be described in different ways based on characteristic features.

(i) It is composed from two alternating atomic layers parallel to the *bc* plane. These atomic layers are identical but offset according to the *C* centring ($\frac{1}{2}$, $\frac{1}{2}$, 0). One such layer is shown in Fig. 2.

(ii) The Ni and Zn atoms form chains of the type Ni2–Ni3–Ni1–Zn1–Ni1–Ni3–Ni2 within the atomic layer. These chains are not connected but are offset against each other, as shown in Fig. 2.

(iii) The Zn1, Ni1 and Ni3 atoms are each coordinated by six Sn atoms forming more or less distorted octahedra, as

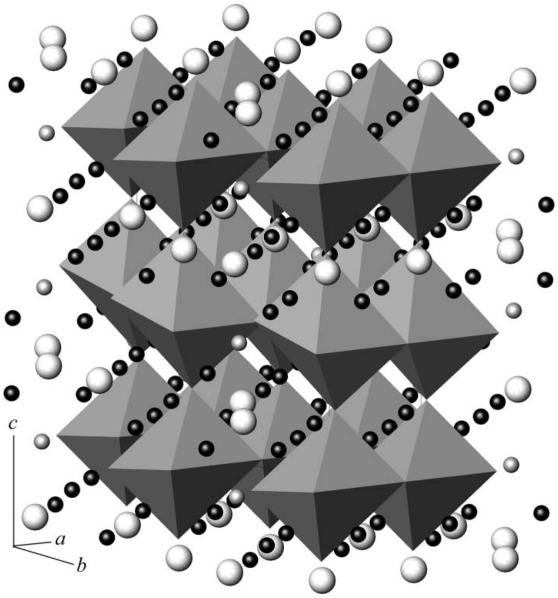

Figure 1
An overall view of the orthorhombic $Ni_{5-\delta}Sn_4Zn$ ($\delta \sim 0.25$) structure based on the coordination of Zn by Sn. Sn atoms are white and Ni atoms black. Zn atoms are at the centres of the polyhedra shown.

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[1] This structure is also registered with Fachinformationszentrum (FIZ) Karlsruhe, D-76344 Eggenstein-Leopoldshafen [Germany, FAX: (49) 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de] under the depository number CSD-421611. Information can be obtained on quoting the CSD number, the name of the author(s) and the citation of the paper.

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shown in Fig. 3 (strongly distorted around Ni1 and almost regular around Ni3). These octahedra include Sn atoms from three neighbouring atomic layers. A full view of the structure based on the Zn-centred octahedra can be seen in Fig. 1. Ni2 is coordinated by only five Sn atoms.

These descriptions are consistent because the Ni and Zn atoms forming the chains are the central atoms of the various octahedra (except Ni2) resulting in a stacking sequence of five octahedra per chain.

The Ni–Sn–Zn phase diagram (Schmetterer *et al.*, 2012) shows the compositional similarity of $Ni_{5-\delta}Sn_4Zn$ ($\delta \sim 0.25$) and Ni_3Sn_2 HT (HT = high temperature) with up to approximately 12 at% Zn dissolved (partially filled $InNi_2$ type) as they are neighbours in the phase diagram. Therefore, structural similarities are to be expected. Indeed, relationships were found between the orthorhombic *a* and *b* cell parameters of $Ni_{5-\delta}Sn_4Zn$ ($\delta \sim 0.25$) and the hexagonal *a* parameter: $a_o \sim a_h$ in the direction $[110]_h$; $b_o \sim [(a_h \times 3^{1/2})^2 + (2 \times c_h)^2]^{1/2}$ in the direction $[2\overline{2}\overline{1}]_h$. The lattice parameters are $a_h = 4.14$, $c_h = 5.29$ and $a_o = 4.1520\ (8)$, $b_o = 12.603\ (2)$, $c_o = 11.657\ (2)$ Å, respectively. Thus, $(100)_o$ can be related to the $(11\overline{2}0)_h$ plane and $(001)_o$ to $(1\overline{1}02)_h$.

However, along the c_o direction, no straightforward relationship with the hexagonal parental cell was found. This situation is shown in Fig. 2 [slice cut out of the $Ni_{5-\delta}Sn_4Zn$ ($\delta \sim 0.25$) structure, *i.e.* the $(11.0)_h$ plane, representing one atomic layer as mentioned above], where the Ni–Zn chains, the orthorhombic unit cell and triplets *ABC* made from the projected outline of the hexagonal cell are represented. This not only shows the relationship between the lattice parameters, but also further structural relations as discussed below.

