sommet. Une analogie demeure cependant dans ces deux sortes de lamellaires dans la manière dont s'imbriquent par les arêtes deux couches successives d'octaèdres et cette disposition entraîne des distorsions dans les distances Nb—O tout à fait comparables.

En conclusion, l'introduction de traces de tungstène dans un mélange d'oxyde de niobium et de carbonate de potassium a permis la synthèse de monocristaux de KNb_3O_8, normalement lamellaires et flexibles, sous forme de prismes rigides, les rendant ainsi aptes à une étude précise par rayons X. La détermination de la structure met en évidence un nouveau type d'enchaînement d'octaèdres imbriqués par les arêtes. Elle prouve que l'existence de ce composé n'est possible que grâce à l'élasticité de la liaison Nb—O qui, normalement voisine de 2 Å, varie de 1,74 à 2,42 Å pour que soit respectée la neutralité électrique locale autour de chaque atome.

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$Y_3(Ni_{0.5}Si_{0.5})_2Si_2$, a Ternary Variant of the Ta_3B_4-Type Structure

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Abstract. $Y_3(Ni_{0.5}Si_{0.5})_2Si_2$, orthorhombic, space group *Immm*, $a = 3.9605$ (5), $b = 4.125$ (1), $c = 17.63$ (1) Å, $Z = 2$, $D_x = 4.72$ Mg m^{-3}, μ(Mo $K\alpha$) = 34.54 mm^{-1}. The crystal structure was determined by direct methods and refined to a conventional R factor of 0.088 for 186 observed reflections and 16 variables. The crystal structure is a ternary variant of the Ta_3B_4-type structure. The structure is characterized by double layers formed by face-sharing trigonal Y prisms. Prism centers are occupied by Ni and Si in a partially ordered arrangement.

Introduction. Ternary systems with rare-earth metals (including Y and Sc), transition metals and semi-metals such as Si, Ge, Al, Ga have a large number of ternary phases. For example in the system Ce–Ni–Si 21 ternary phases have been reported by Bodak, Mis'kiv, Tyvanchuk, Kharchenko & Gladyshevskii (1973). The interpretation of these different structures is a challenging crystal-chemical problem which has been solved only partially. One prerequisite for any general systematic study is the precise knowledge of all compounds and their crystal structures. In the course of our systematic study of the structures of these ternary compounds we have synthesized the compound Y_3NiSi_3 the structure of which we want to report here.

Experimental. Y_3NiSi_3 was prepared from elements of 99.99% purity by arc melting under purified Ar atmosphere. The ingot obtained was wrapped with Ta foil, sealed in an evacuated silica tube and subjected to annealing at 1173 K for a period of two weeks. Well developed single crystals of prismatic to tabular shape could be isolated from the crushed ingot. Preliminary X-ray investigations with Weissenberg and precession techniques showed orthorhombic symmetry. Systematic absences were observed for hkl, $h + k + l \neq 2n$ indicating *Immm*, *Imm*2, $I2_12_12_1$ or *I*222 as possible space groups.

A small single crystal (40 × 60 × 50 µm) was mounted on a computer-controlled four-circle diffractometer (Philips PW1100, graphite-monochromated Mo $K\alpha$ radiation). The lattice constants given in the *Abstract* were obtained from the 2θ values of 32 reflections measured with Mo $K\alpha_1$ radiation ($2\theta >$ 46°). Intensity data were collected in one quadrant of

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Table 1. *Atomic positions and thermal parameters* ($\times 10^2$) *for* $Y_3(Ni_{0.5}Si_{0.5})_2Si_2$ (*space group Immm*)

The equivalent isotropic temperature factors are expressed as $T = \exp[-2\pi^2U(2\sin\theta/\lambda)^2]$ and were obtained from $U = \frac{1}{3}(U_{11} + U_{22} + U_{33})$. E.s.d.'s are given in parentheses.

