

Structure Refinement of Ni₃Sn₄

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Abstract. Ni₃Sn₄, *C2/m*, $a = 12.214$ (6), $b = 4.060$ (2), $c = 5.219$ (3) Å, $\beta = 105.0$ (1)°, $V = 250.0$ Å³, $Z = 2$. The structure was refined from single-crystal X-ray counter data to a conventional R value of 0.056 for 13 variable parameters and 665 structure factors. The original structure determination by Nowotny & Schubert [*Z. Metallkd.* (1946), **37**, 23–31] is confirmed although interatomic distances differ by up to 0.18 Å from the original investigation. Chemical bonding in Ni₃Sn₄ is briefly discussed. It is suggested that the large void in the structure is filled with nonbonding electrons similar to inert pairs in more ionic solids.

Introduction. In the course of our investigations of ternary lanthanoid–nickel–phosphorus systems (Braun & Jeitschko, 1978; Jeitschko & Jaberg, 1980*a,b*) using tin as a flux to grow single crystals of the ternary phosphides, we have frequently observed well developed single crystals of Ni₃Sn₄, especially in samples with high nickel content. The crystal structure of this compound was determined by Nowotny & Schubert (1946) from single-crystal film data. Their trial-and-error refinement of this six-parameter structure led to one rather short Ni–Sn distance. We also decided to refine the structure by least-squares methods from counter data because this compound became of interest as a decomposition product of NiSn on heating, which has found extensive practical application as a corrosion-resistant coating.

The single crystals used for the present investigation were taken from a sample with the overall atomic ratio La:Ni:P:Sn = 3:18:9:70. It was annealed for two weeks at 1000 K and slowly cooled to room temperature at a rate of about 7 K h⁻¹. The tin matrix of the sample was dissolved in concentrated hydrochloric acid. The resulting product consisted mainly of needles of Ni₃Sn₄ with unidentified microcrystalline second- and third-phase material. An X-ray microanalysis of the Ni₃Sn₄ crystals in a scanning electron microscope showed about 1 at.% Si as the only detectable impurity, which presumably was picked up by reduction of the silica tubes. The La and P content of the crystals was less than 0.2 at. %.

Precession photographs showed monoclinic *C2/m* symmetry with the lattice constants refined from Guinier powder patterns and α -quartz ($a = 4.9130$, $c = 5.4046$ Å) as standard. They (see *Abstract*) are within the homogeneity range of Ni₃Sn₄ determined by Nowotny & Schubert (1946).*

The Ni₃Sn₄ crystal used for the collection of the intensity data (length 0.180 mm, diameter 0.020 mm) was mounted with the needle axis approximately parallel to the φ axis of the automated four-circle diffractometer. θ – 2θ scans were taken with graphite-monochromatized Mo $K\alpha$ radiation within one quarter of the reciprocal sphere up to $2\theta = 80^\circ$. The scan speed was 0.05° (2θ) s⁻¹, and the scan width was 2° (2θ). Background was counted for 10 s at both ends of each scan. Because of the small size of the crystal no absorption correction was made ($\mu_{\text{Mo } K\alpha} = 28.8$ mm⁻¹).

The structure was refined in the space group *C2/m* already determined by Nowotny & Schubert (1946). Their positional parameters were used as initial parameters for the full-matrix least-squares refinement with Sheldrick's (1976) program. The scattering factors for neutral atoms (Cromer & Mann, 1968) were corrected for anomalous dispersion (Cromer & Liberman, 1970). Weights were defined by the relation $w = 1/[\sigma^2(F_o) + kF_o^2]$ where k was a least-squares parameter which refined to 0.0073. An isotropic extinction parameter was also refined and applied to the F_c values. The resulting positional and isotropic thermal parameters are listed in Table 1. The corresponding conventional R value is 0.056 for the 665 unique structure factors with $F_o > 3\sigma$ and a total of 13 variables.†

Because Ni₃Sn₄ is known to have a noticeable homogeneity range, we have also refined occupancy parameters for the four atomic sites with a fixed scale factor in one series of least-squares cycles. The re-

* The translation periods given by these authors have to be multiplied by 1.002 to correspond to the present Å unit.

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36340 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic parameters of Ni₃Sn₄

Standard deviations in the least significant digits are given in parentheses. For comparison, the positional parameters reported in the original investigation by Nowotny & Schubert (1946) are given in the lower part of the table.

