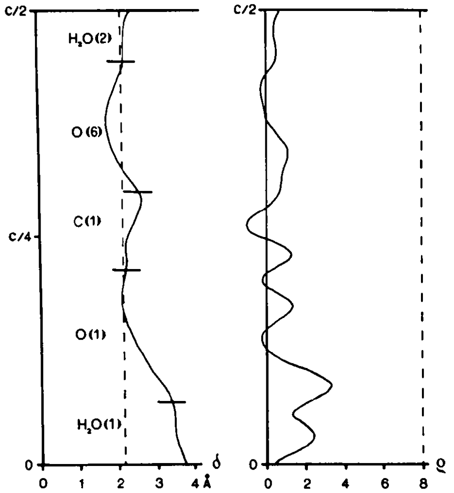

Fig. 2. Plots of: δ, minimum distances from the threefold axis (the broken line represents the minimum H bond); ρ, electron density, on a relative scale, along the same axis, in the interval $0 \leq z \leq \frac{1}{2}$ (the broken line represents the average O electron density).

with the inability of C to form H bonds. There is no evidence in disagreement with our hypothesis, and – with caution – the more likely locations of the last water molecule may be inferred.

Probably, the water distributed in the channel is important for the stability of the entire crystal building.

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Orthorhombic Gadolinium Nickel Silicide Gd_3NiSi_2 with a Filled-up Hf_3P_2 Structure Type

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Abstract

Gd_3NiSi_2 is orthorhombic, space group *Pnma*, with $a = 11{\cdot}398\ (4)$, $b = 4{\cdot}155\ (1)$, $c = 11{\cdot}310\ (1)$ Å, $Z = 4$, $D_x = 7{\cdot}27$ Mg m^{-3}, $\mu(\text{Mo } K\alpha) = 41{\cdot}5$ mm^{-1}, $F(000) = 992$. $R = 0{\cdot}059$ (542 F_o). The rare-earth atoms form trigonal prisms centered by Ni and Si atoms. The Gd and Si arrangement corresponds to that for Hf and P reported for Hf_3P_2. The Ni atoms occupy trigonal prismatic holes leading to the formation of infinite isotactic Si branched chains, –Si–Ni(Si)–, running parallel to **b**. The trigonal prisms are deformed in a

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systematic way. Those centered by Ni are compressed, those containing Si are elongated in accordance with the relative trigonal prism dimensions reported for the binary *R*Ni and *R*Si compounds with FeB or CrB structure types.

Introduction

In an attempt to find new FeB–CrB stacking variants several pseudobinary sections *R*Ni–*R*′Ni (*R* = rare-earth atom or Y), *R*Pd–*R*Ni and *R*Pt–*R*Ni have been investigated (Klepp & Parthé, 1980, 1981*a*,*b*). All these compounds contain compressed transition-metal-centered trigonal prisms of rare-earth atoms of type II (Hohnke & Parthé, 1966). In *R*Si on the other hand, elongated prisms of type I are found. It was of interest to find out whether mixed stacking variants of the FeB–CrB type were possible even if the binary end members have different prism types. For this reason the system GdNi–GdSi was studied where GdNi crystallizes with the CrB-II type and GdSi with the FeB-I type. No FeB–CrB stacking variants were found in this system. Instead a new phase lying on this section was observed, whose crystal structure will be presented in this paper.

Experimental

Several examples in the section GdNi$_x$Si$_{1-x}$ were prepared by arc melting under an atmosphere of purified Ar. High-purity elements were used as starting materials (Gd: 99·9%, Ni: 99·99%, Si: 99·999%). The ingots obtained were wrapped with Ta foil, sealed into evacuated silica capsules and annealed at 1070 K for two weeks.

A preliminary inspection of the powder diagrams indicated the appearance of a new ternary phase in the region x = 0·2–0·6. Single crystals could be isolated from a sample with nominal composition GdNi$_{0\cdot5}$Si$_{0\cdot5}$.