(i) The Ni–Zn chains of the title compound correspond to the Ni1** (the double asterisk ** denotes atom sites in Ni_3Sn_2) chains in Ni_3Sn_2 HT running along the hexagonal *c* direction. These Ni1** chains are continuous, whereas the Ni–Zn chains are interrupted after three 'hexagonal' cells corresponding with the *ABC* cell triplets. One Ni1** atom is therefore replaced by the Zn atom, and in $Ni_{5-\delta}Sn_4Zn$ ($\delta \sim 0.25$) the atoms are slightly displaced as compared to the hexagonal analogue.

(ii) Regular Sn_6 octahedra centred by Ni1** form a building block in the $InNi_2$-type structure of Ni_3Sn_2 HT, similar to the Sn_6 octahedra found in $Ni_{5-\delta}Sn_4Zn$ ($\delta \sim 0.25$). As the Ni1** chains are continuous in Ni_3Sn_2 HT, the octahedra stacking is continuous there, too, but is discontinuous in $Ni_{5-\delta}Sn_4Zn$ ($\delta \sim 0.25$), because of the discontinuity in the Ni–Zn chains (*i.e.* the central atoms of the octahedra).

(iii) In agreement with the structural features just mentioned above, in similarity to the Ni–Zn chains, the *ABC* cell triplets do not form continuous chains, either, as shown in Fig. 2. These triplets in fact form zigzag chains with gaps in between reflecting the offset in the Ni–Zn chains. Furthermore, the atom arrangement in cell *A* corresponds to the arrangement in Ni_3Sn_2 HT, which is not the case in cells *B* and *C*. This is consistent with the variously shaped Sn_6 octahedra in $Ni_{5-\delta}Sn_4Zn$ ($\delta \sim 0.25$) and the fivefold coordination of Ni2 by Sn atoms (Fig. 3).

These structural features cause the lack of an easily visible relationship between the orthorhombic *c* parameter and the hexagonal cell parameters. It can therefore be summarized that structural building blocks from Ni_3Sn_2 HT can be found in the $Ni_{5-\delta}Sn_4Zn$ ($\delta \sim 0.25$) structure, but the structure cannot be constructed from these building blocks alone (the stacking

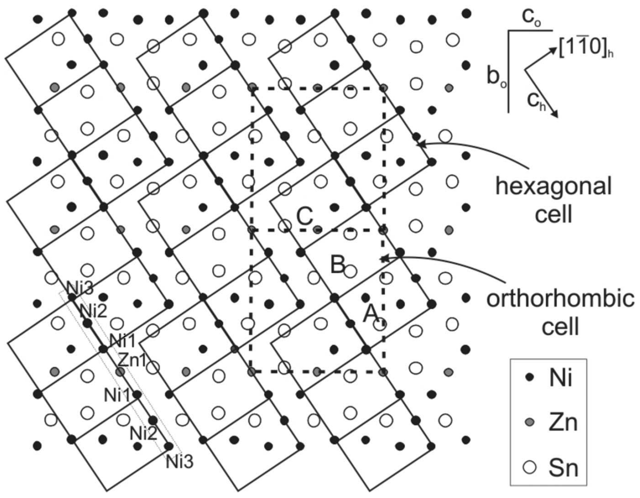
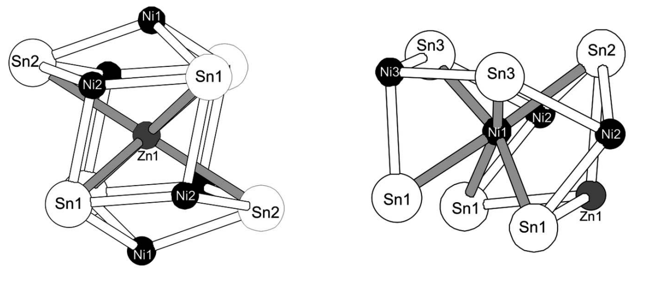
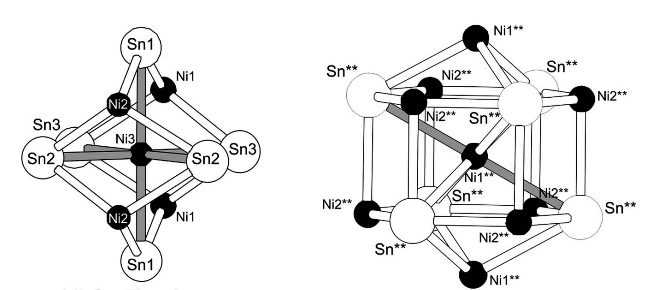


Figure 2
The atomic arrangement in a slice parallel to the *bc* plane of the $Ni_{5-\delta}Sn_4Zn$ ($\delta \sim 0.25$) structure (the orientation is the same as chosen by Bhargava and Schubert); the orthorhombic unit cell is shown (dashed line) as are the triplets formed by the outline of the hexagonal Ni_3Sn_2 HT cell. It is evident that the orthorhombic structure cannot be created only from hexagonal cells. The Ni–Zn chain is indicated by the dotted box and the atom labels. Generic atom labels without symmetry codes have been used.



