The Crystal Structure of Nb_4As_3

BERTIL CARLSSON and STIG RUNDQVIST

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala 1, Sweden

The crystal structure of Nb_4As_3 has been determined, using single-crystal methods. The symmetry is orthorhombic (space group *Cmcm*). The cell dimensions are: $a = 3.516$ Å, $b = 14.660$ Å, $c = 18.830$ Å.

The unit cell contains 32 niobium atoms and 24 arsenic atoms. Two sets of niobium atoms are situated in positions $4a$ and $4c$, respectively, while the remaining niobium atoms occupy $8f$ positions. The arsenic atoms are situated in two sets of $4c$ positions and two sets of $8f$ positions. The structure can be described as a complex arrangement of Nb_6As prisms, with one additional niobium atom situated in an approximately cubic hole between the prisms, and one arsenic atom situated in another hole between the prisms.

In a previous paper [1] on the metal rich part of the niobium-arsenic system, the occurrence of a phase with the approximate composition Nb_4As_3 was reported. In the present paper, the results of further studies of this phase are presented. The structure has been determined and refined by single crystal X-ray methods. The previously suggested ideal crystallographic formula Nb_4As_3 has been confirmed.

EXPERIMENTAL

Preparation. The method of preparation was extensively described and discussed in the previous paper.[1] The crystals were invariably needle-shaped, with very small cross-sections. The single crystal used for the collection of the intensity data was selected from an arc melted alloy, which contained Nb_4As_3 and traces of Nb_5As_3. The crystal was fairly well shaped with the approximate dimensions $0.124 \times 0.038 \times 0.031$ mm (0.124 mm along the rotation axis, which was parallel to the a-axis).

X-Ray investigations. The cell dimensions were determined with a Guinier-Hägg type focusing camera, using strictly monochromatic $CrK\alpha_1$ radiation [$\lambda(CrK\alpha_1) = 2.28962$ Å] and silicon ($a = 5.43054$ Å) as internal calibration standard. Powder diffraction data for Nb_4As_3 are given in Table 1. The intensity data were recorded photographically in a Weissenberg equi-inclination camera, using Zr-filtered $MoK\alpha$ radiation. The multiple film technique was used with thin iron foils interleaving the films. The crystal was rotated about the a-axis, and the $(0kl)$ through $(4kl)$ reflections were recorded. The intensities were estimated visually by comparison with an intensity scale prepared using known exposures of one reflection from the crystal. A total of 396 independent $(0kl)$, 372 $(1kl)$, and 212 $(4kl)$ reflexions were measured.

Table 1. Powder diffraction data for Nb$_4$As$_3$ as measured with a Guinier-Hägg camera, using CrKα_1 radiation.

| | sin$^2\theta \times 10^5$ | | Int. | |
h k l	obs.	calc.	obs.	calc.
0 0 2	1470	1478	W	4.7
0 2 0	2420	2439	VVW	0.5
0 2 1	2793	2809	VVW	1.1
0 2 2		3918		0.3
0 2 3	5761	5766	VW	1.6
0 0 4		5914		0.2
0 2 4		8353		0.1
0 4 0	9752	9756	VVW	0.7
1 1 0		11211		0.1
	11221		M	
0 4 2		11235		4.5
1 1 1	11577	11580	ST	15.7
0 2 5		11680		1.2
1 1 2	12693	12689	VW	2.9
0 4 3		13083		0.9
0 0 6		13306		1.9
1 1 3	14538	14537	VW	4.2
0 4 4		15670		0.7
0 2 6	15748	15745	W	6.2
1 3 0	16084	16089	VVW	2.2
1 3 1	16451	16459	ST	17.9
1 1 4	17137	17125	VVW	1.0
1 3 2		17567		0.2
0 4 5	18998	18997	VW	2.8
1 3 3		19415		0.3
1 1 5	20450	20451	VST	67.7
0 2 7		20550		0.6
0 6 0		21952		0.9
1 3 4	22010	22003	VST	100.0
0 6 1		22321		0.5
0 4 6	23065	23063	M	17.7
0 6 2	23439	23430	ST	33.0
0 0 8	23661	23656	M	19.1
1 1 6		24517		0.4
0 6 3		25278		12.8
	25308		ST	
1 3 5		25329		10.5
1 5 0	25855	25845	M	11.2
0 2 8	26091	26095	M	23.8
1 5 1	26205	26215	VST	61.9
1 5 2		27324		0.5
0 6 4	27862	27866	W	9.3
0 4 7		27868		0.4
1 5 3	29174	29172	M	12.7
1 1 7		29322		2.0
1 3 6	29400	29395	ST	18.4
0 6 5	31190	31192	ST	19.5
1 5 4	31760	31759	M	16.0
0 2 9	32374	32378	W	12.1
0 4 8		33412		1.0
1 3 7	34194	34200	VST	58.0
1 1 8		34866		0.3
1 5 5	35095	35086	VVW	2.0
0 6 6		35258		0.1

Table 1. Continued.