Crystallographic investigations revealed orthorhombic symmetry with systematic absences $hk0$: $h = 2n + 1$, $0kl$: $k + l = 2n + 1$, indicating *Pnma* or $Pn2_1a$ as possible space groups. For the determination of lattice constants and the collection of intensities a single crystal of irregular shape (50 × 40 × 30 μm) was mounted on an automatic four-circle diffractometer (Philips PW 1100). The cell dimensions were obtained by least squares from the 2θ values of 36 centered reflections. The data collection was carried out with graphite-monochromated Mo $K\alpha$ radiation (λ = 0·71069 Å) and the θ–2θ scan mode ($6 \leq 2\theta \leq 54°$). 664 reflections were measured from which 542 with $I > 3\sigma(I)$ were considered as observed. The intensities were corrected for Lorentz and polarization factors and a spherical absorption correction (μR = 0·8) was applied.

Structure determination and refinement

The structure was solved by direct methods with *SINGEN* and *PHASE* of the XRAY system (1976) which generated the phases of 121 reflections with $|E(hkl)|$ > 1·4. The positions of the Gd and Ni atoms were revealed in the corresponding E map, while the Si positions were obtained by difference syntheses. A preliminary least-squares refinement in the centrosymmetric space group, which was suggested by the Wilson statistics, converged to R = 0·073 (isotropic temperature factors). Introduction of anisotropic thermal parameters and application of a correction for isotropic secondary extinction led to a final $R = \sum |F_o - F_c|/\sum |F_o|$ = 0·059 [R_w = 0·070, $w = 1/\sigma^2(F)$] for 37 refined parameters. A difference synthesis showed no physically significant peaks. All calculations were performed with the XRAY system (1976). Scattering factors for neutral atoms were those of Cromer & Mann (1968); anomalous-dispersion corrections were from *International Tables for X-ray Crystallography* (1974). The final atomic positions and the equivalent isotropic temperature factors are listed in Table 1.*

Discussion

A projection of the crystal structure along its short axis is shown in Fig. 1(*a*). The structure is characterized by Ni- or Si-centered trigonal prisms of Gd atoms. Three different types of centered trigonal prisms can be distinguished. Those centered by Si(1) and Ni have their trigonal axes in the (010) plane; the axis of the Si(2)-centered prism is perpendicular to (010). The former two prisms share lateral faces with each other, which leads to the formation of the –Ni–Si–Ni–Si– zigzag chains parallel to **b**. The Si(2)-centered prisms have one rectangular face in common with the Ni-centered prisms which allows further short Ni–Si

Table 1. *Atomic positions and equivalent thermal parameters* (×10^4) *for* Gd$_3$NiSi$_2$

U_{eq}'s are expressed as $T = \exp[-2\pi^2 . 10^{-2}\, U(2\sin\theta/\lambda)^2]$ and were obtained from $U = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq} (Å^2)
Gd(1)	0·3814 (2)	0·25	0·4403 (2)	59 (6)
Gd(2)	0·0576 (2)	0·25	0·3750 (2)	60 (6)
Gd(3)	0·2137 (2)	0·25	0·6976 (2)	69 (6)
Ni	0·1285 (5)	0·25	0·1334 (5)	60 (20)
Si(1)	0·473 (1)	0·25	0·685 (1)	70 (30)
Si(2)	0·303 (1)	0·25	0·005 (1)	110 (40)

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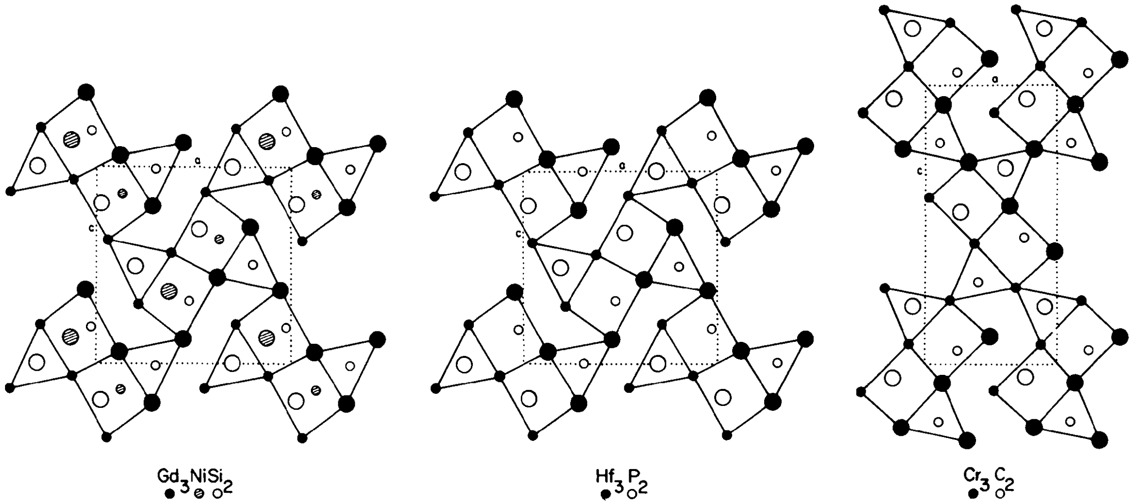
* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36033 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