	Site	x	y	z	U (Å^2)
Y(2)	4(j)	$\frac{1}{2}$	0	0·18307 (9)	0·85 (9)
Si	4(j)	$\frac{1}{2}$	0	0·3599 (3)	1·3 (2)
$Ni_{0.5}Si_{0.5}$	4(i)	0	0	0·4349 (2)	1·2 (1)
Y(1)	2(a)	0	0	0	0·9 (1)

Table 2. *Interatomic distances* (Å) *for* $Y_3(Ni_{0\cdot5}Si_{0\cdot5})_2Si_2$ *up to* 3·8 Å

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

Y(1)—8Ni/Si	3·081 (2)	Y(2)—2Ni/Si	2·929 (3)
—4Si	3·218 (4)	—4Si	2·958 (1)
—4Y(2)	3·787 (2)	—Si	3·118 (6)
		—4Y(2)	3·708 (2)
		—2Y(1)	3·787 (2)
Ni/Si—Ni/Si	2·295 (6)	Si—2Ni/Si	2·381 (4)
—2Si	2·381 (4)	—4Y(2)	2·958 (1)
—2Y(2)	2·929 (3)	—Y(2)	3·118 (6)
—4Y(1)	3·081 (2)	—2Y(1)	3·218 (4)

reciprocal space with the ω–2θ scan mode ($6° \le 2\theta \le 54°$). The usual background, Lorentz and polarization corrections and a spherical absorption correction ($\mu R = 0{\cdot}9$) were applied. Averaging equivalent reflections yielded a unique set of 227 reflections from which 186 with $I > 3\sigma(I)$ were considered as significant.

An estimate of the unit-cell content of ~14 atoms was obtained by comparing the densities of chemically related compounds YNi, YSi and YNiSi (Hovestreydt, Engel, Klepp, Chabot & Parthé, 1982). A further consideration of symmetry, composition and the relative cell dimensions suggested that the new compound might be a ternary representative of the Ta_3B_4-type structure (Kiessling, 1949). A starting model was obtained based on space group *Immm* and the atomic coordinates of Ta_3B_4 assuming Y to be on the Ta positions and Si and $Si_{0\cdot5}Ni_{0\cdot5}$ on the two B positions respectively.

A preliminary least-squares refinement with isotropic thermal parameters converged to an R value of 0·10. A refinement of the occupation of the mixed site indicated no deviation from the assumed stoichiometry. The final refinement with anisotropic temperature factors resulted in an $R = \sum |\Delta F|/\sum |F_o|$ of 0·088 $\{R_w = 0{\cdot}082;\ w = 1/[\sigma(F_o) + 0{\cdot}02F_o]^2\}$.* A corresponding difference Fourier map showed no physically significant peaks. The final positional coordinates and equivalent isotropic temperature factors are given in Table 1. The listed positional coordinates correspond to those given for the Ta_3B_4 structure if (a) the unit-cell axes of the latter are interchanged such that $a < b < c$ and (b) the unit-cell origin is shifted by $00\frac{1}{2}$. A list of interatomic distances of $Y_3(Ni_{0\cdot5}Si_{0\cdot5})_2Si_2$ is given in Table 2. All calculations were performed with programs of the XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Atomic scattering factors for neutral atoms were taken from Cromer & Mann (1968), anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36781 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. A drawing of the $Y_3(Ni_{0\cdot5}Si_{0\cdot5})_2Si_2$ structure is shown in Fig. 1. The structure is characterized by double layers of face-sharing trigonal Y prisms. All Ni and Si atoms occupy the centers of these tricapped trigonal prisms. $Ni_{0\cdot5}Si_{0\cdot5}$ has two Si and one $Ni_{0\cdot5}Si_{0\cdot5}$ neighbor in the prism caps. Si has two $Ni_{0\cdot5}Si_{0\cdot5}$ and one further Y neighbor outside the rectangular face of the trigonal Y prism. With $b/a = 4{\cdot}125/3{\cdot}961 = 1{\cdot}04 > 1$ all trigonal prisms are elongated along the prism axis. The Ta_3B_4 structure is intermediate between the CrB structure with single prism sheets and the AlB_2 structure where the sheets are all connected to form a three-dimensional prism arrangement.

According to Mis'kiv (1973) $Ce_3(Ni_{0\cdot615}Si_{0\cdot385})_4$ is supposed to crystallize with the Ta_3B_4-type structure ($a = 4{\cdot}10$, $b = 4{\cdot}80$, $c = 18{\cdot}4$ Å). No structure refinement was made. At present the experimental data are not sufficient to make any statement on the change of the Ni/Si ratio with a change of the rare-earth component.

