Y_5Bi_3 are higher than those of the corresponding sites in U_3S_5. Effectively, in both compounds all three atoms capping the trigonal prisms are at relatively short distances, two atoms now cap faces of the distorted octahedra. Some of the square pyramids are transformed into octahedra by the approach of a sixth atom and the tetrahedra change into trigonal bipyramids in a similar way. Atoms of the same atomic species should be included in the first coordination shell of the majority atoms for these compounds.

For all iono-covalent compounds and their metallic *anti*-types treated above, the majority atoms are larger than the minority atoms. This is not the case for the compounds belonging to the third group, *i.e.* the strongly distorted intermetallic compounds with the same stoichiometry as the iono-covalent compounds. The interchange in the size of the atoms explains the important distortions observed with respect to the structures of the first two groups of compounds. In Tm_3Ga_5 the homonuclear Ga—Ga distances are shorter than the heteronuclear distances and the Ga atoms of the TPv sites are displaced out of the square pyramids into Tm_4Ga_2 trigonal prisms. The numbers of heteronuclear contacts of the Tm sites are, as expected, higher than for corresponding sites in the chalcogenides and pnictides, ten for the TPc site and nine for the HPb site, respectively.

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Monoclinic NdRuSi₂, a Distortion Derivative of Orthorhombic CeNiSi₂

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Abstract. Neodymium ruthenium disilicide, $M_r = 301.48$, monoclinic, $mP8$, $P2_1/m - e^4$ (No. 11), $a = 4.4620\,(6)$, $b = 4.0451\,(6)$, $c = 8.242\,(2)$ Å, $\beta = 102.23\,(1)°$, $V = 145.39\,(5)$ Å³, $Z = 2$, $D_x = 6.887$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 22.065$ mm⁻¹, $F(000) = 264$, $T = 293$ K, $wR = 0.040$ for 459 contributing unique reflections. The structure is isopointal with $TmLi_{1-x}Ge_2$ ($x = 0.5$), both being distortion variants of the orthorhombic $CeNiSi_2$-type structure. Opposite to what is observed for $TmLi_{0.5}Ge_2$, the distortions in $NdRuSi_2$ are such that all non-metal atoms take part in infinite zigzag chains. Ru—Ru distances of 3.08 Å exist.

Introduction. No systematic investigations of the Nd–Ru–Si system have been reported. The only

compound which has been identified so far is tetragonal $NdRu_2Si_2$ (Ballestracci & Astier, 1978), crystallizing with the $ThCr_2Si_2$ (Ban & Sikirica, 1965) or $CeAl_2Ga_2$-type structure (Zarechnyuk, Kripyakevich & Gladyshevskii, 1965), an ordered substitution variant of the $BaAl_4$-type structure (Andress & Alberti, 1935).

As a guide-line in the search for new ternary intermetallic compounds one can make use of the observation that many compounds in rare-earth–transition-metal–main-group element systems are constructed from intergrown segments characteristic of simple parent structures, which are often found in the same or in related phase diagrams. A large number of ternary intergrowth structures are known where slabs or columns with an atom arrangement corresponding to the $ThCr_2Si_2$ type, or its disordered version the $BaAl_4$ type, are intergrown with segments from other parent structures such as W, Cu or AlB_2.

Since binary $NdSi_2$ crystallizes at high temperature (Brauer & Haag, 1952) with the tetragonal α-$ThSi_2$ type, a stacking variant of AlB_2, and adopts at low temperature (Mayer, Yanir & Shidlovsky, 1967) the $GdSi_2$ type, an orthorhombic deformation derivative of α-$ThSi_2$, it seemed of interest to investigate if for composition $NdRuSi_2$ a structure, where $ThCr_2Si_2$-type slabs are intergrown with AlB_2-type slabs, occurs. Such an atom arrangement, known as the $CeNiSi_2$ structure type (Bodak & Gladyshevskii, 1970), or $BaCuSn_2$ type (May & Schäfer, 1974), has been observed for several silicides and germanides. Various variants of the $CeNiSi_2$ type exist. They are the $TbFeSi_2$ structure with a site exchange between transition-metal and main-group elements in the $ThCr_2Si_2$-type slab (Yarovets & Gorelenko, 1981), the non-stoichiometric $CeNi_{1-x}Si_2$ or $CeNi_{1-x}Si_{2+x}$ structures with vacancies or mixed occupation on the transition-metal site (Dörrscheidt, Savelsberg, Stöhr & Schäfer, 1982; Chabot, Parthé & Steinmetz, 1986), the $CeRh_{1-x}Ge_{2+x}$ structure with a primitive orthorhombic cell and disordered substitution on half of the transition-metal sites (Bodak, Seropegin, Sologub, Pecharskii & Gribanov, 1989), and the $TmLi_{1-x}Ge_2$ structure, a monoclinic distortion variant (Pavlyuk, Bodak, Pecharskii & Gladyshevskii, 1989). Of the related ternary $NdTSi_2$ compounds, two of them: $NdMnSi_2$ and $NdFeSi_2$ (Venturini, Malaman, Meot-Meyer, Fruchart, Le Caer, Malterre & Roques, 1986) have been reported with a $TbFeSi_2$-type structure and four: $NdCoSi_2$ (Pelizzone, Braun & Muller, 1982), $NdNiSi_2$ (Bodak & Gladyshevskii, 1970), $NdRhSi_2$ and $NdIrSi_2$ (Chevalier, Lejay, Etourneau, Vlasse & Hagenmuller, 1982) with a $CeNiSi_2$-type structure. However, the actual site occupation in the last two compounds needs to be verified. An unusual site occupation was reported for $NdCu_{1.6}Si_{1.4}$ (Bodak, Gladyshevskii & Kalychak,

