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The Crystal Structure of Mo_5SiB_2

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The result of an investigation of the Mo-rich corner of the Mo—Si—B system is in accordance with the phase diagram recently given by Nowotny *et al.*[1] The crystal structure of the ternary phase, Mo_5SiB_2, has been determined from single crystal data. There is definite evidence for an ordered distribution of the Si and B atoms. The Mo_5SiB_2-structure is described and discussed in comparison to similar phases, especially the ternary $Me_5Si_3(X')$-phases of the $D8_8$-type, (X′ = B, C, N, O).

After the intensive research during the last few years the binary borides and silicides of the transition metals are so well known that studies on ternary systems containing both these nonmetals have been started. It seems as if metal rich ternary (MeSiB)-phases are not uncommon and the determination of the crystal structures of these should be of a considerable crystallographic interest.

Such a ternary phase was found to exist in the Mo-Si-B system and an investigation of this system was started.* From powder photographs it was concluded that the ternary phase had a composition around Mo_5SiB_2 and that it was bodycentered tetragonal (probably isomorphous [2] with Cr_5B_3). Parthé *et al.*[3] have reported the same structure for Nb_5Si_3 and Ta_5Si_3 and call it the $T2$-structure, a notation that will be used in the following.

Before presenting the results of the refinement of the Mo_5SiB_2-structure some data are given for the Mo-Si-B system.

I. PRELIMINARY SURVEY OF THE Mo—Si—B SYSTEM

Experimental. Some alloys in the Mo—MoB—Mo_5Si_3 region were prepared from Mo powder (99.7 %), Si powder (99.9 %) and B powder of 94 % purity.** Weighed amounts

* In an early stage of this work Prof. Nowotny in Vienna kindly informed me that the same system was being studied at his institute. Therefore this investigation has been mainly devoted to the determination of the crystal structure of the ternary phase from single crystal data. Nowotny *et al.*[1] have later given a report on the Mo—Si—B system in which they stated this ternary phase to have the composition Mo_5SiB_2 and to be of the $T2$-type .

** Some boron was donated by the Borax Consolidated Ltd.

of the elements were melted twice in an arc-furnace. Powder photographs were taken in cameras of the Guinier-type, using Cu$K\alpha$-radiation. The lattice dimensions could be determined with an accuracy of ± 0.1 %.

Results. The phases observed in the powder photographs are consistent with the phase diagram of Nowotny *et al.*[1] The ternary phase was found to be in equilibrium with Mo, Mo_2B, MoB, Mo_3Si and Mo_5Si_3. The lattice parameters (l.p.) of the boundary phases differed very little ($\sim$0.1—0.2 %) from those reported for the binary compounds, indicating that the substitution of Si for B and vice versa is very limited. The smallest l.p. of Mo_5SiB_2 were observed in the Mo_2B-MoB-Mo_5SiB_2 region ($a = 5.99_8$ Å, $c = 11.02_7$ Å) and the largest in the MoB-Mo_5SiB_2-Mo_5Si_3 region ($a = 6.02_8$ Å, $c = 11.07_0$ Å). The results of the chemical analysis indicated that the atomic Si/B ratio of the ternary phase did not exceed 0.5. If the l.p.-variations depend on a variation of this ratio, the homogeneity range of Mo_5SiB_2 should be about $MoSi_{0.14}B_{0.46}$—$MoSi_{0.20}B_{0.40}$ under the applied conditions.

II. REFINEMENT OF THE CRYSTAL STRUCTURE OF Mo_5SiB_2

Experimental. A small single crystal was picked out of an alloy of the approximate composition $MoSi_{0.27}B_{0.36}$ (MoB—Mo_5SiB_2—Mo_5Si_3 region). Weissenberg photographs were taken with MoK-radiation around the a-axis. The layer lines 0—7 were recorded and the intensities of 200 reflexions were visually estimated using the multiple film technique. By plotting log I_o/I_c against $(\sin \Theta/\lambda)^2$ an empirical correction for Θ-dependent adsorption and thermal movement was obtained. Because of the adsorption, log I_o/I_c did not decrease linearly with $(\sin \Theta/\lambda)^2$. The refinement was repeated until the parameters used in the I_c-calculation differed less from the final parameters of the I_o-synthesis than the estimated standard deviation. The Fourier summations were made on the Hägg-Laurent machine [4].

