Acta Cryst. (1964). **17**, 1077

On the crystal structure of $SrB_2O_4.4H_2O$.

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(*Received* 17 *March* 1964)

$SrB_2O_4.4H_2O$ forms colourless needles. Multiple-film Weissenberg photographs were taken with unfiltered Cu radiation from crystals prepared in the Institut für anorganische und anorganisch-technische Chemie der Technischen Universität Dresden (Lehmann & Jäger, 1963).

Crystal data

Space group: $P2_1/c$.
Cell dimensions:

$$a=8{\cdot}20 \text{ (needle axis)},\ b=16{\cdot}07,\ c=10{\cdot}91\ \text{Å};\quad \beta=118{\cdot}5°.$$

Measured density: 2·58 g.cm^{-3} at 25 °C.
Number of molecules per unit cell: $Z=8$.

In addition to the systematic absences corresponding to the space group, systematically weak reflexions were observed for all $F(hkl)$ with $h=2n$, $k=4n+2$ and $h=2n+1$, $k=4n$. This is most probably caused by the fact that all atoms occur in pairs of the same sort, related to each other by a vector with the approximate components $(\frac{1}{2}, \frac{1}{4}, 0)$.

The following positions were obtained for the independent Sr atoms:

	x	y	z
Sr(1)	0,476	0,098	0,216
Sr(2)	−0,012	−0,156	0,214

Reference

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Acta Cryst. (1964). **17**, 1077

The crystal structure of NbAs (comments).

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(*Received* 23 *January* 1964)

A determination of the crystal structure of NbAs has been reported rather recently by Boller & Parthé (1963). An independent investigation has been carried out in Oslo*. Although we have withdrawn our original manuscript some comments seem to be appropriate.

Samples were prepared from spectrographically standardized niobium (Johnson, Matthey & Co., Ltd.) and high purity arsenic (American Smelting and Refining Co.). A series of samples was prepared by heating accurately weighed quantities of the components (in different compositions) in evacuated and sealed silica tubes. The samples were heated at various temperatures between 720 and 1350 °C and quenched in ice water. Certain difficulties in the preparation of the samples resulted from reaction between niobium and the silica (Furuseth & Kjekshus, 1964). Samples of the NbAs phase were therefore also made by thermal decomposition of $NbAs_2$. After complete degradation at 1100 °C the residual crystalline phase was found to contain only the NbAs phase.

Guinier photographs (taken with strictly monochromatized Cu $K\alpha_1$ radiation, $\lambda=1{\cdot}54050$ Å, with potassium chloride, $a=6{\cdot}2919$ Å (Hambling, 1953) added as internal standard) could be indexed on tetragonal axes;

$$a=3{\cdot}4517,\quad c=11{\cdot}680\ \text{Å},\quad c/a=3{\cdot}3838$$

in excellent agreement with the values

$$a=3{\cdot}45_2,\quad c=11{\cdot}67_9\ \text{Å},\quad c/a=3{\cdot}38_4$$

reported by Boller & Parthé (1963). As the lattice constants are almost invariable for specimens with different initial proportions of the components, no composition range of the NbAs phase is indicated.

The composition NbAs was ascertained by density measurements. On the basis of the pycnometric density 7·93 g.cm^{-3} (at 25·00 °C), the unit cell contains 4 NbAs groups ($Z_c=3{\cdot}96$).

The systematic extinctions were of the same type as those reported by Boller & Parthé and accordingly we had the choice between the same six space groups. Our way to the solution of the crystal structure is somewhat different from theirs and some details will be described in the following text.

A tetragonal structure with similar composition, unit-cell dimensions and systematic extinctions in X-ray photographs had been reported for β-NbP by Schönberg (1954). The possibility of the compounds being isostructural was consequently investigated.

The relative intensities of the reflexions on Debye–Scherrer photographs were determined from photometer recordings of the films. (Attempts to obtain single crystals were unsuccessful.) Multiple-film photographs were used to avoid errors in the highest and weakest intensities on the photographs. Corrections for the resolution of $K\alpha_1\alpha_2$ doublets were carried out according to the method of Rae & Barker (1961). F_o^2 values were obtained by multiplication of the corrected intensities

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* *Note added in proof.* — Another independent study of NbAs has been published by Saini, Calvert & Tayler (1964) since this manuscript was accepted for publication. Their lattice dimensions and observed density are:

$$a=3{\cdot}443\pm0{\cdot}002,\quad c=11{\cdot}672\pm0{\cdot}005\ \text{Å},\quad D_m=8{\cdot}11\ \text{g.cm}^{-3}.$$

with $(Lp \times \nu)^{-1}$. (No corrections for absorption and temperature factors were used.) For the calculation of F_c values the atomic scattering factors were taken from Vand, Eiland & Pepinsky (1957).