1971), which crystallizes in a $TbFeSi_2$-type structure with a mixed occupation of the trigonal prismatic site inside the AlB_2-type slabs.

Experimental. Single crystals were found in a sample of nominal composition $Nd_{25}Ru_{25}Si_{50}$, prepared from Nd (99.9%), Ru (99.999%) and Si (99.999%) by arc melting under an argon atmosphere (weight loss 0.4%) and annealed at 1073 K for two weeks in a silica tube under vacuum, and quenched in water. A single crystal [dimensions $\pm$ (100) 0.088, $\pm$ (010) 0.050, $\pm$ (001) 0.030 mm] was mounted on a Philips PW 1100 automatic four-circle diffractometer, Mo $K\alpha$ radiation with graphite monochromator. The unit-cell parameters were refined from 2θ values of 22 reflections (Mo $K\alpha$, $\lambda = 0.71073$ Å, $20 < 2\theta < 38°$). 1026 reflections were collected out to $(\sin\theta/\lambda) = 0.704$ Å^{-1} ($-6 \le h \le 6$, $0 \le k \le 5$, $0 \le l \le 11$ and the anti-reflections) in the ω–2θ-scan mode, yielding 482 unique reflections $(R_{int} = 0.038)$. Two standard reflections, 020 and $\bar{1}\bar{1}1$, were measured with maximum intensity variations 0.4%. Absorption correction was made using the program $LSABS$ (Blanc, Schwarzenbach & Flack, 1991) with maximum and minimum transmission factors of 0.5351 and 0.2465. The anomalous-dispersion coefficients were taken from $International Tables for X-ray Crystallography$ (1974, Vol. IV). Systematic absences led to the following possible space groups: $P2_1$ and $P2_1/m$ ($International Tables for Crystallography$, 1983, Vol. A). The structure was solved in space group $P2_1/m$ by the $MULTAN$87 program (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987) and confirmed by the structure refinement, based on $|F|$ values using the program $CRYLSQ$ (Olthof-Hazekamp, 1990). 26 variables including anisotropic atomic displacement parameters refined to $R = 0.049$ and $wR = 0.040$ [$w = 1/\sigma^2(|F_{rel}|)$, $S = 2.824$] considering 459 contributing unique reflections with $|F_{rel}| > 3\sigma(|F_{rel}|)$. Secondary-extinction correction parameter (Gaussian distribution of mosaic spread) was refined to $G = 0.0014$ (6). The maximum shift/e.s.d. in the last cycle was 0.0003. Final residual electron density $+4.4$ (-5.9) e Å^{-3}. The programs used to

Table 1. *Atomic positional and displacement parameters for* $NdRuSi_2$ *with space group* $P2_1/m$

The equivalent isotropic atomic displacement parameters are expressed as $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

E.s.d.'s are given in parentheses.

	Wyckoff position	x	y	z	U_{eq}(Å² × 100)
Si(1)	2(e)	0.0364 (9)	¼	0.0907 (5)	0.8 (1)
Ru	2(e)	0.1179 (2)	¼	0.3869 (2)	0.56 (3)
Nd	2(e)	0.4130 (2)	¼	0.79904 (9)	0.68 (2)
Si(2)	2(e)	0.6657 (9)	¼	0.4913 (5)	0.8 (1)

refine the structure are all from the *XTAL3.0* system (Hall & Stewart, 1990). The atom positional parameters, standardized by using the *STRUCTURE TIDY* program (Gelato & Parthé, 1987), and displacement parameters are listed in Table 1.*