Ni_5Sn_4Zn phase, coord. of Zn1

Ni_5Sn_4Zn phase, coord. of Ni1



Ni_5Sn_4Zn phase, coord. of Ni3

Ni_3Sn_2 HT

Figure 3
The coordination of Zn1, Ni1 and Ni3 in $Ni_{5-\delta}Sn_4Zn$ ($\delta \sim 0.25$) compared with the coordination of Ni1** in Ni_3Sn_2 HT; a quite similar environment can be seen for the Zn1, Ni1 and Ni3 atoms. Generic atom labels without symmetry codes have been used.

sequence is interrupted), which leads to the lowering in symmetry. The structure of $Ni_{5-\delta}Sn_4Zn$ ($\delta \sim 0.25$) is therefore not a superstructure of Ni_3Sn_2 HT ($InNi_2$).

Similar to neighbouring Ni_3Sn_2 HT, $Ni_{5-\delta}Sn_4Zn$ ($\delta \sim 0.25$) is not a purely stoichiometric phase, but has a considerable homogeneity range of $Ni_{44–49}Sn_{37–44}Zn_{9–14}$ at 973 K (Schmetterer *et al.*, 2012). Liang *et al.* (2011) also mention the existence of a ternary phase with similar composition at 773 K. According to their interpretation this is a stabilization of an incommensurate Ni_3Sn_2 low-temperature phase to higher temperatures. In the light of the present results, however, it is likely to be $Ni_{5-\delta}Sn_4Zn$ ($\delta \sim 0.25$) just as at 973 K. Yuan *et al.* (2011) also report the existence of a ternary phase with a similar composition at 873 K. The stability range of the $Ni_{5-\delta}Sn_4Zn$ ($\delta \sim 0.25$) compound is therefore the subject of ongoing investigations (Rajamohan *et al.*, 2012). In both structures, the Ni sublattice is not fully occupied, since in $Ni_{5-\delta}Sn_4Zn$ ($\delta \sim 0.25$) the Ni2 position has an occupancy significantly below 1. This corresponds to the Ni2** position in Ni_3Sn_2 HT, which is also only partially filled (partially filled $InNi_2$ type).

Experimental

Samples were prepared from the pure metals Ni (99.98%, Advent Research Materials Ltd, Eynsham, Oxfordshire, England), Sn (99.999%, Ventron Alfa Products, Beverly, MA, USA) and Zn (Alfa Aesar, Zn shots, 99.999%). Proper amounts were weighed out and placed in alumina crucibles. They were then sealed in evacuated quartz glass tubes that were flushed with argon before sealing. The use of alumina crucibles was necessary because otherwise frequent breaking of the quartz tubes on quenching after alloying was observed. Alloying was carried out by heating the mixtures to 1453 K. Owing to the use of closed capsules, the loss of Zn by evaporation was negligible. Care had to be taken during cooling of the samples so that material would not be splashed out of the crucible. After alloying, the samples were cut or smashed into several pieces which were again sealed in quartz capsules for equilibrium annealing.

Single crystals were isolated from samples, where the presence of the title compound had been confirmed by powder X-ray diffraction (Bruker D8 powder, Bragg–Brentano geometry, Cu *Kα* radiation).

Crystal data

$Ni_{3.17}Sn_{2.67}Zn_{0.67}$
$M_r = 546.00$
Orthorhombic, *Cmcm*
$a = 4.1520$ (8) Å
$b = 12.603$ (3) Å
$c = 11.657$ (2) Å
$V = 610.0$ (2) $Å^3$
$Z = 6$
Mo *Kα* radiation
$\mu = 34.10$ mm^{-1}
$T = 298$ K
$0.02 \times 0.01 \times 0.01$ mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (120 s, $\Delta = 2$, 626 scans, $dx = 30$)
$T_{min} = 0.6$, $T_{max} = 0.71$
4711 measured reflections
779 independent reflections
693 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.071$
$S = 1.14$
779 reflections
37 parameters
$\Delta\rho_{max} = 1.96$ e $Å^{-3}$
$\Delta\rho_{min} = -2.14$ e $Å^{-3}$

The determination of the distribution of the Ni and Zn atoms is rather impossible using conventional X-ray sources because of the similar scattering power of the two elements, but the final arrangement gave reasonable results and corresponds to the experimentally found composition range determined by scanning electron microscope analysis. The (002) reflection was omitted because of partial overlap with the beam stop. The largest residual electron-density peaks were 0.14, 0.41 and 0.54 Å from the Ni1, Zn1 and Sn2 atoms, respectively.

Data collection: *COLLECT* (Nonius, 2003); cell refinement: *COLLECT*; data reduction: *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ATOMS* (Dowty, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KU3063). Services for accessing these data are described at the back of the journal.

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