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Crystal structure of triniobium triiron chromium hexasilicide $Nb_{\approx 3}Fe_{\approx 3}Cr_{\approx 1}Si_6$: an intergrowth of $Zr_4Co_4Ge_7$ and $Nb_2Cr_4Si_5$ blocks

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Abstract

A new quaternary compound $Nb_{\approx 3}Fe_{\approx 3}Cr_{\approx 1}Si_6$ was studied using single-crystal X-ray diffraction data. The crystal structure is of a new type with space group $P4_2/mbc$ and $Z=8$, $a=b=16.558(3)$ Å, $c=4.940(2)$ Å, $D_x=6.54$ g cm^{-3}, μ(Mo Kα)$=136.5$ cm^{-1}, $F(000)=2470$ and $R=0.034$ ($R_w=0.044$) for 515 contributing unique reflections and 41 parameters. The structure of $Nb_{\approx 3}Fe_{\approx 3}Cr_{\approx 1}Si_6$ can be characterized as a combination of elemental blocks of the $Zr_4Co_4Ge_7$- and $Nb_2Cr_4Si_5$-type structures.

1. Introduction

In recent years, the oxidation behaviour of niobium alloys and protective coatings for niobium alloys has been the subject of intensive research [1]. We have recently developed a protective silicide coating, comprising five discrete layers, which appear to be single phases of new quaternary compounds. As a continuation of our efforts to achieve a better understanding of the crystal chemistry of quaternary transition metal silicides, we have synthesized all of these phases [2]. In this paper, we report the results for a new silicide: $Nb_{\approx 3}Fe_{\approx 3}Cr_{\approx 1}Si_6$.

2. Experimental details

Powders of the initial composition $Nb_{3.1}Fe_{2.9}Cr_1Si_6$, corresponding to the composition determined by microprobe analysis for one of the coating phases [3], were prepared from high purity elements. The samples were homogenized at 1473 K in a sealed quartz tube under vacuum for 2 days. Single crystals were obtained from powder by gas transport using $SiCl_4$ as transport agent (temperature of evaporation zone, 1473 K; temperature of deposition, 1423 K). One of the single crystals was studied by conventional X-ray analysis (oscillating crystal and Weissenberg photographs). The cell is tetragonal and the systematic extinction led to the two space groups $P4_2/mbc$ and $P4_2bc$. The cell parameters (Table 1) were determined by least-squares refinements of 25 reflections measured on the diffractometer (see below).

TABLE 1. $Nb_3Fe_3CrSi_6$: summary of data collection and structure refinement

Molar mass (g)	666.8
Average crystal diameter (μm)	≈ 50
Symmetry	Tetragonal
a (Å)	16.5580(30)
c (Å)	4.9401(2)
V (Å^3)	1354.4
Z	8
ρ_{cal} (g cm^{-3})	6.54
Space group	$P4_2/mbc$
Radiation	Mo Kα (1750 W)
Monochromator	Graphite
Scan mode	θ–ω
Record limits	$\theta < 25°$
Linear absorption coefficient μ(cm^{-1})	136.5
Numbers of intensities:	
recorded	933
unique and non-zero	721
kept ($\sigma(I)/I < 0.30$)	515
Number of parameters	41
Final R value	0.037
Final R_w value	0.044
$w=0.9259/(\sigma^2(F_o)+g(F_o)^2)$	$g=0.003147$

3. Structure determination

3.1. Experimental procedure

A small monocrystalline needle was mounted on a Nonius CAD4 automatic diffractometer. The conditions

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TABLE 2. Atomic coordinates, thermal parameters and occupancy factors

