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Refinement of Nb_3Si and Nb_3As

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Nb_3Si and Nb_3As crystallize in the tetragonal Ti_3P structure type, space group $P4_2/n$ (No. 86); $a=$ 10·224 (3), $c=5·189$ (1) Å for Nb_3Si; $a=10·294$ (4), $c=5·199$ (2) Å for Nb_3As; $Z=8$. Least-squares refinement based on 786 and 964 independent reflexions led to R values of 0·032 and 0·043 for Nb_3Si and Nb_3As respectively. A survey of the known T_3B compounds with Cr_3Si, Ti_3P and Fe_3P structure types indicates that the occurrence of these types is influenced by the electronegativity difference of the component atoms.

Introduction

Nb_3Si and Nb_3As would possibly be good superconductors were it possible to crystallize them in the $A15$ type structure (Johnson & Douglass, 1974; Waterstrat, 1975).

Nb_3Si has been studied by Rossteutscher & Schubert (1965) and Deardorff, Siemens, Romans & McCune (1969). They concluded from X-ray powder diffraction that the structure is of the Ti_3P type (Lundström, 1963) with atomic parameters similar to those reported for Ta_3Si by Rossteutscher & Schubert based on a single-crystal study. They obtained an R value of 0·20. We recalculated the intensities for Ta_3Si from their parameters and found great discrepancies with the calculated values of Rossteutscher & Schubert for certain reflexions. We had to conclude that the atomic parameters reported for Ta_3Si were probably incorrect. Consequently, these values cannot be assumed valid for the Nb_3Si structure. It was thus thought useful to refine the Nb_3Si structure by single-crystal diffraction methods.

Nb_3As has been studied by Ganglberger, Nowotny & Benesovsky (1966*b*) and Rundqvist, Carlsson & Pontchour (1969) by powder methods only. In order to compare the change of the interatomic distances when one changes the group number of the B element, accurate positional parameters are needed and it was thus also of interest to perform a single-crystal study of Nb_3As.

Experimental

Nb_3Si

Crystals of Nb_3Si were obtained from a small cast ingot which was generously sent to us by Deardorff, Siemens, Romans & McCune (1969) at the U.S. Bureau of Mines. The procedures used in preparing the 'chill-cast' ingots are described in their paper. We annealed the ingot in vacuum at 1850°C for 24 h and then quenched it in an argon jet. A single crystal having an irregular shape and approximate dimensions $160\times160\times110$ μm was obtained from the interior of this ingot. Intensities were collected on an automatic four-circle diffractometer (Philips PW 1100) with Mo $K\alpha$ radiation ($\lambda=0·71069$ Å) reflected from a graphite monochromator and scanning in the $\omega/2\theta$ mode. 875 independent reflexions were measured out to a limit of 0·8 $Å^{-1}$ in $\sin\theta/\lambda$, of which 786 had $|F|$ greater than $2\sigma_F$ and were used in the subsequent refinement. A spherical absorption correction [μ(Mo $K\alpha$)$=121·3$ cm^{-1}, $\mu R=1·7$] was applied. Precession photographs were obtained for the $h0l$ and $h1l$ reciprocal lattice planes and the space group was confirmed as $P4_2/n$. Positional parameters, isotropic temperature factors, one scale factor and an isotropic extinction parameter were refined by least-squares calculations with the program *CRYLSQ* (X-RAY System, 1972) starting from the values given for Ti_3P (Lundström, 1963).

Scattering factors were taken from Cromer & Mann (1968) and anomalous dispersion corrections $\Delta f'$ and $\Delta f''$ from *International Tables for X-ray Crystallography* (1962). The weights used for the last cycle were $w=1/\sigma_F^2$ where σ_F is the standard deviation of F_o. The refinement, based on F values and applied

Table 1. *Atomic positional and isotropic thermal parameters for* Nb_3Si (*second description of space group* $P4_2/n$ *with symmetry centre at origin*)

All atoms are in the general point position 8(*g*). Isotropic temperature factors are expressed as $T=\exp[-8\pi^2U(\sin\theta/\lambda)^2]$. E.s.d.'s are in parentheses.