	<i>C2/m</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Ni(1)	2(<i>a</i>)	0	0	0	0.59 (3)
Ni(2)	4(<i>i</i>)	0.2147 (1)	0	0.3369 (3)	0.65 (2)
Sn(1)	4(<i>i</i>)	0.4286 (1)	0	0.6864 (2)	0.92 (1)
Sn(2)	4(<i>i</i>)	0.1718 (1)	0	0.8123 (2)	0.89 (1)
Ni(1)	2(<i>a</i>)	0	0	0	
Ni(2)	4(<i>i</i>)	0.220	0	0.350	
Sn(1)	4(<i>i</i>)	0.428	0	0.675	
Sn(2)	4(<i>i</i>)	0.180	0	0.800	

sulting occupancy factors for Ni(1), Ni(2), Sn(1), and Sn(2) are (with standard deviations of the least significant digits in parentheses): 1.034 (13), 1.040 (9), 1.000 (7), 0.967 (7). Thus, since Ni has less scattering power than Sn, there is a slight indication that some Sn atoms occupy Ni sites and *vice versa*. As could be expected, positional parameters were practically unchanged in this refinement and the *R* value decreased by only 0.0005. A final difference Fourier synthesis resulted in no features higher than +8.2 or less than -9.1 e Å⁻³. Most of these peaks were close to the atomic sites and are probably due to absorption effects. In a refinement with ellipsoidal thermal parameters these extremes reduced to +6.2 and -4.7 e Å⁻³ but stayed close to their previous positions. The highest electron density at a possible additional atomic site was 3.0 e Å⁻³ at the position which is occupied by Co atoms in CoGe with a 'filled' Ni₃Sn₄ structure. Nevertheless, this low electron density is within the error limits and cannot be taken as a proof for any occupancy of this site.

Discussion. The present refinement confirms the structure determination of Nowotny & Schubert (1946). The least-squares treatment of a large number of diffractometer data, however, resulted in a higher accuracy than the original trial-and-error determination from film data. Thus the short Ni(2)-Sn(2) distance of 2.48₅ Å of the original investigation has now increased to 2.665 ± 0.003 Å and is within the expected range.

The interatomic distances (Table 2) indicate strong nickel-tin interactions: the average Ni-Sn distance of 2.654 Å is much shorter than 2.86 Å, which is the sum of the radii for coordination number (CN) 12. On the other hand, the Ni-Ni distances are all longer than the sum of the CN 12 radii (2.48 Å). The shortest Sn-Sn distance of 2.93 Å comes close to the two-electron bond distance of 2.81 Å in gray (α) tin, but only one other distance is shorter than twice the CN 12 radius of Sn (3.24 Å).

Table 2. Interatomic distances (Å) in Ni₃Sn₄

All distances shorter than 4 Å are listed. Standard deviations are all 0.003 Å or less. Distances from the void position at 0.0, ½ are also given.

Ni(1): 2 Sn(2)	2.535	Sn(1): 2 Ni(1)	2.612
4 Sn(1)	2.612	2 Ni(2)	2.663
2 Ni(2)	2.753	1 Ni(2)	2.772
		1 Sn(1)	2.930
Ni(2): 1 Sn(2)	2.651	2 Sn(2)	3.278
2 Sn(1)	2.663	1 Sn(1)	3.287
1 Sn(2)	2.665	1 Sn(2)	3.367
2 Sn(2)	2.685	2 Sn(2)	3.517
1 Sn(1)	2.772	2 Sn(2)	3.759
2 Ni(2)	2.646		
1 Ni(1)	2.753	Sn(2): 1 Ni(1)	2.535
		1 Ni(2)	2.651
Void: 2 Sn(2)	2.300	1 Ni(2)	2.665
4 Sn(1)	2.503	2 Ni(2)	2.685
2 Ni(1)	2.609	2 Sn(2)	3.110
2 Ni(2)	2.959	2 Sn(1)	3.278
4 Ni(2)	3.931	1 Sn(1)	3.367
		2 Sn(1)	3.517
		2 Sn(1)	3.759

The main structural characteristic of intermetallic phases is the high CN's which result from the lack of valence electrons as compared to the number of orbitals available for bonding. Apparently a better overall overlap of bonding orbitals can be achieved if many atoms surround the central atom at a greater distance rather than a few at a short distance. As a consequence intermetallic phases are usually 'close packed' and in the extreme case - when atoms of different sizes are available - only tetrahedral voids are formed (Frank & Kasper, 1958; Shoemaker & Shoemaker, 1971).

