

Ni_{1.282(4)}Si_{1.284(5)}P₃ or NiSi₂P₃: Two Solutions with Different Atom Distributions for One Single-Crystal X-Ray Data Set, Both Refined to Residuals of Less Than 2.5%

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The crystal structure of NiSi₂P₃ (*Imm*2, *a* = 350.5(1) pm, *b* = 1107.1(3) pm, *c* = 530.7(1) pm, *Z* = 2), previously reported with the composition Ni_{1.68}Si_{0.88}P₃, was redetermined from single-crystal X-ray data. The original structure proposed with mixed Ni/Si occupancy of one atomic site and partial Si occupancy of another site was refined to a residual *R* = 0.023. For the correct model with a different atom distribution and full occupancy of all atomic sites, the residual is 0.020 for 739 structure factors and 21 variable parameters. The structure of NiSi₂P₃ corresponds to a superstructure of the cubic sphalerite with the nickel and silicon atoms occupying the zinc positions of ZnS in an ordered manner, while the positions of the phosphorus atoms correspond to the sulfur positions. Consequently the nickel atoms obtain the oxidation number +1, while the unusually high oxidation number +3.88 is obtained for the composition Ni_{1.282(4)}Si_{1.284(5)}P₃ refined for the incorrect model. © 1995 Academic Press, Inc.

1. INTRODUCTION

The ternary system nickel–silicon–phosphorus was investigated by Il'nitskaya and Kuz'ma, who reported seven ternary phases, and for most of these the crystal structures were established (1). For the composition "Ni_{3.36}Si_{1.76}P₆" (=Ni_{1.68}Si_{0.88}P₃) a tetrahedral structure was reported (2), i.e., a structure where all atoms have four near neighbors in a tetrahedral arrangement. This structure seemed to be unusual in that it violated some rules found for other tetrahedral structures (3, 4). For one atomic position a mixed occupancy was reported: 84 at.% Ni and 16 at.% Si. Another position was found to be occupied solely by silicon atoms but with an occupancy of only 56 at.%. With the structural data reported in the original publication (2) we obtain the unusually high fractional oxidation number +3.26 for the nickel atoms. In the course of our work on polyphosphides (5–7) we thought it worthwhile to reinvestigate this compound. To our sur-

prise the previously reported model of the structure could be refined to an incorrect minimum with a residual of *R* = 0.023. Thus, the selection of the correct structure is based essentially on chemical arguments.

2. SAMPLE PREPARATION AND LATTICE CONSTANTS

Starting materials were powders of nickel and silicon (both with nominal purities 99.9%) and red phosphorus (Hoechst, "ultrapure"). The powders were compacted to cold-pressed pellets and annealed in evacuated and sealed silica tubes. The samples were relatively small with a total phosphorus content of 0.1 g for a tube volume of 3 cm³. To prevent the rupture of the tubes the temperature was raised slowly: 1 day at 450°C, 1 day at 750°C, 5 days at 900°C, and 30 days at 800°C. Finally the tubes were quenched in air.

The first sample had a composition which was close to that reported originally with a ratio of Ni : Si : P = 3 : 2 : 6. This sample contained large amounts of the cubic high-pressure modification of NiP₂ (8, 9), apparently stabilized by silicon. In addition the sample consisted of NiSi₃P₄ (10) and well-developed crystals of NiSi₂P₃, which were used for the structure determination. It resulted in the composition Ni : Si : P = 1 : 2 : 3. Subsequently the compound was also prepared with that atomic ratio.

The samples of NiSi₂P₃ have a shiny gray color, similar to that of elemental silicon. They were investigated in a scanning electron microscope, and the composition of the NiSi₂P₃ crystal used for the structure determination was established with an energy dispersive X-ray fluorescence analysis. No impurity elements heavier than sodium were found. The analyses at four different locations of the crystal varied within the following values, assuming a value of 1.00 for nickel as reference point: Si between 2.00 and 2.68, and P between 2.74 and 4.29. The average Si : P ratio was 2 : 3.1 (±0.7), in rather good agreement with the ideal ratio of 2 : 3.