Site	x	y	z	U ($Å^2$) $\times 10^2$
Nb(1)	0·1653 (1)	0·6525 (1)	0·7185 (1)	0·84 (2)
Nb(2)	0·1043 (1)	0·2665 (1)	0·5230 (1)	0·83 (2)
Nb(3)	0·0603 (1)	0·5364 (1)	0·2370 (1)	0·80 (2)
Si	0·0442 (2)	0·2782 (2)	0·0293 (5)	0·95 (5)

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to 18 parameters, gave an $R(=\sum|\Delta F|/\sum F_o|)$ of 0·032. The final atomic parameters are listed in Table 1.

Nb_3As

Crystals of Nb_3As were obtained from an internal cavity in a cast ingot of that composition which had been melted in a beryllium oxide crucible in a high pressure furnace under 40 atm of argon. After melting, the alloy was soaked for 6 h at a temperature somewhat below the solidus for homogenization purposes and then rapidly cooled by turning off the furnace power. The crystals were in the form of needles having a square cross-section. The needle axis coincided with the tetragonal c axis and the four flat faces were indexed as $\{110\}$. The same X-ray procedure was followed with a crystal $30\times30\times350$ μm with the exception that no absorption or extinction corrections were applied [$\mu(\text{Mo } K\alpha)=241{\cdot}1$ cm^{-1}, $\mu R\simeq0{\cdot}5$]. 1040 independent reflexions were collected, 964 of which had $|F|>2\sigma_F$ and were used in the refinement.* The final atomic parameters are listed in Table 2 ($R=0{\cdot}043$).

Table 2. *Atomic positional and isotropic thermal parameters for* Nb_3As (*second description of space group* $P4_2/n$ *with symmetry centre at origin*)

All atoms are in the general point position 8(g). Isotropic temperature factors are expressed as $T=\exp[-8\pi^2U(\sin\theta/\lambda)^2]$. E.s.d.'s are in parentheses.

Site	x	y	z	U (Å^2) × 10^2
Nb(1)	0·1652 (1)	0·6554 (1)	0·7272 (2)	0·34 (2)
Nb(2)	0·1021 (1)	0·2617 (1)	0·5181 (2)	0·31 (2)
Nb(3)	0·0562 (1)	0·5364 (1)	0·2411 (1)	0·33 (2)
As	0·0430 (1)	0·2714 (1)	0·0203 (3)	0·37 (2)

The shortest interatomic distances for Nb_3Si and Nb_3As are listed in Tables 3 and 4 respectively.

Discussion

Table 5 gives a list of all known compounds with the Ti_3P structure type. The atomic position parameters of Nb_3Si are found to be very similar to those of the phosphides and arsenides.

We are particularly interested in compounds between transition elements and non-transition elements which might possibly crystallize in the Cr_3Si ($A15$) structure type. These compounds have the ideal composition T_3B where T is a transition element of the fourth, fifth or sixth groups and B a non-transition element of the (second), third, fourth and fifth B subgroups. Three structure types are found with this composition: the cubic Cr_3Si ($A15$), the tetragonal Ti_3P and the tetragonal Ni_3P (Aronsson, 1955). The latter two are closely related (Rundqvist, 1962b). Fig. 1 is a Mooser–Pearson plot for these compounds with $\bar{n}$, the average principal quantum number as ordinate and Δx, the electronegativity difference between the component atoms, as abscissa. The electronegativities

Table 3. *Interatomic distances* (Å) *in* Nb_3Si

(Maximum distance of 3·77 Å included, e.s.d.'s are given in parentheses).

Nb(1)–Si	2·608 (5)	Nb(2)–Si	2·586 (5)
–Nb(1)	2·644 (10)	–Si	2·637 (2)
–Si	2·651 (8)	–Si	2·642 (7)
–Nb(3)	2·967 (6)	–Si	2·701 (3)
–Nb(3)	3·015 (9)	–Nb(3)	2·887 (6)
–Nb(2)	3·123 (8)	–Nb(3)	2·905 (6)
–Nb(3)	3·130 (5)	–Nb(2)	3·000 (7)
–Nb(2)	3·138 (7)	–Nb(1)	3·123 (8)
–Nb(3)	3·195 (7)	–Nb(1)	3·138 (7)
–4Nb(1)	3·198 (6)	–Nb(3)	3·166 (3)
–Nb(3)	3·221 (10)	–2Nb(2)	3·170 (4)
Nb(3)–Si	2·578 (7)	–2Nb(2)	3·540 (4)
–Si	2·667 (9)	–Nb(3)	3·587 (7)
–Nb(3)	2·849 (6)	Si–Nb(3)	2·578 (7)
–Si	2·857 (8)	–Nb(2)	2·586 (5)
–Nb(2)	2·887 (6)	–Nb(1)	2·608 (5)
–Nb(2)	2·905 (6)	–Nb(2)	2·637 (3)
–Nb(1)	2·967 (6)	–Nb(2)	2·642 (7)
–Nb(1)	3·015 (9)	–Nb(1)	2·651 (8)
–Nb(3)	3·086 (5)	–Nb(3)	2·667 (9)
–Nb(1)	3·130 (5)	–Nb(2)	2·701 (2)
–Nb(2)	3·166 (3)	–Nb(3)	2·857 (8)
–Nb(1)	3·195 (7)	–2Si	3·777 (7)
–Nb(1)	3·221 (10)	–Nb(3)	3·778 (10)
–Nb(2)	3·587 (7)		
–Si	3·778 (10)		