As mentioned the unit cell of Mo_5SiB_2 was similar [2] to that of Cr_5B_3. Bertaut and Blum [2] found that the latter was bodycentered tetragonal ($a = 5.46$ Å, $c = 10.64$ Å) and contained four formula units. The spacegroup was D_{4h}^{18}—$I4/m\,c\,m$ with 16 Cr in 16 (l) ($x = 1/6$, $z = 0.15$) and 4 Cr in 4(c). From spatial considerations the B atoms were placed in 4(a) and 8(h) with $x = 0.375$. (The value of 0.125 given in the paper by Bertaut and Blum is probably due to a misprint.)

From the l.p. of Mo_5SiB_2 it was concluded that there were four formula units in the cell, that is 20 Mo, 4 Si and 8 B atoms. The systematic absences were consistent with the space group D_{4h}^{18}—$I\,4/m\,c\,m$. The preliminary electron density calculations confirmed this spacegroup and showed that 16 Mo atoms were situated in 16 (l) and 4 Mo atoms in 4 (c).

Starting from the parameters of Bertaut and Blum the atomic parameters of the Mo atoms were refined by carrying out successive $\varrho_o(x\,z)$ and ϱ_c $(x\,z)$ projections. (48 $h0l$ reflections were used.) The backshift corrections determined from the last synthesis were less than the standard deviations, computed with Cruickshank's formula [5].

The number of electrons found in the different maxima of the two final syntheses were counted in exactly the same way and a backshift correction

was applied to the scattering parameters obtained from the last $\varrho_o(x\,z)$ synthesis. The final atomic and scattering parameters are

	atomic par.	scattering par.
4 Mo_I in 4 (c)		42.0
16 Mo_{II} in 16 (l)	$x = 0.165_3 \pm 0.0008$	41.9
	$z = 0.138_8 \pm 0.0004$	
4 Si(?) in 4 (a)		14.0

As seen, the $\varrho(x\,z)$ projections strongly suggest that the four Si atoms of the unit cell are situated in the 4(a)-positions. In that case the 8 B atoms which are not revealed by the projection should be found in the 8 (h)-positions.

A three-dimensional F_o—F_c synthesis which was carried out in the $xy0$-section supports this hypothesis. The only significant maximum found in this section had a position corresponding to an atom in 8(h) with $x = 0.37_5$. Electron counts in the $xy0$-section gave the ratio 3.1/42 between the mentioned maximum and that of the Mo atom in origo.

It is difficult to appreciate the reliability of electron counts when atoms of widely different scattering powers are involved. The various formulæ given by Lipson and Cochran [6] suggest a standard deviation of somewhat less than 2 e per peak. The flat background of the final $\varrho(x\,z)$ and $D(xy0)$ syntheses (the background did not exceed 1/3 of the Si or B peakheight, respectively) makes this accuracy seem reasonable. Therefore, the result of the Fourier summations is taken as an evidence for an ordered distribution of the B and Si atoms in Mo_5SiB_2, the Si atoms mainly occupying the 4 (a)- and the B atoms the 8 (h)-positions.

DESCRIPTION OF THE STRUCTURE

Most of the transition metal atoms in the $T2$ phases are arranged in layers of the type shown in Fig. 1 a. Metal atom layers of this type have been called A-layers by Black [7] in his discussion of alloys of Al and transition elements. The simplest way to build up a structure of A-layers is to place successive layers exactly above each other. With this stacking of A-layers (A—A—A— . . .) there will be large cubic and smaller trigonal prismatic holes between the layers. A better packing of A-layers is obtained if every second layer is translated half the base diagonal of the unit cell. (Fulldrawn and dotted A-layers of Fig. 1 c alternate.) With this stacking (A—$A_{\frac{1}{2}\frac{1}{2}}$—$A$—$A_{\frac{1}{2}\frac{1}{2}}$— . . .) the layers fit better in each other and only one type of holes is found between the layers, namely cubic antiprismatic holes.

While the A-layer skeleton in the Al-transition metal alloys [7] consists of Al atoms, it is the transition metal atoms that form layers of this type in the structures of some borides and silicides. In Mo_5SiB_2 the sequence of A-layers (consisting of Mo atoms) is A—A—$A_{\frac{1}{2}\frac{1}{2}}$—$A_{\frac{1}{2}\frac{1}{2}}$— . . . (Two fulldrawn and two dotted layers of Fig. 1 c alternate.) Thus, there are holes of all the three mentioned types: cubic, antiprismatic and trigonal prismatic, filled by Mo, Si and B atoms respectively. The Mo atoms in the cubic holes and the B atoms are in contact and form what can be called subsidiary layers in $z = 0$ and $z = \frac{1}{2}$ (Fig. 1b). The Si atoms are situated between Mo atoms of successive subsidiary layers.