0 0 10		36962	1.6
0 8 0		39026	0.1
0 8 1		39395	0.7
	39371		VVW
0 2 10		39401	6.6
0 4 9		39695	10.6
	39724		M
1 3 8		39744	4.9
1 7 0	40480	40480	VVW 3.6
0 8 2		40504	1.0
1 7 1	40836	40850	VVW 9.7
1 1 9		41150	0.8
0 8 3	42335	42352	ST 17.1
2 0 0	42434	42404	ST 68.4
1 7 3		43806	2.6
2 0 2		43882	0.2
1 5 7		43957	0.5
2 2 0		44843	0.1
0 8 4	44949	44939	VVW 6.5
2 2 1		45212	0.1
0 6 8		45607	0.8
1 3 9	46041	46028	VW 15.4
1 7 4		46394	0.3
0 4 10		46718	0.1
0 2 11	47176	47163	VVW 10.2
2 2 3		48169	0.4
1 1 10		48172	4.0
0 8 5		48266	4.1
2 0 4		48318	0.1
1 5 8	49534	49501	VVW 6.2
1 7 5		49720	3.2

Table 2. Structure data for Nb_4As_3. Space group *Cmcm* $Z = 8$. $a = 3.5161(3)$ Å, $b = 14.6605(10)$ Å, $c = 18.8303(11)$ Å.

		x	y	z	B (Å²)
Nb1	in 8*f*	0	0.26241 (11)	0.83821 (8)	0.38 (2)
Nb2	in 8*f*	0	0.46616 (10)	0.88002 (8)	0.31 (2)
Nb3	in 8*f*	0	0.33177 (11)	0.02848 (8)	0.36 (2)
Nb4	in 4*a*	0	0	0	0.22 (2)
Nb5	in 4*c*	0	0.94676 (15)	1/4	0.29 (2)
As1	in 8*f*	0	0.09818 (12)	0.88215 (9)	0.41 (2)
As2	in 8*f*	0	0.15774 (12)	0.07725 (9)	0.39 (2)
As3	in 4*c*	0	0.30758 (19)	1/4	0.48 (3)
As4	in 4*c*	0	0.58790 (17)	1/4	0.41 (3)

Calculations. All the calculations were performed on the Control Data (CD 3600) computer in Uppsala, using the programs listed in Table 1, Ref. 2.

The cell dimensions were refined by the least squares method. Lp- and absorption corrections were applied to the intensity data, using eight limiting planes of the form {001}, {021}, {031}, and {100}, and a linear absorption coefficient of 301 cm⁻¹. In the calculation of structure factors, atomic scattering factors (including the real part of the anomalous dispersion) were taken from Ref. 3. The refinement of the structure was performed with a full matrix least squares program.

DETERMINATION OF THE STRUCTURE

The magnitude of the cell volume indicates a cell content of about 56 atoms, which would correspond to eight formula units of Nb_4As_3. The oscillation and Weissenberg photographs showed orthorhombic symmetry. Extinctions were observed for hkl reflexions, when $h + k = 2n + 1$, and for $h0l$ reflexions, when $l = 2n + 1$. In the previous report, the space group symmetry $C222_1$ was suggested on the basis of a rather limited survey of the reciprocal space. Additional data showed, however, that the extinctions covered a larger portion of the reflexions than was initially assumed. If the extinctions observed are systematic, the possible space groups are $Cmcm$, $Cmc2_1$, and $C2cm$.