The samples were characterized by their Guinier pow-

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TABLE 1
Guinier Powder Pattern of NiSi₂P₃^a

<i>h</i>	<i>k</i>	<i>l</i>	<i>H</i>	<i>K</i>	<i>L</i>	<i>Q</i> _o	<i>Q</i> _c	<i>I</i> _o	<i>I</i> _c
0	2	0				325	326	m	9
0	1	1				434	437	m	12
1	1	0				894	896	w	5
0	3	1	1	1	1	1089	1089	vs	99
1	0	1	1	1	1	1170	1169	vs	100
0	4	0				—	1305	—	<1
0	0	2	2	0	0	—	1420	—	<1
1	2	1				1495	1495	w	4
1	3	0	2	0	0	1545	1548	vw	1
0	2	2				1746	1746	vw	2
1	1	2				2317	2316	vw	2
0	5	1				2392	2395	vw	2
1	4	1				2476	2475	vw	2
0	4	2				—	2725	—	1
1	5	0				—	2854	—	<1
0	6	0	2	2	0	2938	2937	s	24
1	3	2	2	2	0	2971	2968	vs	95
2	0	0	2	2	0	3257	3257	m	21
0	1	3				—	3277	—	<1
2	2	0				—	3583	—	<1
2	1	1				3690	3693	vw	1
0	3	3	3	1	1	3930	3929	m	19
1	0	3	3	1	1	4008	4009	m	13
1	6	1	3	1	1	4108	4106	s	32
1	5	2				4272	4274	vw	1
1	2	3				—	4335	—	1
2	3	1	3	1	1	4348	4346	s	27

^a The diagram was recorded with CuK α_1 radiation. The *Q* values are defined by $Q = 100/d^2$ (nm⁻²). For the intensity calculations (11) the positional parameters of the refined structure were used. The second column contains the indices *HKL* of the corresponding sphalerite subcell reflections.

der patterns using α -quartz ($a = 491.30$ pm, $c = 540.46$ pm) as an internal standard. The evaluation of such a pattern is listed in Table 1. The following lattice constants were obtained by a least-squares fit: $a = 350.5(1)$ pm, $b = 1107.1(3)$ pm, $c = 530.7(1)$ pm, and $V = 0.2059$ nm³.

3. STRUCTURE REFINEMENTS

The single crystal used for the data collection on an automated four-circle diffractometer had the dimensions $100 \times 70 \times 50$ μm^3 . Graphite-monochromated MoK α radiation was used with a scintillation counter and a pulse-height discriminator. The scans were along 2θ with background counts on both sides of each scan. An empirical absorption correction was made from psi-scan data. A total of 4330 reflections was measured in the whole reciprocal space to $2\theta = 100^\circ$. The data averaging ($R_i = 0.030$) resulted in 1214 reflections, of which 739 had an intensity of $I_o > 3\sigma(I_o)$.

For the full-matrix least-squares refinements atomic

scattering factors were used (12), corrected for anomalous dispersion (13). An extinction correction parameter was refined, and the weighting scheme included a term which accounted for the counting statistics. The structure was refined in the polar space group *Imm2*, and when we cite residuals we always cite the lower one for the correct handedness.

Many structural models were refined. First we describe the optimization of the originally proposed model (2), which is shown in Table 2A. With our data set of 739 structure factors—using exactly the same (fixed) positional, thermal, and occupancy parameters as reported before and in Table 2A—we obtained a residual of $R = 0.103$. In optimizing this model we varied all parameters which were varied originally and, in addition, we allowed anisotropic displacement parameters for all atoms. This resulted in the surprisingly low residual of $R = 0.023$. The occupancy parameter of the nickel position was found to be 0.8206(9) and that of the silicon position 0.566(2). Assuming the nickel position to be fully occupied by nickel and silicon atoms, this corresponds to the composition Ni_{1.282(4)}Si_{1.284(5)}P₃. The occupancy parameters of the phosphorus atoms were assumed to be ideal, as before (2). A final difference Fourier analysis gave no hint for occupancy of an additional atomic site. The highest residual peak had an electron density of 0.49 e/Å³. The results of this least-squares refinement are listed in Table 2B.

As was already pointed out above, this refinement, although highly acceptable in view of the low residual, was somewhat doubtful from the chemical point of view: mixed and/or fractional occupancies—although frequently observed in typical intermetallic compounds—are rarely found in the predominantly covalently bonded tetrahedral structures, and with our present refinements the nickel atoms obtain the unusually high oxidation number of +3.88! On the other hand, the interatomic distances—usually a reliable indicator of a wrong structure—were all reasonable.