distances. Thus the arrangement of the Ni and Si atoms can be described as an infinite, Si(2)-branched isotactic chain, —Si—Ni(Si)—. No other ternary structure is known with such a chain. However, a homoatomic chain of this type is formed by B atoms in $Ru_{11}B_8$ (Åselius, 1960).

The structure of Gd_3NiSi_2 can be related to that of Hf_3P_2 (Lundström, 1968), Fig. 1(*b*). This structure type is also found with Hf_3As_2 (Rundqvist & Carlsson, 1968), Zr_3As_2 (Carlsson, Gölin & Rundqvist, 1976) and with Sc_3P_2 and Sc_3As_2 (Berger, 1980). The two structure types have the same space group, similar unit-cell ratios and atomic coordinates, except that in Hf_3P_2 one third of the trigonal prismatic sites, corresponding to those of Ni in Gd_3NiSi_2, remain unoccupied. Hence no P chains are formed in Hf_3P_2, which is in accordance with the weaker tendency of self-catenation of the Group V elements. Gd_3NiSi_2 may therefore be regarded as a filled-up derivative structure of the Hf_3P_2 type.

Another structure which is related to Hf_3P_2 is Cr_3C_2 (Rundqvist & Runnsjö, 1969), Fig. 1(*c*). It is composed of analogous columnar building blocks and differs only in the way in which these blocks are linked with each other. The close relationship between Hf_3P_2 and the Cr_3C_2 structure type is further demonstrated by their coexistence in Sc_3P_2 and Sc_3As_2 (Berger, 1980). Thus, in contrast to earlier assumptions by Lundström (1968) and Shoemaker (1973), the radius ratio of the constituent atoms does not seem to be the criterion which controls the choice between these two structure types. The close relationship is also reflected in the derivation of their prism linkage coefficients (Parthé & Moreau, 1977), Table 2. It appears therefore reasonable to speculate that a filled-up derivative structure of the Cr_3C_2 structure type may also exist.

The interatomic distances, Table 3, show that the coordination figure around Ni and Si is a tricapped trigonal prism. Since Ni is the branching point of the mixed chain, it has three close Si neighbors in addition to the six Gd atoms which form the trigonal prism. The additional coordination partners of Si(1) are the two Ni atoms of the chain and one further Gd atom, the latter contact being created by waist contact with a prism from an adjacent building block. Si(2) has only one Ni neighbor and two Gd neighbors from waist contacts. In



(*a*) (*b*) (*c*)

Fig. 1. Projections of the crystal structures of (*a*) Gd_3NiSi_2, (*b*) Hf_3P_2 and (*c*) Cr_3C_2 along [010]. Atoms at $y = \frac{3}{4}$ are indicated by large circles, those at $y = \frac{1}{4}$ by small circles. The origin of the cell of Hf_3P_2 has been shifted by $\frac{1}{2}$,0,0 to correspond with the origin of the unit cell chosen for Gd_3NiSi_2.

Table 2. *Calculation of the prism linkage coefficients for the* Gd_3NiSi_2, Hf_3P_2 *and* Cr_3C_2 *structure type*

Gd_3NiSi_2
Pnma
All atoms in equipoint 4(*c*)

	Gd(1)	Gd(2)	Gd(3)
Si(1)	3	2	1
Si(2)	2	2	2
Ni	3	1	2
	8	5	5

LC = 4 × (8 + 5 + 5)/12 = 6
$Gd_6M_{LC} = Gd_6M_6 = Gd_3NiSi_2$

Hf_3P_2
Pnma
All atoms in equipoint 4(*c*)

	Hf(1)	Hf(2)	Hf(3)
P(1)	2	2	2
P(2)	2	3	1
	4	5	3

LC = 4 × (4 + 5 + 3)/12 = 4
$Hf_6P_{LC} = Hf_6P_4 = Hf_3P_2$

Cr_3C_2
Pnma
All atoms in equipoint 4(*c*)