A careful visual inspection of the Weissenberg films showed that the intensity ratio between corresponding hkl and $h + 2,kl$ reflexions was apparently constant. This observation, combined with the fact that the length of the a axis is only 3.516 Å, indicates that the atoms are confined to two planes perpendicular to the a axis and spaced $a/2$ apart. In this case, the Patterson section $P(0vw)$ should contain all relevant maxima of the whole three-dimensional Patterson function. The Patterson section $P(0vw)$ was calculated using the intensity material from the layer lines $(0kl)$ and $(1kl)$. A simple superposition analysis yielded a structure proposal, which explained all significant maxima in the Patterson section. The atomic arrangement obtained appeared to be centrosymmetric, and it could be described in terms of $Cmcm$ symmetry, with niobium atoms in one $4a$, one $4c$, and three $8f$ positions, and arsenic atoms in two $4c$, and two $8f$ positions. This corresponds to the ideal crystallographic formula Nb_4As_3. The electron density section $P(0yz)$ was computed for the structure proposal, and maxima appeared with the expected locations and heights. A backshift correction was applied to the atomic positions obtained from the electron density map, and the resulting values were used as starting parameters in a subsequent least squares refinement. The refinement included observed structure factors for reflexions from the layer lines $(0kl)$, $(1kl)$, and $(4kl)$. The reflexions were weighted according to the formula $w = 1/(a + |F_o| + c|F_o|^2 + d|F_o|^3)$. The constants were adjusted on the basis of weight analyses calculated after each refinement cycle, and the final values adopted were $a = 60$, $c = 0.002$, and $d = 0.0009$. $Cmcm$ symmetry was assumed, and the following parameters were refined: 1 scale factor for each of the three layer lines, 13 positional parameters, and 9 isotropic temperature factors. The comparison between observed and calculated structure factors indicated extinction effects for the strongest reflexions, but the number of reflexions affected appreciably was quite small, and no correction was therefore applied. The refinement converged rapidly, and the final conventional R value for the 980 reflexions was 0.099. A final difference Fourier synthesis showed no abnormal features. The largest positive and negative parts of the difference map were less than 10 % of the arsenic peaks in the F_o-synthesis. The results of this refinement are given in Table 2, and the observed and calculated structure factors are listed in Table 3.

Although the refinement yielded a satisfactory result in terms of $Cmcm$ symmetry, the possibility still remained that one of the lower space groups $Cmc2_1$ or $C2cm$ might represent a better alternative. A decision between

CARLSSON AND RUNDQVIST

Table 3. Observed and calculated structure factors. The observed structure factors are corrected for absorption.

h	k	l	$|F_o|$	$|F_c|$	h	k	l	$|F_o|$	$|F_c|$	h	k	l	$|F_o|$	$|F_c|$	h	k	l	$|F_o|$	$|F_c|$	h	k	l	$|F_o|$	$|F_c|$

Table 3. Continued.