Nevertheless, we refined all possible atom distributions for the four atomic sites determined before, excluding only the extreme compositions NiP₃ and NiSi₅, and assuming full occupancy of all atomic sites. It soon turned out that the nickel atoms can only occupy the $2b$ position with positional parameters similar to those found before for the silicon atom on that site. Not all results can be reported here because of space limitations. As will be discussed further below, the structure with the lowest residual and with the most reasonable occupancy and thermal parameters (which were always refined simultaneously) is also the structure which is most reasonable from a chemical standpoint. The results for the correct structure are listed in Tables 2C and 2D. The results in Table 2C should be compared with those in 2B. These two refinements have the same number of variable param-

TABLE 2
Results of the Least-Squares Refinements^a

Atom	Site	Occupancy (%)	x	y	z	B (10 ⁻² nm ²)
A. Results of Ref. (2): $R = 0.038$ (293 F values, 15 variables); formula Ni _{1.68(4)} Si _{0.88(4)} P ₃						
Ni/Si	4d	84(2)Ni/16(2)Si	0	0.16771(8)	0 ^b	0.97(5)
Si	2b	56	0	1/2	0.0189(15)	0.26(4)
P1	2a	100	0	0	0.2386(5)	0.26(4)
P2	4d	100	0	0.3303(1)	0.2471(3)	0.34(4)
B. Present data, structure model of Ref. (2): $R = 0.023$, $R_w = 0.028$ (739 F values, 23 variables); formula Ni _{1.282(4)} Si _{1.284(5)} P ₃						
Ni/Si	4d	64.1(2)Ni/35.9(2)Si	0	0.16757(3)	0.0000(1)	0.626(4)
Si	2b	56.6(2)	0	1/2	0.0179(2)	0.10(1)
P1	2a	100	0	0	0.2388(2)	0.50(1)
P2	4d	100	0	0.33043(7)	0.248 ^b	0.620(7)
C. Present data, correct solution: $R = 0.018$, $R_w = 0.021$ (739 F values, 23 variables); formula NiSi ₂ P ₃						
Ni	2b	103.6(2)	0	1/2	-0.0088(9)	0.621(3)
Si	4d	99.3(2)	0	0.16505(3)	0.0000(1)	0.431(5)
P1	2a	100	0	0	0.2434(1)	0.590(8)
P2	4d	100	0	0.33630(3)	0.234 ^b	0.418(5)
D. Present data, correct solution with ideal occupancy values after STRUCTURE TIDY (14): $R = 0.020$, $R_w = 0.025$ (739 F values, 21 variables); formula NiSi ₂ P ₃						
Ni	2b	100	0	1/2	0.2516(1)	0.607(4)
Si	4d	100	0	0.16512(3)	0.2435(1)	0.532(6)
P1	4d	100	0	0.33617(4)	0.009 ^b	0.489(6)
P2	2a	100	0	0	0.0000(1)	0.662(9)

^a The last column lists the equivalent thermal parameters B with the exception of the refinement in A, where the light atoms were refined with isotropic B values. The residuals R and R_w are the conventional residual on F values and the weighted residual, respectively. The weights are defined by $w = F_o^2/(\sigma_f^2 + 0.03F_o^2)$.

^b This parameter was held constant to fix the origin of the cell.

eters. The refinement in Table 2D was obtained with the ideal occupancy parameters and with the equivalent standardized setting obtained with the program STRUCTURE TIDY (14). The residual of this refinement is 0.020 for the correct handedness, and for the incorrect handedness it increases to $R = 0.044$. A final difference Fourier synthesis for the correct solution of the structure resulted in an electron density of 0.52 e/Å³ for the highest residual peak. Listings of the structure factors and anisotropic thermal parameters are available from the authors. The structure is shown in Fig. 1 and the interatomic distances are listed in Table 3.

4. DISCUSSION

As already noted above, the structure of this nickel–silicon–phosphorus compound was originally refined to a low residual value with an incorrect atom distribution. Our refinement of that wrong model resulted in the composition Ni_{1.282(4)}Si_{1.284(5)}P₃ with a residual of $R = 0.023$. We do not know of any structure determination with such a low residual for a substantially incorrect structure. Obviously, the low residual for the incorrect structure results from the fact that the atomic positions of both models are the same and correspond to those of the sphalerite structure. The atomic order is reflected mainly by the