Atom	Position	x	y	z	B_j (Å^2)	Occupancy factor
Fe_1	16i	0.3454(1)	0.4470(1)	0.2508(5)	0.56(4)	1.0
T_1	8h	0.3830(1)	0.0430(1)	0	0.53(7)	0.42(12)Cr; 0.58(12)Fe
T_2	8g	0.3729(1)	0.8729(1)	1/4	0.53(6)	0.46(11)Cr; 0.54(11)Fe
Nb_1	8h	0.2824(1)	0.2963(1)	0	0.44(3)	1.0
Nb_2	8h	0.2938(1)	0.6033(1)	0	0.51(3)	1.0
M_1	8h	0.4707(1)	0.2113(1)	0	0.42(4)	0.12(2)Cr; 0.88(2)Nb
Si_1	8h	0.4299(3)	0.3614(3)	0	0.49(9)	1.0
Si_2	8h	0.0207(3)	0.4325(3)	0	0.70(9)	1.0
Si_3	8h	0.1320(3)	0.2467(3)	0	0.42(7)	1.0
Si_4	8h	0.2263(3)	0.4518(3)	0	0.53(9)	1.0
Si_5	8h	0.4371(3)	0.5307(3)	0	0.61(9)	1.0
Si_6	8g	0.1638(2)	0.6638(2)	1/4	0.38(5)	1.0

for the collection of the data and the refinement of the structure are listed in Table 1. Absorption has been neglected ($\mu_r \ll 1$). Atomic scattering factors for neutral atoms and anomalous dispersion corrections were taken from ref. 4. All computer programs used were taken from refs. 5 and 6. A list of the structure factors can be obtained from the authors on request.

3.2. *Structure refinement*

The structure refined satisfactorily in the centrosymmetric space group $P4_2/mbc$. The atomic positions obtained using direct methods [6] and "difference" Fourier synthesis [5] yielded in a first step the formula (Table 2) $M_{24}T_{32}Si_{48}$ where T stands for (Fe,Cr) and M for Nb. In this hypothesis, a refinement with a general temperature factor (B_g) yielded a reliability factor $R=0.042$ (for an average $f_j(T)=f_{Fe}$ and $f_j(M)=f_{Nb}$). At this stage, the refinement of the occupancy factor (m_j) shows a slight decrease for the three atomic sites denoted T_1, T_2 and M_1 in Table 2. Due to the small amount of chromium in this compound, Cr was introduced on the T_1, T_2 and M_1 sites and its distribution was calculated thanks to a special procedure of the SHELX program [5].

Finally, the best refinement, with individual isotropic thermal factors (B_j), gave a residual value of $R=0.037$ ($R_w=0.044$) corresponding to the formula $Nb_{23}Fe_{25}Cr_8Si_{48}$. The very small crystal size hampered microprobe analysis; nevertheless the composition determined from X-ray analysis is close to that of the starting powder ($Nb_{24.8}Fe_{23.2}Cr_8Si_{48}$). It should be noted that less than 12% of chromium is substituted for niobium on the M_1 site and that the (Fe,Cr) atom mixture on the T_1 and T_2 sites is measured with rather poor accuracy owing to the small difference in scattering factors of chromium and iron.

The crystallographic results were confirmed by Mössbauer spectrometry, which shows the occurrence of three different Fe sites (T_1, T_2 and Fe_1). The relative intensities of the different subspectra lead to a distribution of Fe and Cr atoms on both the T_1 and T_2 sites very close to that calculated by the crystallographic refinement (Table 3).

TABLE 3. Mössbauer spectrometry results

	T_1	T_2	Fe_1
EQ[a] (mm s^{-1})	0.64(1)	0.41(1)	0.46(1)
IS[b] (mm s^{-1})	0.45(1)	0.28(1)	0.15(1)
Site occupancy by Fe atoms	0.47(3)	0.52(3)	1.0
Site occupancy by Fe atoms (crystallographic result)	0.58(12)	0.54(11)	1.0

[a] EQ, quadrupole splitting.
[b] IS, isomer shift.

The atomic and thermal parameters are listed in Table 2, whereas the main interatomic distances are collected in Table 4.