Table 4. *Interatomic distances* (Å) *in* Nb_3As

(Maximum distance of 3·85 Å included, e.s.d.'s are given in parentheses.)

Nb(1)–Nb(1)	2·617 (6)	Nb(2)–As	2·610 (8)
–As	2·623 (7)	–As	2·660 (5)
–As	2·649 (6)	–As	2·669 (9)
–Nb(3)	3·018 (8)	–As	2·683 (5)
–Nb(3)	3·025 (5)	–Nb(3)	2·885 (8)
–Nb(2)	3·125 (7)	–Nb(3)	2·922 (7)
–Nb(3)	3·146 (5)	–Nb(2)	3·057 (10)
–Nb(2)	3·149 (9)	–Nb(1)	3·125 (7)
–4Nb(1)	3·191 (4)	–Nb(1)	3·149 (9)
–Nb(3)	3·239 (7)	–Nb(3)	3·208 (6)
–Nb(3)	3·253 (8)	–2Nb(2)	3·239 (7)
Nb(3)–As	2·608 (8)	–2Nb(2)	3·527 (7)
–As	2·667 (10)	–Nb(3)	3·536 (8)
–Nb(3)	2·859 (7)	As–Nb(3)	2·608 (8)
–Nb(2)	2·885 (8)	–Nb(2)	2·610 (8)
–Nb(2)	2·922 (7)	–Nb(1)	2·623 (7)
–As	2·964 (8)	–Nb(1)	2·649 (6)
–Nb(1)	3·018 (8)	–Nb(2)	2·660 (5)
–Nb(3)	3·025 (7)	–Nb(3)	2·667 (10)
–Nb(1)	3·025 (5)	–Nb(2)	2·669 (9)
–Nb(1)	3·146 (5)	–Nb(2)	2·683 (5)
–Nb(2)	3·208 (6)	–Nb(3)	2·964 (8)
–Nb(1)	3·239 (7)	–Nb(3)	3·670 (10)
–Nb(1)	3·253 (8)	–2As	3·860 (8)
–Nb(2)	3·536 (8)		
–As	3·670 (10)		

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* Tables of observed and calculated structure factors for Nb_3Si and Nb_3As have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31089 (19 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 5. *Structure data for compounds with* Ti_3P *structure type*