h	k	l	$\|F_o\|$	$\|F_c\|$
0	30	23	-	12.4
0	30	24	-	43.5
0	30	25	-	41.5
0	30	26	93.2	102.8
0	30	27	-	11.2
0	30	28	-	48.2
0	30	29	-	25.3
0	30	30	-	20.2
0	30	31	-	31.7
0	30	32	76.9	53.8
0	30	33	-	32.1
0	30	34	85.4	95.9
0	30	35	-	7.0
0	30	36	-	19.2
0	32	0	76.4	77.5
0	32	1	-	39.0
0	32	2	-	28.3
0	32	3	-	2.1
0	32	4	-	47.8
0	32	5	-	1.6
0	32	6	84.6	88.5
0	32	7	-	33.3
0	32	8	70.3	77.5
0	32	9	70.0	58.6
0	32	10	69.6	77.0
0	32	11	-	9.4
0	32	12	-	1.8
0	32	13	-	47.1
0	32	14	-	44.5
0	32	15	-	3.8
0	32	16	134.0	141.7
0	32	17	-	26.0
0	32	18	-	26.1
0	32	19	-	0.3
0	32	20	-	18.4
0	32	21	-	20.1
0	32	22	-	9.6
0	32	23	-	42.3
0	32	24	66.5	69.6
0	32	25	-	12.3
0	32	26	67.5	74.1
0	32	27	-	14.8
0	32	28	-	33.2
0	32	29	-	26.3
0	32	30	58.0	62.1
0	32	31	-	22.9
0	32	32	-	10.3
0	32	33	-	5.6
0	34	0	-	44.3
0	34	1	-	63.4
0	34	2	-	22.5
0	34	3	-	28.8
0	34	4	-	10.8
0	34	5	-	51.6
0	34	6	74.2	68.5
0	34	7	-	18.4
0	34	8	-	47.6
0	34	9	-	45.4
0	34	10	-	13.0
0	34	11	-	25.0
0	34	12	-	40.1
0	34	13	-	53.2
0	34	14	-	3.2
0	34	15	-	20.9
0	34	16	-	16.6
0	34	17	-	37.4
0	34	18	-	59.3
0	34	19	-	13.7
0	34	20	-	49.6
0	34	21	-	13.5
0	34	22	-	3.3
0	34	23	-	81.2
0	34	24	-	43.7
0	34	25	-	7.7
0	34	26	-	0.3
0	34	27	-	19.2
0	34	28	-	14.3
0	34	29	-	6.3
0	34	30	-	25.1
0	36	0	-	22.6
0	36	1	-	34.8
0	36	2	-	19.2
0	36	3	-	32.7
0	36	4	119.5	133.8
0	36	5	-	14.1
0	36	6	-	11.3
0	36	7	68.8	78.8
0	36	8	-	60.6
0	36	9	-	61.2
0	36	10	-	12.0
0	36	11	-	32.7
0	36	12	-	18.1
0	36	13	-	1.5
0	36	14	-	33.1
0	36	15	94.7	96.7
0	36	16	-	33.3
0	36	17	-	18.8
0	36	18	87.0	71.1
0	36	19	-	4.8
0	36	20	-	45.7
0	36	21	-	38.3
0	36	22	-	14.0
0	36	23	-	18.1
0	36	24	-	4.4
0	36	25	-	35.7
0	36	26	-	45.5
0	38	0	50.1	48.7
0	38	1	-	40.1
0	38	2	-	5.2
0	38	3	49.7	39.8
0	38	4	-	11.2
0	38	5	58.6	57.0
0	38	6	-	6.3
0	38	7	54.4	63.6
0	38	8	-	18.4
0	38	9	-	7.0
0	38	10	-	1.2
0	38	11	-	35.0
0	38	12	81.0	95.1
0	38	13	-	28.4
0	38	14	53.8	56.9
0	38	15	51.7	57.7
0	38	16	-	14.7
0	38	17	-	1.4
0	38	18	-	29.7
0	38	19	45.7	58.7
0	38	20	-	24.3
0	40	0	-	22.4
0	40	1	-	37.2
0	40	2	-	27.1
0	40	3	52.1	66.6
0	40	4	-	24.3
0	40	5	-	15.3
0	40	6	-	2.3
0	40	7	-	8.8
0	40	8	-	29.1
0	40	9	-	16.6
0	40	10	-	44.2
0	40	11	-	37.7
0	40	12	-	19.9
0	40	13	-	6.2
1	1	0	-	19.0
1	1	1	-	217.4
1	1	2	-	97.4
	1	3	142.9	126.2
1	1	4	69.3	65.8
1	1	5	421.0	591.6
1	1	6	54.1	51.7
1	1	7	113.0	115.8
1	1	8	48.4	47.7
1	1	9	69.7	71.3
1	1	10	126.7	151.3
1	1	11	95.6	102.2
1	1	12	237.9	255.5
1	1	13	43.3	40.2
1	1	14	196.1	226.2
1	1	15	171.4	194.6
1	1	16	95.9	109.2
1	1	17	211.6	242.3
1	1	18	74.8	80.0
1	1	19	150.6	161.8
1	1	20	91.0	107.1
1	1	21	191.5	198.4
1	1	22	107.0	100.5
1	1	23	-	26.5
1	1	24	57.8	56.7
1	1	25	107.0	126.0
1	1	26	100.3	91.3
1	1	27	178.7	170.8
1	1	28	96.8	97.0
1	1	29	-	49.0
1	1	30	-	12.1
1	1	31	-	31.0
1	1	32	-	59.6
1	1	33	-	69.4
1	1	34	-	22.4
1	1	35	-	27.5
1	1	36	-	35.2
1	1	37	-	39.8
1	1	38	-	43.6
1	1	39	-	11.5
1	1	40	-	13.7
1	1	41	120.2	123.3
1	1	42	-	5.7
1	1	43	-	59.8
1	1	44	-	24.9
1	1	45	-	24.6
1	1	46	-	28.0
1	1	47	-	37.1
1	1	48	-	11.1
1	1	49	-	25.1