A set of F_c^2 values calculated on the basis of a 'β-NbP' type atomic arrangement gave a disappointingly high reliability index, $R^* = \Sigma|F_c^2 - F_o^2|/\Sigma F_o^2 = 0{\cdot}86$. (In the first stage of the structure determination only reflexions with $\sin^2\theta \leq 0{\cdot}5$ were included.) Attention was then turned to the space groups $I4_1$ and $I4_1md$ having a fourfold position (a) with a variable z parameter. R^* was now calculated as a function of z_{As} with the niobium atoms defining the origin, $z_{\mathrm{Nb}} = 0$. From Fig. 1 a marked minimum in R^* will be seen. When all reflexions are taken into account a sharper minimum is obtained (see Fig. 1), whereas the position of the minimum is not shifted. In agreement with convention the final parameter is taken equal to $z = 0{\cdot}416 \pm 0{\cdot}001$, *i.e.* the z value at the minimum; F_o is listed in Table 1 together with F_c for $z = 0{\cdot}416$ ($R = \Sigma||F_c| - |F_o||/\Sigma|F_o| = 0{\cdot}053$).

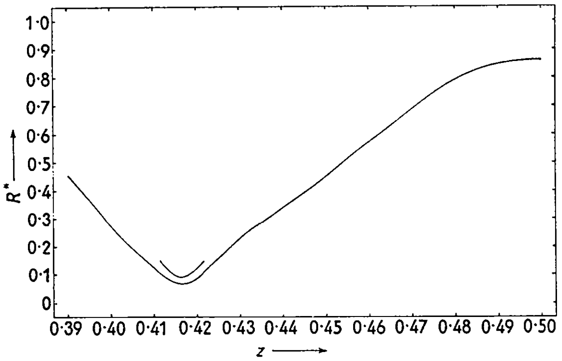

Fig. 1. Reliability index R^* as a function of the z parameter of the arsenic atoms. The lower curve includes reflexions with $\sin^2\theta \leq 0{\cdot}5$. All possible reflexions have been included in the upper curve around the minimum value.

Table 1. *Observed and calculated structure factors for* NbAs

hkl	F_o	$10\lvert F_c\rvert$	*hkl*	F_o	$10\lvert F_c\rvert$
101	488	480	1,0,11	—	256
004	1224	1208	219	784	720
103	1072	1152	0,0,12	1408	1424
112	1880	1864	321	—	288
105	1344	1376	316	—	176
200	1928	1896	307	840	952
211	392	360	228	704	736
116	—	224	323	728	704
107	1176	1208	325	880	920
204	848	896	2,1,11	—	256
008	912	888	1,1,13	—	280
213	880	880	400	1392	1312
215	1160	1152	309	736	648
220	1728	1608	2,0,12	1296	1296
109	888	784	411	—	240
301	312	320	327	904	864
217	1072	1056	404	592	640
224	600	784	413	624	632
208	744	776	332	1128	1072
303	776	776	3,1,10	1008	1080
312	1424	1304	1,1,14	1080	1040
1,1,10	1416	1312	415	600	832
305	1064	1008			

Within the limited accuracy the present value is in agreement with $z = 5/12 = 0{\cdot}4167$ reported by Boller & Parthé (1963). Although the two studies show the same result, the present determination should for the following two reasons be regarded as a more accurate confirmation of the value of the z parameter:

1. The 116 reflexion is neither sufficiently sensitive nor accurately enough observed by Boller & Parthé to determine z with the present degree of precision.
2. The geometrical considerations are only of limited value when the c/a ratio differs $\sim 2{\cdot}5\%$ from the ideal value.

At $z = 0{\cdot}5$, *i.e.* the parameter value reported by Schönberg (1954) for 'β-NbP', the z, R^* curve has a flat maximum. (The curve is symmetric around $z = 0{\cdot}5$.) It should be pointed out in this connection that although changes in a parameter alone do not normally justify the term 'a new structure type', Boller & Parthé's distinction between the 'β-NbP' and NbAs types is appropriate, as the geometry of the coordination polyhedra has been completely altered.

The shortest interatomic distances are only slightly altered by the present investigation. According to our data:

Nb(As)–4 Nb(As) : 3·3919 Å
–4 Nb(As) : 3·4517 Å
–2 As(Nb) : 2·595 ± 0·009 Å
–4 As(Nb) : 2·630 ± 0·005 Å ,

there seems nevertheless to be a slight mistake in the values listed by Boller & Parthé (1963). Instead of six equivalent Nb(As)–As(Nb) distances there are two different sets (2 + 4) of distances. With $c/a = 3{\cdot}3838$ the z parameter making the six Nb(As)–As(Nb) distances alike, appears to be 0·406. The same correction should also be applied to the distances listed for NbP and TaAs by Boller & Parthé.

For a detailed description of the structure and its relationship to other common structure types reference is made to Boller & Parthé.

The authors express their appreciation to Prof. Haakon Haraldsen for his interest in this study and for making laboratory facilities available.

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