4. Discussion

4.1. *Structure description*

A [001] projection of the structure is given in Fig. 1. It is characterized by parallel infinite rectilinear columns (along the [001] axis) of (Fe_1 and T_2) centred face-sharing octahedra formed by Si atoms. These rows of octahedra are linked by edge sharing and generate double channels filled by infinite chains of T_1–Nb(M_1) square antiprisms centred by silicon atoms.

The Nb(M_1) atoms have a sevenfold silicon coordination building pentagonal dipyramids, whereas the T_1 site, with a 5+2 silicon coordination (Table 4), keeps the first five nearest neighbours to yield a polyhedron similar to a trigonal dipyramid. Some interatomic Fe(Cr)–Si and Nb(M_1)–Si distances are short

TABLE 4. Interatomic distances (up to 3.4 Å) and rounded values Δ (%) = 100($d - \Sigma r$)/Σr. The atomic radii were taken from ref. 7. The estimated standard deviations are given in parentheses

Atom	To atom	d (Å)	Δ (%)
Nb_1	Si_3	2.621(5)	−5.9
	Si_1	2.669(5)	−4.2
	$2Si_6$	2.671(3)	−4.2
	Si_4	2.737(5)	−1.9
	$2Si_3$	2.782(2)	−0.1
	$2Fe_1$	2.975(2)	
	$2Nb_1$	3.081(2)	
	$2Nb_2$	3.112(1)	
	$2T_2$	3.122(2)	
Nb_2	Si_5	2.661(5)	−4.5
	Si_3	2.672(5)	−4.1
	$2Si_6$	2.676(3)	−4.0
	Si_4	2.746(5)	−1.5
	$2Si_1$	2.767(2)	−0.7
	$2Fe_1$	2.945(2)	
	$2Fe_1$	2.994(2)	
	$2M_1$	3.077(1)	
	T_1	3.092(3)	
	$2Nb_1$	3.112(1)	
M_1	Si_2	2.520(5)	−8.8
	Si_1	2.575(5)	−6.8
	$2Si_6$	2.665(3)	−3.6
	Si_3	2.761(5)	−0.1
	$2Si_4$	2.795(2)	+1.0
	$2Fe_1$	2.882(2)	
	$2T_1$	2.931(1)	
	$2Nb_2$	3.077(1)	
	T_1	3.141(3)	
	$2T_2$	3.190(2)	
Fe_1	Si_4	2.330(4)	−10.1
	Si_1	2.345(4)	−9.5
	Si_3	2.356(4)	−9.3
	Si_1	2.396(4)	−7.6
	Si_5	2.398(4)	−7.5
	Si_5	2.400(4)	−7.4
	Fe_1	2.462(4)	−3.3
	Fe_1	2.478(4)	−2.7
	M_1	2.881(2)	
	Nb_2	2.945(2)	
	Nb_1	2.975(2)	
	Nb_2	2.994(2)	
T_1	Si_2	2.316(5)	−10.8
	Si_4	2.357(5)	−9.2
	Si_2	2.428(5)	−6.5
	$2Si_6$	2.474(3)	−4.7
	$2Si_2$	2.808(2)	+8.1
	$2M_1$	2.930(1)	
	$2T_1$	3.016(2)	
	$2T_2$	3.079(2)	
	Nb_2	3.092(2)	
	M_1	3.141(2)	
T_2	$2Si_2$	2.366(4)	−8.9
	$2Si_3$	2.429(4)	−6.5
	$2Si_4$	2.435(4)	−6.2
	$2T_2$	2.407(1)	−3.3
	$2T_1$	3.079(2)	
	$2Nb_1$	3.122(2)	
	$2M_1$	3.190(2)	
Si_1	$2Fe_1$	2.345(4)	
	$2Fe_1$	2.396(4)	
	M_1	2.575(4)	
	Nb_1	2.669(4)	
	$2Nb_2$	2.766(2)	
	Si_5	2.806(6)	
	Si_5	2.836(6)	
	$2Si_5$	2.846(3)	
Si_2	T_1	2.316(5)	
	Si_2	2.339(9)	−11.3
	$2T_2$	2.366(4)	
	T_1	2.428(5)	
	M_1	2.520(4)	
	$2Si_2$	2.702(3)	
	$2T_1$	2.808(2)	
	$2Si_2$	3.220(6)	
Si_3	$2Fe_1$	2.356(4)	
	$2T_2$	2.429(4)	
	Nb_1	2.621(4)	
	Nb_2	2.672(4)	
	M_1	2.761(4)	
	$2Nb_1$	2.782(2)	
	$2Si_4$	2.868(3)	
Si_4	$2Fe_1$	2.330(4)	
	T_1	2.357(5)	
	$2T_2$	2.435(4)	
	Nb_1	2.727(4)	
	Nb_2	2.746(4)	
	$2M_1$	2.794(2)	
	$2Si_3$	2.868(3)	
Si_5	Si_5	2.317(9)	−12.1
	$2Fe_1$	2.398(4)	
	$2Fe_1$	2.400(4)	
	Nb_2	2.660(4)	
	Si_1	2.806(6)	
	Si_1	2.836(6)	
	$2Si_1$	2.846(3)	
	$4Si_5$	2.964(3)	
Si_6	$2Si_6$	2.470(1)	−6.4
	$2T_1$	2.474(3)	
	$2M_1$	2.664(2)	
	$2Nb_1$	2.670(2)	
	$2Nb_2$	2.675(2)	