1	1	50	-	25.5
1	1	51	-	31.4
1	1	52	-	56.7
1	3	0	161.9	134.8
1	3	1	291.1	276.7
1	3	2	31.7	27.8
1	3	3	39.3	36.1
1	3	4	547.1	740.5
1	3	5	225.1	252.1
1	3	6	304.2	347.6
1	3	7	472.4	631.5
1	3	8	173.0	182.2
1	3	9	266.7	306.7
1	3	10	199.2	198.0
1	3	11	211.1	254.0
1	3	12	171.0	187.7
1	3	13	-	15.5
1	3	14	193.0	200.9
1	3	15	382.4	460.1
1	3	16	133.7	137.0
1	3	17	300.6	291.6
1	3	18	113.4	124.4
1	3	19	-	14.1
1	3	20	227.3	240.1
1	3	21	79.4	72.2
1	3	22	-	9.2
1	3	23	133.8	150.3
1	3	24	-	25.5
1	3	25	60.3	53.6
1	3	26	146.3	171.1
1	3	27	-	45.6
1	3	28	129.1	123.9
1	3	29	173.2	186.6
1	3	30	148.4	146.6
1	3	31	181.3	190.8
1	3	32	184.9	182.7
1	3	33	-	27.4
1	3	34	-	17.0
1	3	35	-	65.9
1	3	36	148.4	147.5
1	3	37	135.6	121.2
1	3	38	-	58.9
1	3	39	162.4	152.5
1	3	40	-	35.6
1	3	41	-	29.1
1	3	42	-	34.4
1	3	43	-	2.6
1	3	44	71.9	88.0
1	3	45	-	51.5
1	3	46	-	45.7
1	3	47	-	36.9
1	3	48	-	32.5
1	3	49	-	11.5
1	3	50	64.4	69.7
1	3	51	-	40.7
1	3	52	-	25.7
1	5	0	363.2	370.3
1	5	1	525.7	619.2
1	5	2	64.3	54.9
1	5	3	289.0	288.4
1	5	4	324.2	328.7
1	5	5	133.5	117.6
1	5	6	-	12.4
1	5	7	59.7	54.3
1	5	8	178.2	185.6
1	5	9	296.2	287.0
1	5	10	85.7	88.2
1	5	11	127.8	125.6
1	5	12	239.4	296.1
1	5	13	254.0	262.7
1	5	14	286.3	301.8
1	5	15	-	26.0
1	5	16	-	34.9
1	5	17	131.2	124.7
1	5	18	-	31.4
1	5	19	64.2	65.7
1	5	20	234.3	198.9
1	5	21	-	17.4
1	5	22	265.7	251.7
1	5	23	405.0	434.9
1	5	24	-	22.7
1	5	25	-	15.5
1	5	26	-	38.7
1	5	27	-	38.7
1	5	28	119.4	116.9
1	5	29	-	13.4
1	5	30	113.7	92.8
1	5	31	140.0	121.1
1	5	32	-	49.5
1	5	33	-	48.0
1	5	34	74.3	64.0
1	5	35	86.6	91.1
1	5	36	-	2.3
1	5	37	-	38.2
1	5	38	94.2	77.7
1	5	39	-	10.2
1	5	40	-	37.8
1	5	41	-	50.8
1	5	42	-	42.4
1	5	43	-	56.5
1	5	44	-	4.9
1	5	45	116.6	119.6
1	5	46	77.2	80.6
1	5	47	67.6	68.1
1	5	48	-	42.4
1	5	49	-	19.7
1	5	50	-	7.4
1	5	51	-	16.6
1	5	52	-	26.3
1	7	0	231.0	218.8
1	7	1	282.1	255.0
1	7	2	-	0.2
1	7	3	132.6	129.2
1	7	4	56.3	45.5
1	7	5	139.4	133.3
1	7	6	-	9.3
1	7	7	185.5	231.6
1	7	8	69.2	67.2
1	7	9	131.6	125.7
1	7	10	-	9.0
1	7	11	156.6	139.8
1	7	12	313.0	381.3
1	7	13	277.6	253.2
1	7	14	210.2	211.1
1	7	15	144.7	159.9
1	7	16	67.4	60.6
1	7	17	-	33.2
1	7	18	52.1	49.3
1	7	19	-	25.1
1	7	20	99.1	90.9
1	7	21	-	14.4
1	7	22	-	29.0
1	7	23	240.6	213.4
1	7	24	145.1	145.1
1	7	25	86.8	80.2
1	7	26	89.0	73.8
1	7	27	-	46.1
1	7	28	-	51.0
1	7	29	-	41.9
1	7	30	-	37.8
1	7	31	-	6.1
1	7	32	-	11.7
1	7	33	-	13.5
1	7	34	86.5	90.7
1	7	35	103.8	112.6
1	7	36	-	40.5
1	7	37	-	15.0
1	7	38	-	71.1
1	7	39	66.1	79.4
1	7	40	-	30.5
1	7	41	-	29.6
1	7	42	-	1.1
1	7	43	-	15.1
1	7	44	-	17.7
1	7	45	79.4	78.1
1	7	46	-	5.9
1	7	47	-	7.0
1	7	48	-	35.7
1	7	49	-	7.2
1	7	50	-	38.9
1	7	51	-	1.0
1	7	52	-	33.7
1	9	0	92.5	97.6
1	9	1	145.5	150.5
1	9	2	249.3	358.3
1	9	3	-	15.7
1	9	4	73.4	72.3
1	9	5	205.9	193.4
1	9	6	250.8	243.8
1	9	7	77.6	64.7
1	9	8	288.0	287.0
1	9	9	150.9	161.3
1	9	10	211.4	252.1
1	9	11	-	13.3
1	9	12	361.1	400.0
1	9	13	58.9	49.6
1	9	14	106.2	113.6
1	9	15	58.6	51.0
1	9	16	-	32.4
1	9	17	95.9	103.4
1	9	18	108.1	92.3
1	9	19	77.4	61.1