	Cr(1)	Cr(2)	Cr(3)
C(1)	2	2	2
C(2)	2	1	3
	4	3	5

LC = 4 × (4 + 3 + 5)/12 = 4
$Cr_6C_{LC} = Cr_6C_4 = Cr_3C_2$

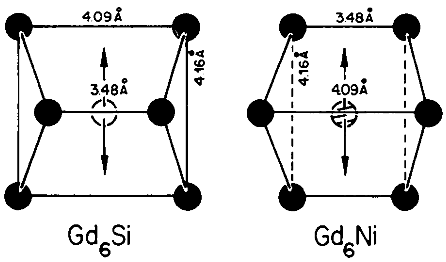
Table 3. *Interatomic distances* (Å) *for* Gd_3NiSi_2 *up to* 4·3 Å

E.s.d.'s are given in parentheses and refer to the last significant figure. The Gd atoms forming the surrounding trigonal prism are marked with asterisks.

Gd(1)–Ni	2·937 (6)	Gd(2)–Ni	2·850 (6)	Gd(3)–2Ni	2·843 (4)
–2Ni	3·016 (4)				
		–2Si(2)	3·001 (9)	–Si(1)	2·96 (1)
–Si(1)	2·96 (1)	–2Si(1)	3·011 (9)	–2Si(2)	3·02 (1)
–2Si(1)	3·010 (9)	–Si(2)	3·20 (1)	–Si(1)	3·05 (1)
–2Si(2)	3·044 (9)			–Si(2)	3·62 (1)
		–2Gd(2)	3·747 (3)		
–Gd(3)	3·482 (3)	–Gd(1)	3·764 (3)	–Gd(1)	3·482 (3)
–2Gd(3)	3·609 (3)	–2Gd(3)	3·814 (3)	–2Gd(1)	3·609 (3)
–2Gd(1)	3·668 (3)	–2Gd(3)	3·891 (3)	–2Gd(2)	3·814 (3)
–Gd(2)	3·764 (3)	–Gd(3)	4·060 (3)	–2Gd(2)	3·891 (3)
–Gd(2)	4·092 (3)	–Gd(1)	4·092 (3)	–Gd(2)	4·060 (3)
–2Gd(1)	4·155 (1)	–2Gd(2)	4·155 (1)	–2Gd(3)	4·155 (1)
Ni–2Gd(3)*	2·843 (4)	Si(1)–Gd(1)*	2·96 (1)	Si(2)–2Gd(2)*	3·001 (9)
–Gd(2)*	2·850 (6)	–Gd(3)*	2·96 (1)	–2Gd(3)*	3·02 (1)
–Gd(1)*	2·937 (6)	–2Gd(1)*	3·010 (9)	–2Gd(1)*	3·044 (9)
–2Gd(1)*	3·016 (4)	–2Gd(2)*	3·011 (9)	–Gd(2)	3·20 (1)
		–Gd(3)	3·05 (1)	–Gd(3)	3·62 (1)
–2Si(1)	2·449 (7)				
–Si(2)	2·46 (1)	–2Ni	2·449 (7)	–Ni	2·46 (1)
–Si(1)	4·01 (1)	–Ni	4·01 (1)		
				–Si(1)	4·11 (2)
–2Ni	4·155 (1)	–Si(2)	4·11 (2)	–2Si(2)	4·155 (1)
		–2Si(1)	4·155 (1)	–Si(1)	4·29 (2)
		–2Si(2)	4·29 (2)		

contrast to Si(1), the Si–Gd distances due to the waist contacts are larger (3·20 and 3·68 Å) than the Gd–Si distances within the Si(2)Gd_6 prism. The average Gd–Ni and Gd–Si distances [$\bar{d}_{\text{Gd–Ni}} = 2{\cdot}92$, $\bar{d}_{\text{Gd–Si(1)}} = 3{\cdot}00$ and $\bar{d}_{\text{Gd–Si(2)}} = 3{\cdot}02$ Å with waist contacts omitted] are smaller than the sum of the metallic radii ($r_{\text{Gd}} + r_{\text{Ni}} = 3{\cdot}03$, $r_{\text{Gd}} + r_{\text{Si}} = 3{\cdot}11$ Å). Ni–Si(1) and Ni–Si(2) are practically identical (2·45 and 2·46 Å) and shorter by 0·1 Å than the sum of the metallic radii (2·56 Å). The Si–Ni angle within the chain is 116·0 (5) and the Si(1)–Ni–Si(2) angle 121·5 (3)°. Si(2) is slightly tilted out of the plane defined by the atoms of the zigzag chain. Each of the three different Gd atoms is coordinated by 17 neighbors (up to 4·3 Å). The ratio of homoatomic *vs* heteroatomic neighbors is, however, different for the Gd atoms. The highest number of Gd neighbors is found with the Gd(2) atoms which form the link between the columnar building blocks, whereas the highest number of heteroatomic neighbors is found with the Gd(1) atoms which form the common triangular face of the Si(1)- and Ni-centered prisms.