compared with the sum of the atomic radii, with contractions reaching 10% and 8% respectively. The T_2–T_2 (Fe,Cr) interatomic distances correspond to half of the c parameter and are slightly contracted compared with the metallic state. Finally, the short distances of the Si_2–Si_2 and Si_5–Si_5 dumbbells complete this list (Fig. 1).

4.2. *Structural relationships*

The occurrence of a tridimensional framework of TSi_6 (T ≡ Fe, Cr) octahedra is a common feature in many ternary compounds such as $TiMnSi_2$, $ZrFeSi_2$, $ZrMnSi_2$, $LuMnGe_2$, $Zr_4Co_4Ge_7$ and $Nb_2Cr_4Si_5$ [8–13]

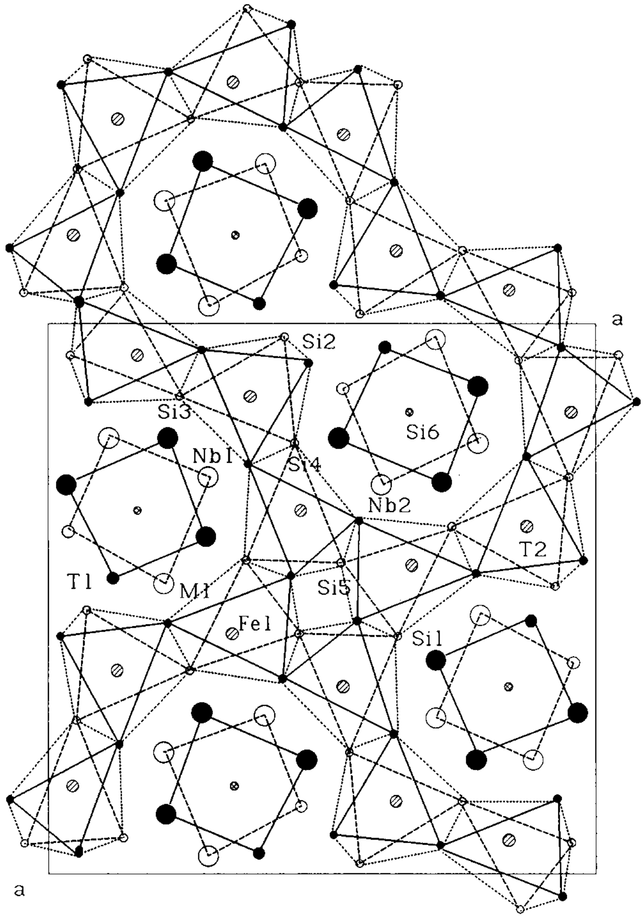


Fig. 1. [001] projection of the $Nb_3(Cr,Fe)_4Si_6$ structure (white circles, $z=0$; black circles, $z=\frac{1}{2}$; hatched circles, $z\approx\frac{1}{4}$).