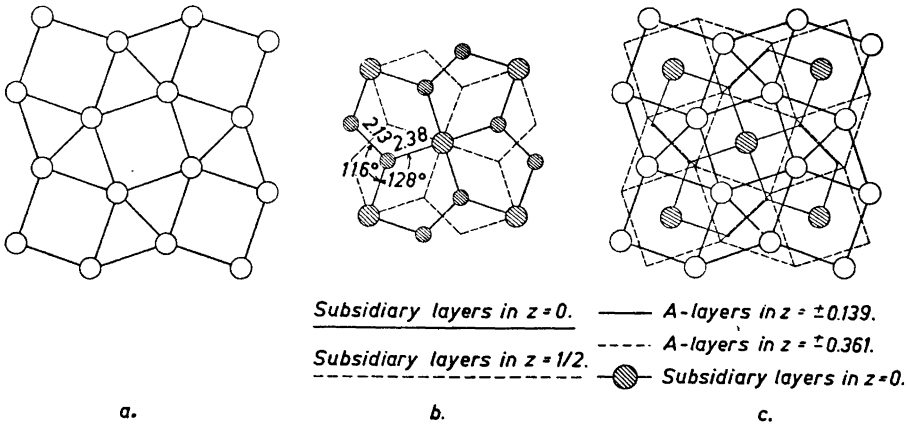

Fig. 1. a) *A*-type layer: b) Subsidiary layers of Mo and B atoms in $z = 0, \frac{1}{2}$; c) The Mo_5SiB_2-structure, projected along the *c*-axis.

As pointed out in Refs. [1,2], the atomic environments in Mo_5SiB_2 are similar to those found in related phases. The ninefold coordination around the B atoms (6 neighbours situated at the corners of a trigonal prism and 3 outside the square faces of this prism) has been found in a number of borides [8]. The ninth neighbour is a B atom at a distance of 2.13 Å. This points to a weak interaction but is another manifestation of the tendency towards B—B bonding revealed in a number of boride structures [8]. The Mo—B—Mo angle in the subsidiary layers is the same as the B—B—B angle in the boron chains of MoB (128°). The antiprismatic environment of the Si atoms (with two additional remote contacts outside the square faces of the prism) has earlier been found in the silicides of the $CuAl_2$- and W_5Si_3-types.

Table 1. Interatomic distances in Å (Estimated accuracy ±0.03 Å)

	In Mo_5SiB_2	In Mo_2B	In Mo_5Si_3*
B	— 2 Mo_I 2.38 (2)	B — 8 Mo 2.37 (8)	
	— 6 Mo_{II} 2.34 (4) 2.36 (2)	— 2 B 2.37 (2)	
	— 1 B 2.13		
Si	— 2 Mo_I 2.77 (2)		Si — 2 Si 2.45 (2)
	— 8 Mo_{II} 2.56 (8)		— 8 Mo 2.56 (8)
Mo_I	— 4 B 2.38 (4)		
	— 2 Si 2.77 (2)		
	— 8 Mo_{II} 2.72 (8)		
Mo_{II}	— 2 B 2.34, 2.36		
	— 2 Si 2.56 (2)		
	— 2 Mo_I 2.72 (2)		
	— 9 Mo_{II} 2.82, 2.85, 3.07, 3.17 (2), 3.18 (4)		

* The l.p. given in Ref.[11] have been used. Less accurate l.p. of Mo_5Si_3 have earlier been reported by this author. A redetermination has confirmed the values of Dauben, Templeton and Myers [11] within 0.05 %.

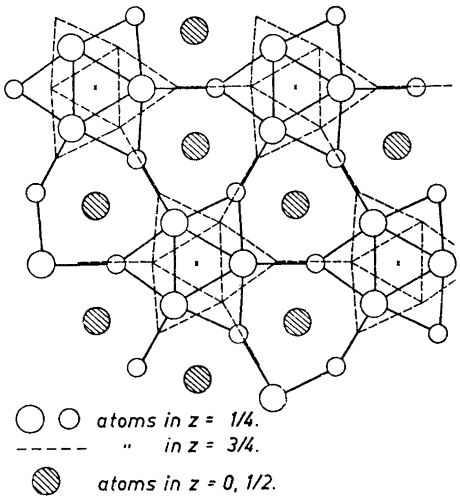

Fig. 2. The $D8_a$-structure. The position of the octahedral holes are marked with **x**.