Fig. 1(*a*) shows that the prisms centered on the Si(1) and those on the Ni atoms are deformed in a different way. In Fig. 2 the two prisms are shown on a larger scale. The different deformations of the Si(1)- and Ni-centered prisms can be explained in a qualitative way by making reference to the relative prism dimensions in equiatomic *R*Si and *R*Ni compounds with FeB or CrB structure type. Hohnke & Parthé (1966) showed that in FeB- and CrB-type structures the relative prism dimensions, expressed as the ratio of prism height to width of the prism parallel to the chain of atoms centering the prisms, allow one to classify the compounds into two groups. Group I compounds with prism ratios >0·95 have elongated prisms and are found with *R*Si, *R*Ge and *R*Ga compounds, group II compounds with prism ratios <0·95 have compressed prisms and are found with *R*Ni, *R*Pt, *R*Cu and *R*Rh compounds. Also in Gd_3NiSi_2 the Ni atoms prefer compressed prisms and the Si atoms elongated prisms. Since Ni- and Si-centered prisms are joined by common lateral prism faces, a compromise is obtained by deforming the prisms as shown in Fig. 2.



$$\frac{\text{prism height}}{\text{prism width}} = \frac{4{\cdot}09}{4{\cdot}16} = 0{\cdot}98 \qquad \frac{\text{prism height}}{\text{prism width}} = \frac{3{\cdot}48}{4{\cdot}16} = 0{\cdot}83$$

Fig. 2. The deformed trigonal prisms around Si(1) and Ni atoms. The arrows indicate the direction of the infinite –Si–Ni– chain.

The ternary systems R–T–M (R = rare-earth metal, T = transition metal, M = main-group element of Groups III and IV) have been and are still being intensively investigated. However, only a few phases with composition RT_xM_{1-x} have been detected so far, namely hexagonal R_2NiSi (R = La, Ce, Pr) (Gladyshevskii, Bodak & Mys'kiv, 1972), Ho_5Ni_4Ga (Yarmolyuk & Grin', 1977), $R_{10}Co_7Ga_3$ (R = La, Y) (Grin', Yarmolyuk & Gladyshevskii, 1979) and $Ce_7Ni_2Si_5$ (Mys'kiv, 1974). The latter two, also crystallizing with space group *Pnma*, show structural principles similar to Gd_3NiSi_2. Their structures are exclusively built up by centered trigonal rare-earth prisms, whose axes are parallel and normal to [010]. The small central atoms form branched chains, which are, however, of a more complex type than those of Gd_3NiSi_2.

Only a few intermediate ternary phases have so far been reported for the Gd—Ni—Si system. $GdNi_2Si_2$ (Bodak, Gladyshevskii & Kripyakevich, 1966) crystallizing with the tetragonal $ThCr_2Si_2$ structure type, $Gd_3Ni_6Si_2$ (Gladyshevskii, Kripyakevich & Bodak, 1966) crystallizing with an ordered cubic Ca_3Ag_8 structure type, $GdNiSi_2$ with the orthorhombic $CeNiSi_2$ type (Bodak & Gladyshevskii, 1970) and finally $Gd(Ni,Si)_{13}$ (Bodak & Gladyshevskii, 1969*a*) with the hexagonal $NaZn_{13}$ structure type. In view of the large number of intermediate phases reported for the related Ce—Ni—Si (Bodak & Gladyshevskii, 1969*b*; Bodak, Gladyshevskii, Tyvanchuk, Kharchenko & Mys'kiv, 1973), it appears reasonable to expect a large number of ternary phases also for the Gd—Ni—Si system.

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