and the structural relationships with the last two compounds are particularly close. Figures 2(a), 2(b) and 2(c) show [001] projections of $Nb_3(Cr,Fe)_4Si_6$, $Zr_4Co_4Ge_7$ and $Nb_2Cr_4Si_5$ structures. It can be seen that $Nb_3(Cr,Fe)_4Si_6$ (Fig. 2(a)) comprises two types of columns with square and rhombic sections which are the elemental building blocks of the $Zr_4Co_4Ge_7$ and $Nb_2Cr_4Si_5$ structures (Figs. 2(b) and 2(c)) respectively.

The intergrowth ability of such blocks is obvious since they have the same atomic arrangement at their interfaces and their dimensions are quite similar. The interface dimensions in the three related structures are given by the following relations (see Fig. 2):

$Nb_{\approx 3}(Cr,Fe)_4Si_6$	$Nb_4Fe_4Si_7$	$Nb_2Cr_4Si_5$
Cell parameters	Cell parameters	Cell parameters
$a''=16.558$ Å	$a=12.652$ Å	$a'=15.81$ Å
$b''=16.558$ Å	$b=12.652$ Å	$b'=7.497$ Å
$c''=4.9401$ Å	$c=4.981$ Å	$c'=4.879$ Å
Interface	Interface	Interface
$l''=a\{(0.5-2x_{Si6})^2+0.25\}^{1/2}$	$l=\frac{a}{2^{1/2}}$	$l'=\frac{1}{2}(a'^2+b'^2)^{1/2}$
$l''=8.710$ Å	$l=8.946$ Å	$l'=8.749$ Å
$h''=c''=4.9401$ Å	$h=c=4.981$ Å	$h'=c'=4.879$ Å

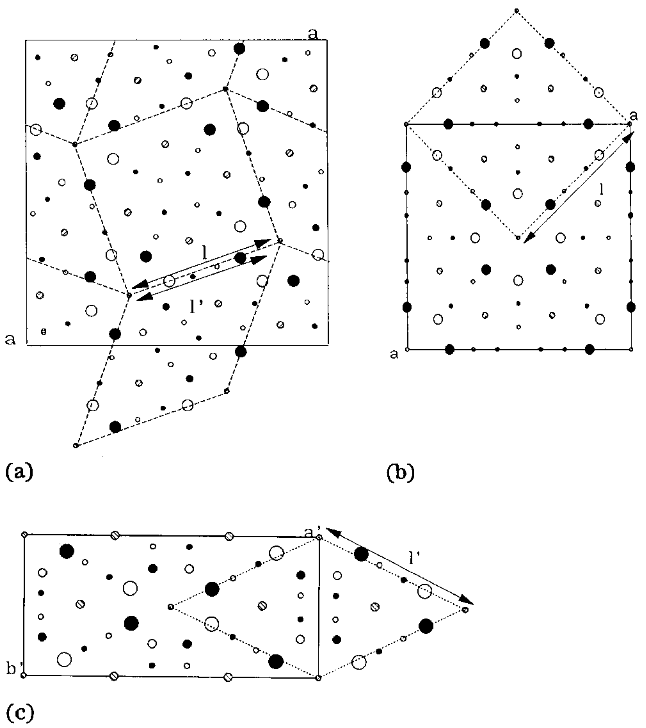


Fig. 2. (a) $Nb_3(Fe,Cr)_4Si_6$: [001] projection; (b) $Nb_4Fe_4Si_7$($Zr_4Co_4Ge_7$-type): [001] projection; (c) $Nb_2Cr_4Si_5$(V_6Si_5-type derivative): [001] projection.