Discussion. The structure of NdRuSi$_2$ is a distorted variant of the orthorhombic CeNiSi$_2$ type, which, as mentioned above, can be considered as an intergrowth of AlB$_2$- and ThCr$_2$Si$_2$-type slabs. It is also a filled-up derivative of the CaSb$_2$ type (Deller & Eisenmann, 1976) which crystallizes in the same space group, $P2_1/m$. A similar, isopointal structure was recently reported for TmLi$_{0.5}$Ge$_2$ (Pavlyuk *et al.*, 1989), where, however, the site inside the square antiprisms in the ThCr$_2$Si$_2$-type slab is only partly occupied by Li. Very short distances are observed around this site (four Ge at 2.06 – 2.17 Å), which

* Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54573 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

seem to indicate that the reported positional coordinates only correspond to average values. Projections of the structures of NdRuSi$_2$ and TmLi$_{0.5}$Ge$_2$ along [010], together with a directly comparable projection of CeNiSi$_2$, are presented in Fig. 1.* Interatomic distances up to 3.9 Å in CeNiSi$_2$ and corresponding distances in the two monoclinic deformation variants are listed in Table 2.

It can be seen from the figure that the distortions from the CeNiSi$_2$ structure are more pronounced in NdRuSi$_2$ than in TmLi$_{0.5}$Ge$_2$, the cell of which is pseudo-orthorhombic [$2c \cos(180° - \beta) \simeq a$]. Deformations are observed in particular at the interface of the two ThCr$_2$Si$_2$-type slabs where the square-mesh Si net is strongly distorted. The Si atoms are displaced from the ideal sites, parallel to [100], so that

* A similar description is obtained for TmLi$_{0.5}$Ge$_2$, originally reported with the *c* axis unique, by applying the following unit-cell vector transformation: $\mathbf{a}' = -\mathbf{a}$, $\mathbf{b}' = \mathbf{c}$, $\mathbf{c}' = \mathbf{a} + \mathbf{b}$ followed by a $\frac{1}{2}0\frac{1}{2}$ origin shift. This cell does not correspond to the 'best' monoclinic cell (Parthé & Gelato, 1985) but is, due to the pseudo-orthorhombicity of the structure, very similar to it. The standardized description of CeNiSi$_2$ is shifted by $0\frac{1}{2}\frac{1}{2}$ with respect to the originally published data.
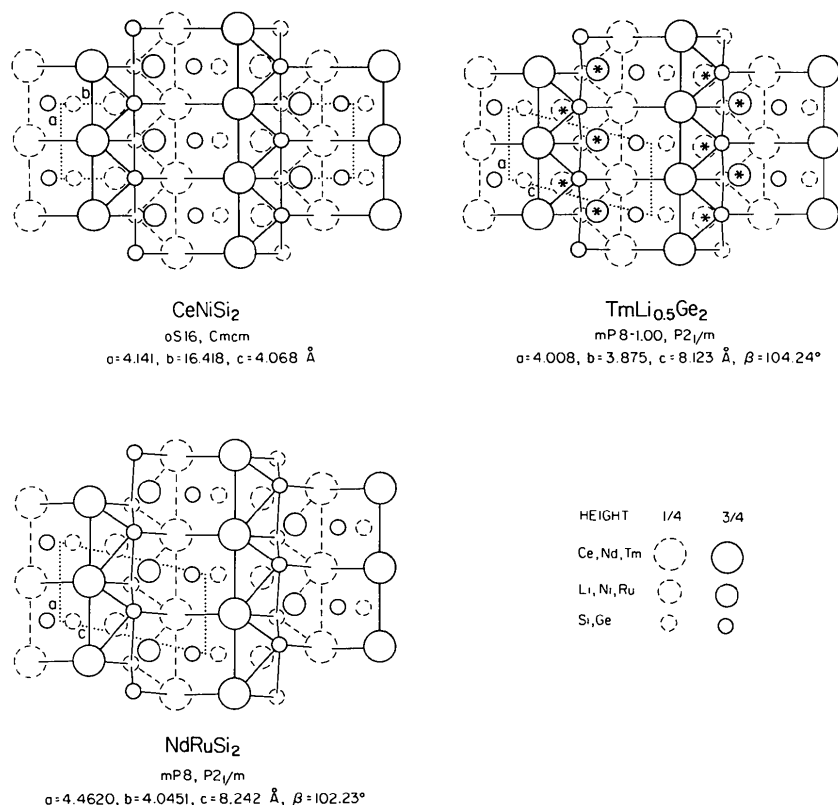

CeNiSi$_2$
oS16, Cmcm
o=4.141, b=16.418, c=4.068 Å

TmLi$_{0.5}$Ge$_2$
mP8-1.00, P2$_1$/m
o=4.008, b=3.875, c=8.123 Å, β=104.24°

NdRuSi$_2$
mP8, P2$_1$/m
o=4.4620, b=4.0451, c=8.242 Å, β=102.23°

HEIGHT	1/4	3/4
Ce,Nd,Tm	⌣	◯
Li,Ni,Ru	⌣	○
Si,Ge	⌣	○

Fig. 1. Projections of the structures of NdRuSi$_2$ and TmLi$_{0.5}$Ge$_2$ along [010] and of CeNiSi$_2$ along [001]. The contours of the trigonal prisms in the AlB$_2$-type slabs and of the square antiprisms in the ThCr$_2$Si$_2$-type slabs are emphasized. The asterisks in the circles corresponding to the Li atoms in TmLi$_{0.5}$Ge$_2$ are a reminder that these sites are only 50% occupied.