1	9	20	103.8	103.6
1	9	21	55.9	58.0
1	9	22	-	49.1
1	9	23	93.0	84.4
1	9	24	87.8	76.2
1	9	25	-	48.9
1	9	26	99.6	82.8
1	9	27	60.2	51.3
1	9	28	-	5.4
1	9	29	63.7	97.5
1	9	30	-	54.5
1	9	31	-	53.6
1	9	32	110.9	102.7
1	9	33	-	57.2
1	9	34	252.4	254.6
1	9	35	-	13.5
1	9	36	-	22.0
1	9	37	-	13.9
1	9	38	-	2.0
1	9	39	-	5.1
1	9	40	-	23.9
1	9	41	-	33.3
1	9	42	86.9	94.4
1	9	43	-	1.5
1	9	44	-	13.8
1	9	45	-	28.4
1	9	46	-	42.6
1	9	47	-	22.4
1	9	48	-	25.6
1	9	49	-	3.4
1	9	50	-	6.5
1	9	51	-	40.0
1	11	0	166.5	145.3
1	11	1	-	21.2
1	11	2	152.7	139.3
1	11	3	397.2	440.2
1	11	4	442.7	474.1
1	11	5	78.3	82.9
1	11	6	309.4	293.8
1	11	7	54.7	43.1
1	11	8	67.9	74.9
1	11	9	56.2	43.4
1	11	10	263.8	254.5
1	11	11	325.9	330.0
1	11	12	143.2	133.0
1	11	13	103.2	99.6
1	11	14	164.4	162.4
1	11	15	44.5	38.1
1	11	16	58.6	54.8
1	11	17	122.7	123.5
1	11	18	379.1	431.4
1	11	19	153.5	152.9
1	11	20	109.2	102.6
1	11	21	207.6	207.9
1	11	22	47.5	34.5
1	11	23	116.9	126.6
1	11	24	99.2	86.5
1	11	25	189.5	176.3
1	11	26	252.9	250.0
1	11	27	81.4	71.7
1	11	28	154.8	167.9
1	11	29	-	30.7
1	11	30	-	36.7
1	11	31	-	33.0
1	11	32	-	13.9
1	11	33	124.2	131.7
1	11	34	113.9	109.0
1	11	35	76.4	72.4
1	11	36	67.1	59.5
1	11	37	-	20.1
1	11	38	-	8.9
1	11	39	-	13.3
1	11	40	67.8	74.5
1	11	41	-	23.4
1	11	42	121.5	129.0
1	11	43	97.1	121.4
1	11	44	-	7.2
1	11	45	-	17.7
1	11	46	-	0.6
1	11	47	-	9.9
1	11	48	-	14.5
1	11	49	47.6	49.3
1	11	50	78.7	114.0
1	13	0	149.1	127.3
1	13	1	134.5	123.3
1	13	2	161.8	155.3
1	13	3	67.1	58.8
1	13	4	56.7	54.7
1	13	5	321.6	311.0
1	13	6	202.5	195.9
1	13	7	204.8	184.9
1	13	8	102.9	115.0
1	13	9	-	23.0
1	13	10	195.8	207.6
1	13	11	-	17.1
1	13	12	-	13.6
1	13	13	100.8	96.6
1	13	14	147.5	155.3
1	13	15	179.2	163.9
1	13	16	228.5	259.2
1	13	17	98.8	94.7
1	13	18	-	0.8
1	13	19	191.4	175.2
1	13	20	64.2	66.2
1	13	21	97.6	89.8
1	13	22	83.3	78.0
1	13	23	55.6	46.2
1	13	24	103.3	96.0
1	13	25	70.6	56.9
1	13	26	141.5	136.0
1	13	27	203.2	179.5
1	13	28	-	76.1
1	13	29	-	25.5
1	13	30	71.1	72.0
1	13	31	-	27.1
1	13	32	-	30.2
1	13	33	-	3.1
1	13	34	80.7	65.0
1	13	35	-	51.0
1	13	36	-	23.6
1	13	37	-	25.3
1	13	38	-	6.7
1	13	39	-	35.7
1	13	40	96.0	89.4
1	13	41	93.0	100.2
1	13	42	-	43.9
1	13	43	-	15.6
1	13	44	-	33.8
1	13	45	-	15.7
1	13	46	-	2.6
1	13	47	-	36.0
1	13	48	-	17.9
1	13	49	-	48.6
1	13	50	-	47.3
1	15	0	271.4	266.8
1	15	1	-	47.4
1	15	2	89.0	89.6
1	15	3	98.1	89.1
1	15	4	98.4	97.4
1	15	5	-	23.1
1	15	6	362.0	309.0
1	15	7	-	30.6
1	15	8	122.1	126.4
1	15	9	123.6	100.7
1	15	10	57.9	59.7
1	15	11	114.5	109.3
1	15	12	-	14.0
1	15	13	-	1.6
1	15	14	90.8	85.5
1	15	15	101.0	94.4
1	15	16	112.8	96.4
1	15	17	-	3.2
1	15	18	53.0	65.0
1	15	19	-	37.3
1	15	20	-	1.0
1	15	21	-	28.1
1	15	22	69.6	63.9
1	15	23	57.8	50.8
1	15	24	71.8	63.9
1	15	25	-	10.2
1	15	26	-	6.7
1	15	27	61.0	57.2
1	15	28	-	46.2
1	15	29	-	12.8
1	15	30	124.5	116.4
1	15	31	-	44.9
1	15	32	150.9	159.3
1	15	33	-	5.4
1	15	34	61.9	55.1
1	15	35	-	42.6
1	15	36	78.2	65.7
1	15	37	-	38.3
1	15	38	75.1	54.6
1	15	39	-	20.7
1	15	40	-	15.8
1	15	41	-	5.6
