

A Ternary W_5Si_3 -type Phase in the Ni-Si-B System

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In the course of studies of ternary Ni-Si-B alloys by one of the authors (A.A.U.) the occurrence of a new ternary phase was observed. Preliminary X-ray diffraction data indicated that the new phase might be isostructural with $Co_{4.7}Si_3B$ and $Fe_{4.86}Si_3B$. Aronsson and Lundgren¹ have shown that $Co_{4.7}Si_3B$ crystallizes with a structure closely related to the W_5Si_3 type. The W_5Si_3 structure is tetragonal and the space group is $I4/mcm$. The unit cell contains twenty tungsten atoms situated on one $16k$ and one $4b$ position, and twelve silicon atoms on one $8h$ and one $4a$ position. In $Co_{4.7}Si_3B$, the silicon atoms occupy the $8h$ position and the boron atoms the $4a$ position. The $16k$ position is fully occupied by cobalt atoms, while the $4b$ position is only partially occupied by cobalt atoms. Aronsson and Engström² found an analogous situation in the structure of $Fe_{4.86}Si_3B$. It seemed possible that the Ni-Si-B phase might exhibit the same type of defect structure, and it was decided to analyze the structure in some detail.

A single crystal was selected from an alloy, which according to powder diffraction analysis contained only faint traces of Ni_3Si in addition to the ternary phase. The unit cell dimensions were determined

from Guinier-Hägg type powder films, using $CuK\alpha_1$ radiation and silicon ($a=5.4305$ Å) as the internal calibration standard. The crystal was mounted with the tetragonal axis as the rotation axis, and photographic intensity data for the layer lines ($hk0$) through ($hk3$) were recorded in a Weissenberg camera with filtered MoK radiation. The intensities of the reflexions were estimated visually. The absorption in the crystal was calculated to be very small, and no correction was considered necessary.

Preliminary calculations showed that the structure is closely similar to that of $Co_{4.7}Si_3B$. The structure data reported¹ for $Co_{4.7}Si_3B$ were therefore taken as the starting values in a structure refinement by the least squares method. The calculations were made on a CDC 3600 computer using the program ORFLS.³ Atomic scattering factors were interpolated from tables given in Ref. 4, and weights of the reflexions were applied according to the formula $w=1/(a+|F_o|+c|F_o|^2)$, with $a=2.5$ and $c=0.1$.

In the first stage of refinement, scale factors (one for each of the four layer lines), positional parameters and individual isotropic temperature factors were varied. The R value for the 117 observed reflexions did not drop below 0.15 and the temperature factor for the $4b$ nickel position was very large. In the case of $Co_{4.7}Si_3B$ and $Fe_{4.86}Si_3B$ strong evidence was presented^{1,2} to show that the low scattering power of the $4b$ position is associated with metal vacancies rather than metal/nonmetal substitution. Accordingly, the degree of occupation of the $4b$ nickel position was included among the variable parameters in the next step of refinement. The R value now dropped to 0.085. The results of this refinement are presented in Table 1.

As seen in Table 1, the temperature factor associated with the $4b$ position is negative. There is a strong correlation

Table 1. Structure data for $Ni_{4.6}Si_3B$. Space group $I4/mcm$. $a=8.632$ (2) Å, $c=4.290$ (1) Å.

	x	y	B (Å ²)	Occupation parameter
Ni 1 in $16k$	0.0787 (2)	0.2033 (2)	0.34 (6)	—
Ni 2 in $4b$	—	—	-0.08 (10)	0.58 (3)
Si in $8h$	0.1588 (6)	—	0.58 (11)	—
B in $4a$	—	—	1.5 (8)	—

Standard deviations are given in parenthesis and refer to the last decimal places of the respective values.

between the temperature factor and the occupational parameter, and it was found that a positive value for the temperature factor was obtained in a refinement, where the occupational parameter was held fixed at a value exceeding that given in Table 1 by one standard deviation.

With the fractional occupation of the 4b nickel position as obtained from the refinement, the composition of the crystal is calculated to be $\text{Ni}_{1.6}\text{Si}_{1.6}\text{B}$. While the phase relationships in the Ni—Si—B system still remain to be clarified in detail, the result of the present structure analysis is taken as a strong indication that the ternary W_5Si_5 -type phase in this system exhibits a similar nonstoichiometric behaviour as the corresponding phases in the Co—Si—B and Fe—Si—B systems.

Acknowledgements. The work has been financially supported by the *Swedish Natural Science Research Council*. One of the authors (A.A.U.) is indebted to *The International Seminar in Physics*, Uppsala, and the *Swedish International Development Authority (SIDA)* for financial support.

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Received May 20, 1970.

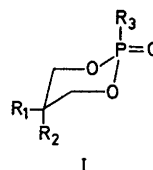
Equilibration of *cis* and *trans* 6-Methyl-2-oxo-2-ethoxy-1,2- oxaphosphorinane

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The conformational energies of substituents on cyclohexane rings have been widely studied, both because of the wide occurrence and importance of this ring system, and also because of the simplicity of the theoretical treatment of the data so obtained.^{1,2} In contrast to the abundance of information in the cyclohexane area, there has been, until very recently, a paucity of data concerned with conformational preferences in heterocyclic systems, with the result that relatively little is known regarding the conformational consequences of introducing one or more heteroatoms into a six-membered ring.^{3,4} This paper reports the conformational equilibria of the *cis* and *trans* isomers of 6-methyl-2-ethoxy-2-oxo-1,2-oxaphosphorinane (II). The preparation of the geometric isomers has been reported in a previous paper.⁴

In analogy with cyclohexanes it has been found by X-ray diffraction method, and proton magnetic resonance studies that the 1,3,2-dioxaphosphorinane (I) ring⁵⁻⁷ exists in a chair-like structure where the phosphoryl oxygen atom occupies the equatorial position.



Proton magnetic resonance and infrared spectra of *cis* and *trans* isomers of 6-methyl-2-oxo-2-alkoxy-1,2-oxaphosphorinanes⁸ indicate difference in the configuration around the phosphorus atom. The 6-methyl group is found to occupy the equatorial position in both isomers.