			T(1)			T(2)			T(3)			*B*			
Compound	*a* (Å)	*c* (Å)	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	Reference
Borides															
$(Fe_{0·8}Re_{0·2})_3B$	8·683	4·329													5
$\varepsilon_1Fe_3(P_{0·37}B_{0·63})$	8·812	4·375	0·1678	0·6422	0·7312	0·1115	0·2813	0·5187	0·0742	0·5317	0·2424	0·0450	0·2949	0·016	1
Silicides, germanides															
Ti_3Si	10·196	5·097													4
Zr_3Si	11·01	5·45													4
Zr_3Ge	11·08	5·48													4
Hf_3Ge	10·92	5·42													4
Nb_3Si	10·21	5·19													4,12
	10·224	5·189	0·1653	0·6525	0·7185	0·1043	0·2665	0·5230	0·0603	0·5364	0·2370	0·0442	0·2782	0·0293	13
Ta_3Si	10·193	5·175	0·148	0·665	0·719	0·105	0·231	0·529	0·037	0·560	0·237	0·041	0·231	0·013	4
Ta_3Ge	10·28	5·22													4
Phosphides, arsenides															
Ti_3P	9·9592	4·9869	0·16613	0·64275	0·7153	0·11009	0·27849	0·5295	0·06957	0·53342	0·2407	0·04395	0·29188	0·0354	2
Zr_3P	10·7994	5·3545													8
Zr_3As	10·9734	5·4499													8
Hf_3P	10·6683	5·2948													6,9
V_3P	9·387	4·756	0·1665	0·65468	0·72644	0·10311	0·26491	0·51546	0·05892	0·53459	0·24033	0·04081	0·27668	0·02159	3
Nb_3P	10·1282	5·0891	0·1634	0·6529	0·7256	0·1051	0·2632	0·5154	0·0590	0·5368	0·2406	0·0425	0·2748	0·0185	6,10,11
Nb_3As	10·2937	5·1971													6,7
	10·294	5·199	0·1652	0·6554	0·7272	0·1021	0·2617	0·5181	0·0562	0·5364	0·2411	0·0430	0·2714	0·0203	13
Ta_3P	10·154	5·012	0·1649	0·6423	0·7131	0·1128	0·2777	0·5274	0·0707	0·5346	0·2367	0·0443	0·2910	0·0328	6,11

(1) Rundqvist(1962*a*). (2) Lundström & Snell (1967). (3) Jawad, Lundström & Rundqvist (1971). (4) Rossteutscher & Schubert (1965). (5) Ganglberger, Nowotny & Benesovsky (1966*a*). (6) Ganglberger, Nowotny & Benesovsky (1966*b*). (7) Rundqvist, Carlsson & Pontchour (1969). (8) Lundström (1966). (9) Lundström & Tansuriwongs (1968). (10) Rundqvist (1966). (11) Nawapong (1966). (12) Deardorff, Siemens, Romans & McCune (1969). (13) This study.

used are those given by Evans (1964). Compounds with a large electronegativity difference form the Ti_3P or Ni_3P type structures while compounds with small differences form the Cr_3Si (*A*15) type structure. It appears that one would probably obtain an even better separation of these structure types by adopting a more realistic set of electronegativities (for example Evans gives identical values for Pb, Sn, Ge and Si despite much evidence that the electronegativities increase in passing from Pb to Si).

By arranging certain *B* elements as they appear in the periodic table (Fig. 2) one can see that Si and As can be regarded as the end members of two distinct series of elements which form compounds with Nb having the T_3B stoichiometry. In each of these two series one observes that the Cr_3Si (*A*15) type structure is replaced by a Ti_3P type structure as one proceeds in the direction of a greater *B* element electronegativity. Ge seems to occupy a critical position near the border line where the Cr_3Si (*A*15) type structure is becoming increasingly unstable. Thus, the stoichiometric compound Nb_3Ge can be obtained only in a metastable condition and, when equilibrium conditions are obtained, one observes the non-stoichiometric composition $Nb_{82}Ge_{18}$ for the Cr_3Si (*A*15) structure.

The Ti_3P type structure seems to represent a compromise between the tendencies toward close packing for atoms of the transition elements and a less dense packing around the atoms of the *B* element. The coordination polyhedra around Nb(1) and Nb(3) resemble to some extent the Kasper polyhedron having CN14 which contains only tetrahedral interstices between its atoms. The coordination polyhedra around Si or As, however, contain some octahedral interstices and this, apparently, restricts the formation of Kasper polyhedra on the adjoining Nb sites. Thus Nb(2), with CN15, bears little or no resemblance to the CN15 Kasper polyhedron.

B-elements arranged as in the periodic table	Corresponding crystal structure types
Si	Ti_3P
→Ga Ge As	→Cr_3Si Cr_3Si Ti_3P
Sn	Cr_3Si
Pb	Cr_3Si
↑	↑
(a)	(b)

Fig. 2. Relationship between crystal structure type and location of the *B* element in the periodic table for some T_3B compounds where T is Nb. Arrows indicate the direction of increasing eletronegativity for each elemental series.