1	15	42	-	46.6
1	15	43	-	17.1
1	15	44	-	40.8
1	15	45	-	2.1
1	15	46	-	8.2
1	15	47	-	20.3
1	15	48	-	23.1
1	15	49	-	24.3
1	17	0	-	4.4
1	17	1	95.3	92.5
1	17	2	105.0	83.9
1	17	3	105.5	106.3
1	17	4	127.5	133.8
1	17	5	106.5	98.6
1	17	6	166.4	149.4
1	17	7	265.1	270.4
1	17	8	267.1	256.5
1	17	9	120.4	116.4
1	17	10	65.0	54.5
1	17	11	85.0	63.3
1	17	12	-	8.4
1	17	13	-	35.5
1	17	14	-	22.0
1	17	15	290.3	278.7
1	17	16	324.2	302.1
1	17	17	-	22.3
1	17	18	-	7.5
1	17	19	-	38.0
1	17	20	151.8	147.2
1	17	21	140.5	125.0
1	17	22	83.4	63.9
1	17	23	-	17.2
1	17	24	92.3	89.6
1	17	25	111.4	98.6
1	17	26	-	43.6
1	17	27	-	41.2
1	17	28	113.9	97.1
1	17	29	76.6	71.6
1	17	30	76.6	84.5
1	17	31	105.0	97.2
1	17	32	62.1	71.0
1	17	33	-	20.1
1	17	34	-	30.1
1	17	35	-	60.5
1	17	36	-	0.1
1	17	37	81.5	79.2
1	17	38	94.4	90.5
1	17	39	91.3	90.5
1	17	40	79.7	79.1
1	17	41	49.8	51.0
1	17	42	-	10.6
1	17	43	-	45.1
1	17	44	-	27.3
1	17	45	-	18.8
1	17	46	-	16.3
1	17	47	-	30.3
1	17	48	-	59.7
1	19	0	369.5	432.9
1	19	1	123.0	124.1
1	19	2	62.4	60.4
1	19	3	174.6	164.0
1	19	4	86.5	87.6
1	19	5	-	17.7
1	19	6	73.5	71.5
1	19	7	-	27.4
1	19	8	180.1	163.1
1	19	9	197.8	152.4
1	19	10	-	47.2
1	19	11	241.5	197.3
1	19	12	243.8	206.6
1	19	13	-	27.4
1	19	14	-	7.9
1	19	15	72.8	81.2
1	19	16	215.1	168.9
1	19	17	-	16.0
1	19	18	63.1	65.6
1	19	19	99.5	93.8
1	19	20	-	13.1
1	19	21	-	34.0
1	19	22	147.3	155.9
1	19	23	148.6	153.4
1	19	24	233.8	237.4
1	19	25	-	68.7
1	19	26	95.6	107.5
1	19	27	-	31.0
1	19	28	-	20.2
1	19	29	-	26.6
1	19	30	88.1	76.7
1	19	31	104.1	99.6
1	19	32	-	60.3
1	19	33	-	41.4
1	19	34	-	50.7
1	19	35	-	49.9
1	19	36	-	66.5
1	19	37	-	45.4
1	19	38	-	16.8
1	19	39	-	17.1
1	19	40	-	44.9
1	19	41	-	8.2
1	19	42	-	33.1
1	19	43	-	55.5
1	19	44	-	49.0
1	19	45	-	59.4
1	19	46	74.0	84.4
1	21	0	98.5	89.5
1	21	1	90.8	87.7
1	21	2	220.7	186.9
1	21	3	99.0	99.2
1	21	4	70.3	62.5
1	21	5	-	0.5
1	21	6	-	32.1
1	21	7	84.5	88.0
1	21	8	176.1	166.4
1	21	9	-	40.8
1	21	10	163.0	142.5
1	21	11	-	35.0
1	21	12	216.3	193.1
1	21	13	-	22.2
1	21	14	-	58.7
1	21	15	-	8.5
1	21	16	90.5	73.4
1	21	17	77.1	73.0
1	21	18	-	1.1
1	21	19	-	54.7
1	21	20	78.9	69.9
1	21	21	-	31.2
1	21	22	-	19.8
1	21	23	95.1	91.1
1	21	24	-	26.0
1	21	25	-	4.6
1	21	26	67.5	60.8
1	21	27	67.3	68.3
1	21	28	-	50.6
1	21	29	-	50.7
1	21	30	-	1.5
1	21	31	-	7.9
1	21	32	70.7	59.5
1	21	33	-	3.0
1	21	34	156.9	167.2
1	21	35	-	8.9
1	21	36	-	28.5
1	21	37	-	18.6
1	21	38	-	9.7
1	21	39	-	28.0
1	21	40	-	49.4
1	21	41	-	12.9
1	21	42	57.8	57.8
1	21	43	-	33.8
1	21	44	-	7.5
1	21	45	-	9.8
1	23	0	-	2.0
1	23	1	80.3	71.6
1	23	2	80.4	72.6
1	23	3	-	43.3
1	23	4	-	6.0
1	23	5	104.6	103.2
1	23	6	152.2	140.2
1	23	7	-	30.4
1	23	8	-	34.2
1	23	9	-	31.7
1	23	10	-	14.6
1	23	11	-	39.2
1	23	12	131.0	109.0
1	23	13	100.9	90.2
1	23	14	-	39.2
1	23	15	-	45.3
1	23	16	-	11.5
1	23	17	-	39.5
1	23	18	148.7	151.2
1	23	19	-	30.4
1	23	20	113.2	123.9
1	23	21	-	4.4
1	23	22	-	27.8
1	23	23	104.7	92.9
1	23	24	-	56.0
1	23	25	-	41.7
1	23	26	-	3.3
1	23	27	-	42.0
1	23	28	-	34.0
1	23	29	-	23.7