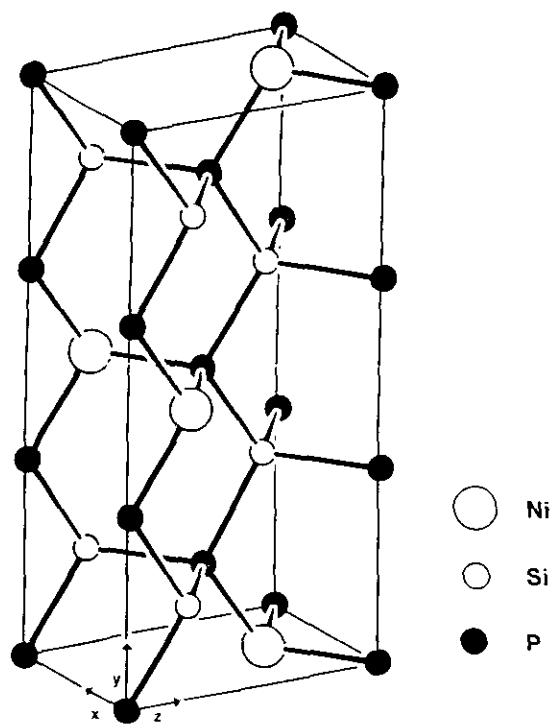


FIG. 1. One unit cell of NiSi₂P₃. All atoms are tetrahedrally coordinated.

TABLE 3
Interatomic Distances in NiSi₂P₃^a

Ni	2P2	219.3	P1	1Ni	222.4
	2P1	222.4		2Si	224.9
Si	1P2	223.9	P2	1Si	226.6
	2P1	224.9		2Ni	219.3
	1P1	226.6		2Si	223.9

^a All atomic distances shorter than 300 pm are listed. Standard deviations are all equal to or less than 0.1 pm.

weak superstructure reflections, and apparently for many of these the absolute values of the structure factors are similar for both models, while the phases may be different. This, however, was not worked out in detail. Our model with the composition NiSi₂P₃ and a residual of $R = 0.020$ is to be preferred not only because of the slightly lower residual and the more reasonable occupancy and thermal parameters, but also, more importantly, for the more plausible structural chemistry with full occupancy of all atomic sites and the more reasonable oxidation number for the nickel atoms. It also agrees with the EDAX analysis and with the placement of this composition in the reported phase diagram of the system nickel–silicon–phosphorus (1).

In both models the more electropositive nickel and silicon atoms have only the more electronegative phosphorus

atoms as neighbors, and these are the only atom distributions for the four sites of the structure where the nickel atoms have no silicon neighbors. The difference between the two models lies essentially in the interchange of the silicon and nickel positions. The refinement of the occupancy parameters resulted in the full occupancy of all positions for the correct model. In contrast, for the incorrect model, the position of the silicon atoms is found to be occupied to only 56.6(2)%, even though this is the position of the heavier nickel atoms in the correct structure! Thus, we have an unusual situation in which the refinement of this occupancy parameter leads away from the correct solution. This may explain how the incorrect model was considered to be correct by the previous investigators.

The structure of NiSi₂P₃ belongs to a large family of tetrahedral structures (3, 4) where all atoms have tetrahedral coordination. The unit cell and the atomic positions of this structure actually are the same as found previously for Cu₂GeSe₃ (15); however, the copper positions of the latter compound are occupied by the silicon atoms of NiSi₂P₃. In that sense the structure of NiSi₂P₃ may be considered as a partial “anti”-type of Cu₂GeSe₃, while the incorrect model of our nickel–phosphorus compound with the ideal composition Ni₂SiP₃ would be completely isotypic with Cu₂GeSe₃. A similar case of such a partial anti-type relationship is known for the compounds NiSi₃P₄ (10) and Cu₃AsS₄ (16).