Thus we can easily summarize the close relationships between the three silicides by the following equation

"4/4/7 block"		"2/4/5 block"		
$4Nb_4Fe_4Si_7$	$+$	$4Nb_{1.75}Fe_{2.25}Cr_2Si_5$	$=$	$Nb_{23}Fe_{25}Cr_8Si_{48}$
$Zr_4Co_4Ge_7$		$Nb_2Cr_4Si_5$		
structure type		structure type		

The two block compositions are in agreement with the structural properties of the $Zr_4Co_4Ge_7$- and $Nb_2Cr_4Si_5$-type structures. $Zr_4Co_4Ge_7$, as well as the isostructural intermetallic compounds, has a very narrow homogeneity range and a single cobalt site (Fe in $Nb_4Fe_4Si_7$), whereas the V_6Si_5-type structure, adopted by many ternary silicides (for example, $Nb_2Cr_4Si_5$ [14]), is well known to be amenable to various kinds of atom substitutions, as demonstrated by several workers [14, 15]. Thus in $Nb_3(Cr,Fe)_4Si_6$, the Fe_1 and Nb_2 sites belong to the "4/4/7 block" and are pure, whereas the T_1 and T_2 sites of the "2/4/5 block" are mixed (Fe + Cr). Finally, the two remaining metallic sites are located in the interfaces between the two blocks. One is pure (Nb_1) and the second (M_1) is a mixture of Cr and Nb atoms. This last observation is in agreement with the distribution of these elements on a very similar site present in the structure of the first quaternary silicide detected in this series, which adopts an Mn_5Si_3-type structure [2].

Finally, it is worth noting that the very short Si_5–Si_5 distance occurs in the "4/4/7" block. Such a covalent-like distance has already been observed and discussed for $Zr_4Co_4Ge_7$ isotypic compounds [16].

4.3. *$Nb_3(Cr,Fe)_4Si_6$ as a member of a structural series*

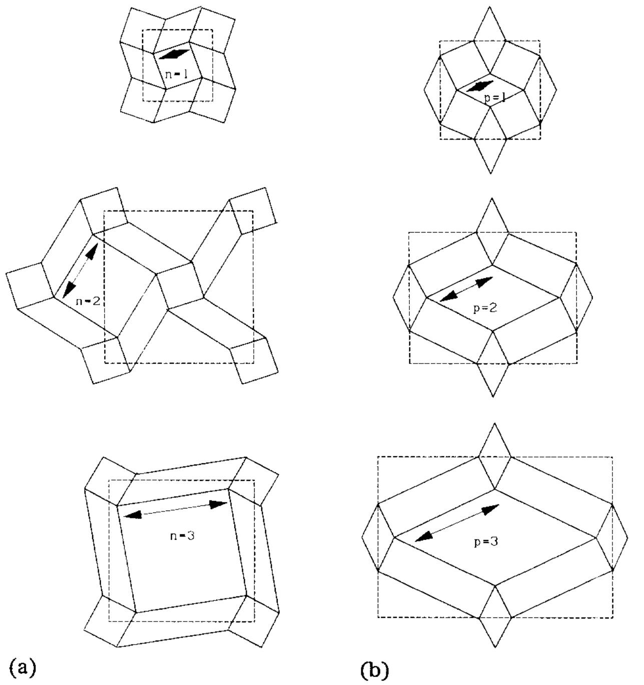
Such similarities in size and atomic distributions at the interface mean that infinite combinations of these blocks making different structure types can be perceived. Two particularly simple structural series can be distinguished. They are schematically drawn in Fig. 3 and can be used as a guide for workers investigating this composition range.