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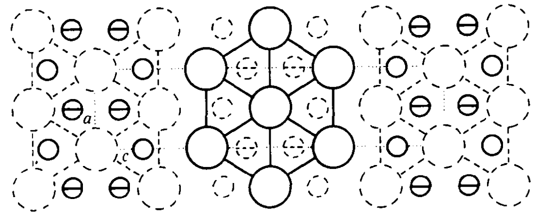

Fig. 1. Projection along **b** of $Y_3(Ni_{0\cdot5}Si_{0\cdot5})_2Si_2$ with Ta_3B_4-type-derivative structure. Large circles: Y, small empty circles: Si, small circles with a bar across: $Ni_{0\cdot5}Si_{0\cdot5}$. Dashed circles at $y = 0$ and fully drawn circles at $y = \frac{1}{2}$.

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The Structure of 8,8′-μ-Methoxo-3,3′-*commo*-bi[1,2-dicarba-3-ferra-*closo*-dodecaborane(11)]

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Abstract. $OCH_3(B_9C_2H_{10})_2Fe$, M_r = 349·89, orthorhombic, $P2_12_12_1$, a = 12·128 (2), b = 21·521 (3), c = 6·991 (4) Å, V = 1825 (1) Å^3, Z = 4, D_c = 1·27 Mg m^{-3}. The structure was refined to R = 5·6% for 2167 counter reflections. Two dicarbollide ligands sharing the Fe atom as a common apex are linked by a monoatomic oxygen bridge to which a CH_3 group is bound. The molecule is compared with its Co analogue.

Introduction. In 1976 we reported the crystal structure of the uncharged zwitterionic compound 8,8′-OCH_3-$(B_9C_2H_{10})_2Co$ (Šubrtová, Petříček, Línek & Ječný, 1976). Thus we found the first case of a metallocarborane with a monoatomic bridge in which the pentagonal faces of the two dicarbollide ligands are mutually inclined. However, the crystals which we studied were not good enough to obtain the necessary experimental data for the refinement of this structure and the precise estimation of all distances and angles. For this reason we studied the ionic compound $C_{11}H_{38}B_{18}CoNO$ with the anion $O(B_9C_2H_{10})_2Co^-$ where the same inclination (28°) of the dicarbollide ligands occurs (Petřina, Petříček, Malý, Šubrtová, Línek & Hummel, 1981).

The purpose of the present study was to determine the molecular dimensions of the sandwich metallocarborane in which the central atom is Fe, and to compare these with the situation in the Co sandwich regarding the inclination of ligand planes and bond lengths between the central ion and the ligand vertices.

Crystals were prepared from $(C_2B_9H_{11})Fe^-$ and formaldehyde in the presence of hydrochloric acid, as for the Co analogue (Plešek, Heřmánek, Baše, Todd & Wright, 1976).

Whereas the structure of the Co analogue could be deduced from ^1H and ^{11}B NMR spectroscopy, this was not possible for the Fe compound since the central ion is paramagnetic. Hence only X-ray diffraction can give information about this structure.

Experimental. The brown transparent crystals are air stable and do not decompose in X-rays. Preliminary lattice constants and the space group were obtained from photographs (Fe $K\alpha$ radiation); final cell parameters were calculated by least squares from 50 reflections centred on the diffractometer (Shoemaker, 1970).

A crystal 0·1 × 0·1 × 0·5 mm was used for intensity measurement on a Hilger & Watts diffractometer with Mo $K\alpha$ radiation (Zr filter). The ω–2θ scan technique was used with a constant scan speed of 2° min^{-1} over a range of 2° to measure 2531 independent reflections to 2θ = 56°. 364 reflections were classified as unobserved [$I < 2\sigma_1(I)$; $\sigma(I)$ was calculated from counting statistics]. Backgrounds were measured at the scan limits for half of the scan time.

The intensities of three standard reflections measured after every ten reflections showed no significant variation. The data were corrected for Lorentz and polarization factors but were not corrected for absorption or extinction.

The structure was solved by the heavy-atom method. The coordinates of the Fe atom were determined from Patterson maps. An electron density synthesis based on

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