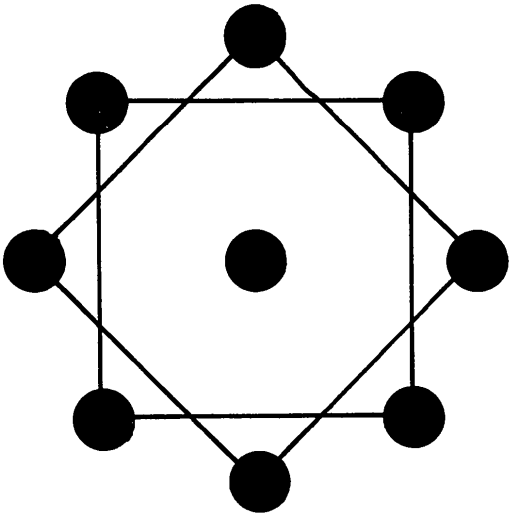

Fig. 3. Square-planar configuration observed in Nb_5Si_3 and Nb_3Si. A silicon atom is located in the centre between the two planar squares of Nb atoms and two Nb atoms are located coaxially above and below.

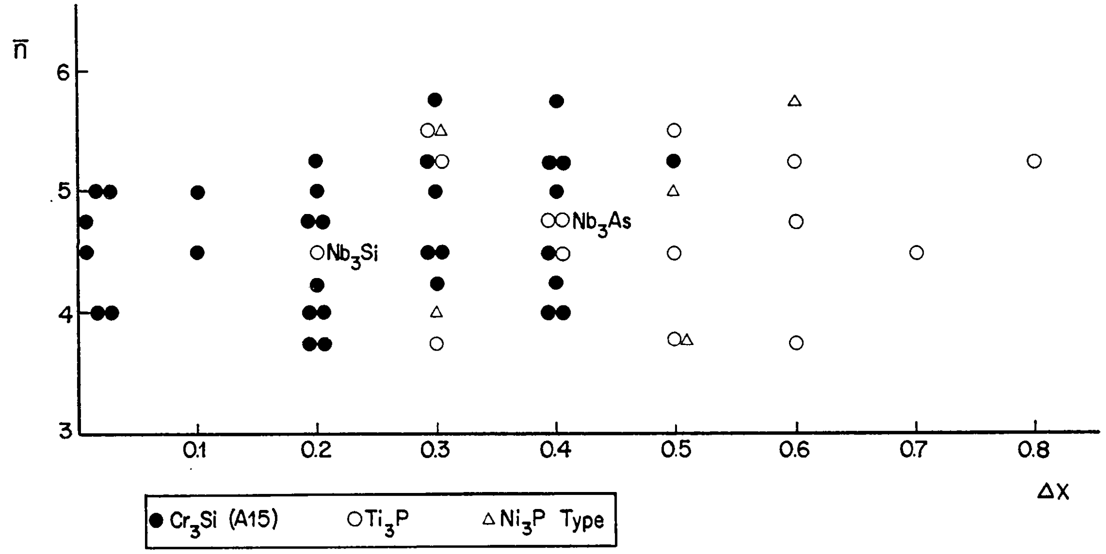

Fig. 1. Mooser–Pearson diagram for T_3B compounds.

The polyhedra around Si or As have CN10 and resemble a cubic Archimedean antiprism. It is noteworthy and probably significant that the Si atoms in Nb_5Si_3 (Cr_5B_3 type structure) are surrounded by similar cubic antiprisms of Nb atoms which, in this case, possess a perfect regularity. The Nb atoms in Nb_5Si_3 form precise square-planar configurations (Fig. 3). This characteristic configuration around the Si atoms is retained in Nb_3Si, although with some loss of regularity. However, since Si atoms constitute only 25% of the atoms in the Nb_3Si structure, it is remarkable that this characteristic configuration is so fully retained in competition with the packing requirements of the Nb atoms which constitute a 75% majority. This suggests that the Nb–Si bonding interactions are strongly dominant in the Nb_3Si structure and might involve directional bonds of a partially covalent nature.

As a result of this study, one may compare the coordination polyhedron around the Si atoms in Nb_3Si with that around the As atom in Nb_3As. As atoms are normally somewhat larger than Si and this produces a lattice expansion. The atomic configuration, however, is quite similar in both cases and one sees little evidence of any unusual distortions which might indicate an incipient instability. Nevertheless, if one replaces the ten-coordinated As atom in Nb_3As with the slightly larger Ge atom, one now obtains the *A*15 type compound Nb_3Ge in which the Ge atom has CN12. The change from CN10 to CN12 as one replaces As with Ge should probably be attributed mainly to the electronegativity factor since there is little difference in the atomic sizes.

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