The first structure type, which is called the "tetragonal series", has $Nb_3(Cr,Fe)_4Si_6$ as the starting point and extends to the $Zr_4Co_4Ge_7$-type structure by increasing the size of the corresponding blocks. The first members of the series are given in Fig. 3(a). Calling n the number of "$Zr_4Co_4Ge_7$" units along the larger "$Zr_4Co_4Ge_7$-type block" and according to the idealized compositions of the building blocks $M_4T_4X_7$ and $M_2T_4X_5$, the general formula is given by $M_{4n+4(n^2+1)}T_{8n+4(n^2+1)}X_{10n+7(n^2+1)}$.

For $n>1$, the maximal symmetry class will be $4/m$ and the Bravais lattice will be primitive for odd n and body-centred for even n.

The approximate cell parameters are given by the following relations

$$a_T = \frac{a}{2^{1/2}} (1+n^2+2n \sin 2\alpha)^{1/2}$$



(a) (b)

Fig. 3. (a) First members of the $(NbFeCr)_7Si_6 \rightarrow Zr_4Co_4Ge_7$ series. (b) First members of the $(NbFeCr)_7Si_6 \rightarrow Nb_2Cr_4Si_5$ series.

where

$$\alpha = \arctan\left(\frac{b'}{a'}\right)$$

$$c_T = c$$

a, c and a', b', c' are the cell parameters of the $Zr_4Co_4Ge_7$- and $Nb_2Cr_4Si_5$-type structures respectively (see Section 4.2). The a_T parameter is given for the primitive tetragonal cell (n odd). For the body-centred cell (n even), it will be multiplied by $2^{1/2}$.

The second series, called the "orthorhombic series", has the same starting point and extends to $Nb_2Cr_4Si_5$ by increasing the size of the corresponding blocks. The first members of the series are given in Fig. 3(b). Calling p the number of $Nb_2Cr_4Si_5$ units along the larger $Nb_2Cr_4Si_5$ block, the general formula is given by $M_{8p+2(p^2+1)}T_{8p+4(p^2+1)}X_{14p+5(p^2+1)}$.

For $p>1$, the maximal symmetry class will be mmm and the corresponding space groups are $Pnnm$ for odd p and $Ibam$ for even p.

The approximate cell parameters are given by the following relations

$$a_o = pa' + b'$$

$$b_o = pb' + a'$$

$$c_o = c'$$

In the case of the actual $Nb_3(Cr,Fe)_4Si_6$-type structure ($n=1$, $p=1$) the above-mentioned equations give $a_T=16.852$ Å, $c_T=4.981$ Å, $a_o=23.307(=16.48\times 2^{1/2})$, $b_o=23.307(=16.48\times 2^{1/2})$, $c_o=4.879$ Å, which are close to the experimental values $a=16.558$ Å and $c=4.940$ Å.

5. Conclusions

Investigations in the quaternary Nb–Fe–Cr–Si system have led to the discovery of a new compound $Nb_{\approx 3}Fe_{\approx 3}Cr_{\approx 1}Si_6$. This new type of structure is characterized by an intergrowth of elemental blocks of $Zr_4Co_4Ge_7$- and $Nb_2Cr_4Si_5$-type structures.

$Zr_4Co_4Ge_7$-type compounds are formed with transition metals belonging to the right-hand side of the Periodic Table (T ≡ Mn, Fe, Co, Ni), whereas $Nb_2Cr_4Si_5$-type compounds are formed with intermediate T atoms (T ≡ V, Cr, Mn). The occurrence of the $Nb_3(Cr,Fe)_4Si_6$-type structure provides a method to generate structures of quaternary compounds when the metal to metalloid ratio is close to unity.

The occurrence of Mn compounds belonging to the two structural types "4/4/7" and "2/4/5" would imply the existence of the ternary silicide $Nb_3Mn_4Si_6$. Investigations in quaternary systems involving the combination of appropriate ratios of two or more different T atoms, such as Cr and Ni or V and Co, may allow some of the previously defined hypothetical phases to be synthesized. Such experiments are in progress.

Acknowledgments

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