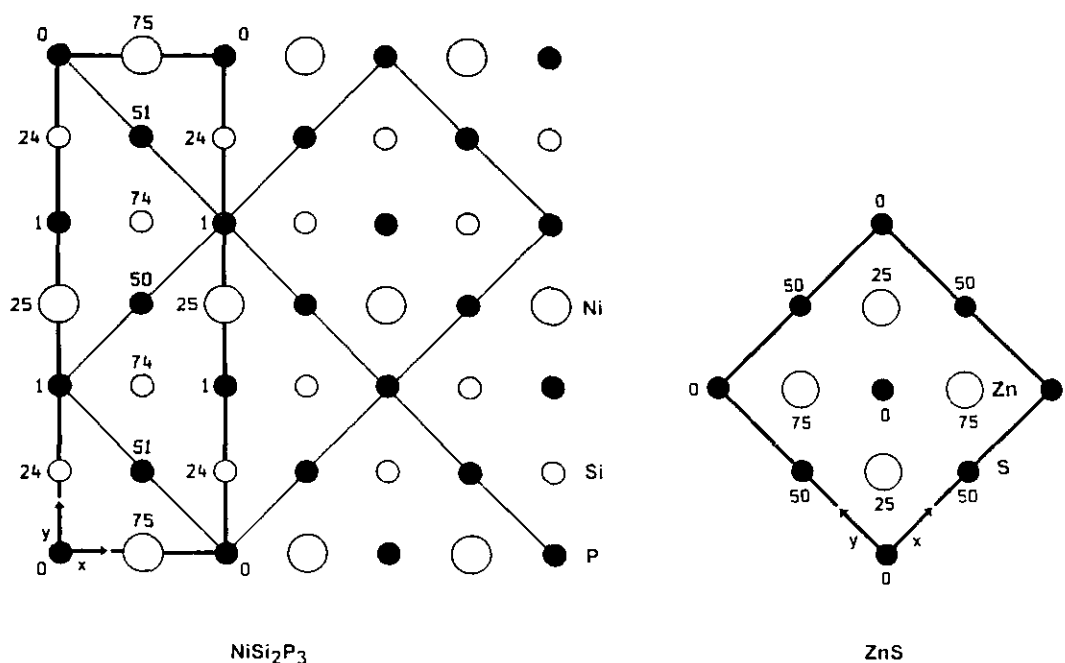


FIG. 2. The crystal structure of NiSi₂P₃ as compared to the cubic zinc blende structure. The heights of the atoms in the projection direction are given in hundredths.

Both of these structures are superstructures of the cubic zinc sulfide (sphalerite) structure, and this is also the case for NiSi_2P_3 , as demonstrated in Fig. 2. It can be seen that the nickel and silicon atoms occupy the positions of the zinc atoms of sphalerite in an ordered manner, while the positions of the phosphorus atoms correspond to the sulfur sites. The approximate lattice constants of the orthorhombic structure of NiSi_2P_3 can be obtained from the cubic ZnS lattice constant a_{ZnS} by the relations $a = a_{\text{ZnS}}/\sqrt{2}$, $b = 3a_{\text{ZnS}}/\sqrt{2}$, and $c = a_{\text{ZnS}}$. As can be seen from the powder pattern (Table 1) the sphalerite subcell is pronounced; nevertheless, many superstructure reflections can be observed. The semiconducting compounds CuSi_2P_3 (17) and CuGe_2P_3 (17, 18) were reported to crystallize with a disordered sphalerite structure. It seems possible that they are isotypic with NiSi_2P_3 . For CuGe_2P_3 the superstructure may be very difficult to observe, because copper and germanium have very similar scattering power; however, the orthorhombic distortion may be detectable from the line splitting.

Since phosphorus is the most electronegative component of NiSi_2P_3 and since the phosphorus atoms do not form P–P bonds, they obtain the oxidation number -3 , while $+4$ may be ascribed to the silicon atoms. As a result, the nickel atoms obtain the oxidation number $+1$, corresponding to the formula $\text{Ni}^+(\text{Si}^{+4})_2(\text{P}^{-3})_3$. The most common oxidation number of nickel is $+2$; however, Ni^+ with tetrahedral coordination has been observed before in $\text{Ni}(\text{PPh}_3)_3\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) (19), $\text{Ni}[\text{MeC}(\text{CH}_2\text{PPh}_2)_3]\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) (20), $\text{Ni}[\text{MeC}(\text{CH}_2\text{PPh}_2)_3]\text{I}$ (20, 21), and $[\text{Ni}(\text{PMe}_3)_4]\text{BPh}_4$ (22). The crystal structures for the latter two compounds were determined. There the Ni–P distances range between 221.1(3) and 222.4(4) pm, in good agreement with the corresponding distances of 219.3(1) and 222.4(1) pm in NiSi_2P_3 . The Si–P bond distances in this tetrahedral compound are between 223.9(1) and 226.6(1) pm, which is in good agreement with the range of the average bond distances varying between 223 and 227 pm in ZnSiP_2 (23), CeSiP_3 (24), AlSiP_3 (25), Ba_4SiP_4 (26), $\text{Sn}_{4.2}\text{Si}_9\text{P}_{16}$ (27), and NiSi_3P_4 (10).

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