Table 1 shows that an ordered distribution of the Si and B atoms gives Mo—B and Mo—Si distances that agree much better with those observed in Mo_2B [9] and Mo_5Si_3 [10, 11] than a disordered one. The Mo—Si distances especially would be abnormally short in a disordered structure. The fact that the atomic Si/B ratio in Mo_5SiB_2 does not exceed 0.5 probably indicates that the Si atoms can not occupy the positions giving such short distances.

DISCUSSION

As evident from the preceding paragraph the structural details of Mo_5SiB_2 are in accordance with the crystal chemical principles which have emerged from earlier studies on metal rich compounds between the transition metals and small nonmetals.

It seems as if the size factor is quite important in determining the structures in which these compounds crystallize. Hägg [12] has shown that a large number of borides, carbides, nitrides and hydrides can be classified from spatial considerations. When $r_X/r_{Me} < 0.59$ (X = nonmetal, Me = transition metal) the nonmetals are conveniently accommodated in the holes (tetrahedral, octahedral or trigonal prismatic) of simple metal lattices. When the radius ratio exceeds 0.59 these simple structures do not permit a good packing of the atoms and other structures are formed where the transition metal atoms are arranged so as to give the nonmetals larger "holes" to occupy.

The trigonal prismatic and cubic antiprismatic holes found in metal skeletons built up from *A*-type metal layers, would be suitably sized for nonmetals with r_X/r_{Me} in the range 0.65—0.85. Thus, it is not surprising that metal lattices of this type have been found among borides and silicides, *e.g.* in the

$T2$ structure. The occurrence of these structures may to a considerable extent depend on the fact that they permit a good packing of atoms with radius ratio in the above mentioned range. As pointed out by Nowotny *et al.*[1] the known $T2$ phases (Ta_5Ge_3[13], Ta_5Si_3[3], Nb_5Si_3[3], $W_5(Si, B)_3$[1], Mo_5SiB_2,[1] Cr_5B_3[2]) do indicate that the radius ratio is important for the stability of this structure. The ordered distribution of the Si and B atoms in Mo_5SiB_2 means that the B atoms occupy the smaller and the Si atoms the large holes in the Mo lattice and this also points to an influence from the size factor.

From the spatial discussion of the interstitial phases we would expect the holes in an A-type metal skeleton to be too large for carbon and nitrogen atoms (X'atoms) — especially with metal atoms from the IVa—VIa groups. Consequently we would not expect to find ternary (MeSiX') phases of the $T2$ type but rather that such phases had structures in which the Me—Si skeleton should contain octahedral holes where the X' atoms could be accommodated and thus obtain the same environment as in the wellknown stable carbides and nitrides of MeX' ($B1$ type) and Me_2X' types. (Boron and oxygen may also behave as X' elements in special cases.)

A number of ternary (MeSiX') phases have been found [14–17] for the IVa—VI a groups metals. All these phases have the composition $Me_5Si_3(X')$ and crystallize in the $D8_8$-structure [18]. They often contain quite small amounts of the X' element. It has been hinted [14, 15] that the small atoms might function interstitially but no comprehensive discussion of this possibility seems to have appeared. I think that the "stabilization" of the $D8_8$-silicides by X' atoms to some extent depends on the filling up of the octahedral holes in the $D8_8$ structure [18]. This would account for the increasing l.p. of Zr_5Si_3 (C) and Nb_5Si_3 (C) [14] with increasing carbon content and it would give some explanation to the fact that the $D8_8$-silicides have a much greater ability to dissolve X' atoms than have silicides with other structures.

It seems reasonable to assume that the interstitial solubility of X' atoms in the $D8_8$-silicides is most important for the group IV a metals and that the carbon-silicon substitution as found by Nowotny *et al.* in Mo_5Si_3 (C) will be of increasing importance with increasing group number of the metal.

The size factor has evidently a considerable influence on the occurrence of the structures mentioned in this paper and discussion from size considerations may still be of some value for the description and classification of the compounds formed by the transition metals and the small nonmetals.

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