Table 2. *Interatomic distances up to* 3.9 Å *in* CeNiSi₂ *and corresponding distances in* TmLi₀.₅Ge₂ *and* NdRuSi₂

For NdRuSi₂ e.s.d.'s are less than 0.005 Å.

CeNiSi₂		TmLi₀.₅Ge₂		NdRuSi₂	
Ce—4Si(1)	3.087	Tm—{ 2Ge(1)	2.900	Nd—{ 2Si(1)	3.116
		{ 2Ge(1)	2.899	{ 2Si(1)	3.163
2Si(2)	3.116	2Ge(2)	3.045	2Si(2)	3.096
2Si(2)	3.121	{ Ge(2)	3.022	{ Si(2)	2.986
		{ Ge(2)	3.019	{ Si(2)	3.737
4Ni	3.167	{ 2Li	2.974	{ 2Ru	3.242
		{ 2Li	3.236	{ 2Ru	3.490
2Si(1)	3.218	{ Ge(1)	3.177	{ Si(1)	3.212
		{ Ge(1)	3.178	{ Si(1)	3.269
Ni	3.428	Li	3.255	Ru	3.373
Ni—2Si(2)	2.297	Li— 2Ge(2)	2.146	Ru— 2Si(2)	2.371
Si(1)	2.318	Ge(1)	2.168	Si(1)	2.391
2Si(2)	2.342	{ Ge(2)	2.059	{ Si(2)	2.355
		{ Ge(2)	2.415	{ Si(2)	2.413
4Ce	3.167	{ 2Tm	2.974	{ 2Nd	3.242
		{ 2Tm	3.236	{ 2Nd	3.490
Ce	3.428	Tm	3.255	Nd	3.373
4Ni	3.618	{ 2Li	3.146	{ 2Ru	3.082
		{ 2Li	3.620	{ 2Ru	4.062
Si(1)— Ni	2.318	Ge(1)— Li	2.168	Si(1)— Ru	2.391
2Si(1)	2.476	2Ge(1)	2.556	2Si(1)	2.496
4Ce	3.087	{ 2Tm	2.900	{ 2Nd	3.116
		{ 2Tm	2.899	{ 2Nd	3.163
2Ce	3.218	{ Tm	3.177	Nd	3.212
		{ Tm	3.178	Nd	3.269
Si(2)—2Ni	2.297	Ge(2)— 2Li	2.146	Si(2)— 2Ru	2.371
2Ni	2.342	{ Li	2.059	{ Ru	2.355
		{ Li	2.415	{ Ru	2.413
4Si(2)	2.903	{ 2Ge(2)	2.787	{ 2Si(2)	2.527
		{ 2Ge(2)	2.790	{ 2Si(2)	3.582
2Ce	3.116	2Tm	3.045	2Nd	3.096
2Ce	3.121	{ Tm	3.022	{ Nd	2.986
		{ Tm	3.019	{ Nd	3.737

the shortest Si(2)—Si(2) distances become contact distances, just as the shortest distances between Si(1) atoms are (2.53 compared to 2.50 Å in NdRuSi₂ but 2.90 compared to 2.48 Å in CeNiSi₂ and 2.79 compared to 2.56 Å for Ge—Ge distances in TmLi₀.₅Ge₂. Atoms from both sites form infinite zigzag chains parallel to [010]. At the same time large differences are observed in the distances between transition-metal atoms, two of the Ru atoms of the neighbouring square being now at a shorter distance (two Ru at 3.08 and two Ru at 4.06 Å, compared to four Ni at 3.62 Å in CeNiSi₂).

As expected the coordination polyhedron around the Si site inside the AlB₂-type slab [Si(1)], a trigonal Nd₆ prism capped by two Si and one Ru atom, is little affected by the deformation. The Ru₄ tetrahedron around the other Si site [Si(2)] also remains relatively regular, but one of the four atoms of the surrounding rare-earth-atom tetrahedron is now at a considerably longer distance (3.74 compared to 3.12 Å in CeNiSi₂). As a consequence the rare-earth site has only nine, instead of ten, near Si neighbours. The Si₅ and Nd₅ square pyramids around the

transition-metal site are slightly larger than corresponding polyhedra around Ni in CeNiSi₂, the square bases of the Si₅ pyramids being distorted as mentioned above. There is no evidence for vacancies or mixed occupation on any of the crystallographic sites.

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