It is therefore surprising that the structure of Ni₃Sn₄ contains a large void with CN 10 (Fig. 1). In the structure of CoGe this void is filled by a Co atom (Bhan & Schubert, 1960). The low electrical conductivity and its temperature dependence (Kleshchinskii, Popov, Romanenko, Sobolev & Sidorov, 1970) suggests that CoGe is a semimetal. Band filling is also indicated for Ni₃Sn₄ by its diamagnetism (Michel, 1963). Thus both compounds seem to have similar band structures, *i.e.* they are isoelectronic if one disregards nonbonding (core) electrons. Since Ni has one more electron than Co, the three additional valence electrons of the three Ni atoms in Ni₃Sn₄ could occupy the same place in the band structure as the (three) electrons of the fourth Co atom in one formula Co₄Ge₄. They are therefore likely to be located in filled orbitals of the Sn atoms pointing at the void position of Ni₃Sn₄ in much the same way as lone pairs take up space in more ionic solids.

It is interesting that the fourth Co atom in Co₄Ge₄ has an approximately octahedral Ge environment which is eminently suited for Co³⁺ with a (low-spin) *d*⁶ system to form six more or less covalent bonds (*via* the

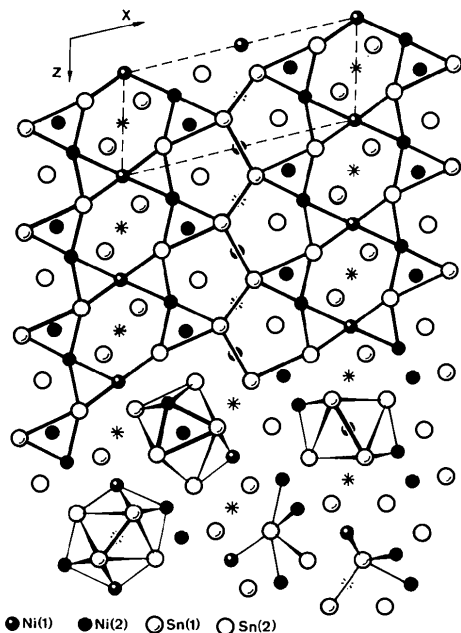


Fig. 1. The crystal structure of Ni₃Sn₄. In the upper part of the drawing atoms at $y = 0$ are connected by thick lines, and atoms at $y = \frac{1}{2}$ are not connected. The positions of the large voids are marked with asterisks. In the lower part of the figure the coordination polyhedra of the Ni atoms and the void position are shown. In the sketches of the near-neighbor environments of the Sn atoms only atoms closer than 3.25 Å are connected to the central atoms.

d^2sp^3 hybrid) to the six Ge neighbors. It is, however, not possible to rationalize the whole structure of CoGe (or Ni₃Sn₄) with classical two-electron bonds.

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Structure of Trirubidium Heptabromodimanganate

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Abstract. Rb₃Mn₂Br₇, tetragonal, $I4/mmm$, $a = 5.37(1)$, $c = 27.80(5)$ Å, $D_o = 3.80$, $D_x = 3.84$ Mg m⁻³, $Z = 2$. The final R was 10.0% for 149 visually estimated reflexions. The structure is composed of discrete double-perovskite-type layers stacked parallel to (001), alternate layers being displaced $a/\sqrt{2}$ in the [110] direction. Mn and Rb(2) ions lie within the layers such that each Mn is octahedrally coordinated by Br ions and each Rb(2) ion is in contact with 12 Br ions. Br ions lying in the surface of a layer are linked to

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Rb(1) ions in the surface of the adjacent layer, each Rb(1) ion being coordinated by nine Br ions. The structure is isomorphous with that of Sr₃Ti₂O₇.

Introduction. A number of complex halides of composition $A_3B_2X_7$ have been reported as having a body-centred tetragonal cell containing two formula units with an axial ratio $c/a \sim 5$. Such structures are likely to be isomorphous with that of Sr₃Ti₂O₇ (Ruddlesden &

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