Table 3. Continued.

h	k	l	$|F_o|$	$|F_c|$	h	k	l	$|F_o|$	$|F_c|$	h	k	l	$|F_o|$	$|F_c|$	h	k	l	$|F_o|$	$|F_c|$	h	k	l	$|F_o|$	$|F_c|$

Table 3. Continued.

h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$
4	20	7	-	46.9	4	22	20	107.1	103.4	4	24	35	-	5.6	4	28	16	-	32.5	4	32	8	-	60.4
4	20	8	74.3	78.4	4	22	21	-	52.9	4	24	36	-	33.7	4	28	17	-	40.4	4	32	9	-	44.9
4	20	9	164.1	154.4	4	22	22	-	5.8	4	24	37	-	5.3	4	28	18	98.5	105.6	4	32	10	-	60.2
4	20	10	-	16.0	4	22	23	-	42.0	4	26	0	-	44.2	4	28	19	-	8.8	4	32	11	-	7.9
4	20	11	-	41.7	4	22	24	-	51.1	4	26	1	-	32.0	4	28	20	-	19.5	4	32	12	-	0.4
4	20	12	127.4	112.9	4	22	25	-	63.9	4	26	2	-	10.6	4	28	21	-	47.3	4	32	13	-	35.9
4	20	13	-	68.6	4	22	26	-	21.5	4	26	3	-	7.0	4	28	22	-	75.5	4	32	14	-	35.3
4	20	14	-	28.7	4	22	27	-	32.7	4	26	4	-	24.3	4	28	23	-	27.5	4	32	15	-	3.3
4	20	15	-	50.2	4	22	28	-	19.1	4	26	5	-	34.0	4	28	24	-	24.0	4	32	16	94.4	110.6
4	20	16	139.9	127.7	4	22	29	119.6	116.1	4	26	6	-	6.9	4	28	25	-	57.8	4	32	17	-	20.3
4	20	17	-	58.7	4	22	30	-	9.4	4	26	7	-	6.3	4	28	26	-	53.1	4	32	18	-	21.1
4	20	18	-	25.9	4	22	31	75.1	79.8	4	26	8	-	14.5	4	28	27	-	18.4	4	32	19	-	0.0
4	20	19	-	27.0	4	22	32	-	69.7	4	26	9	-	55.1	4	28	28	-	36.6	4	32	20	-	14.6
4	20	20	-	66.8	4	22	33	-	3.3	4	26	10	-	23.3	4	28	29	-	16.4	4	32	21	-	15.7
4	20	21	-	42.9	4	22	34	-	18.1	4	26	11	123.8	111.8	4	28	30	-	26.9	4	32	22	-	7.5
4	20	22	-	14.8	4	22	35	-	44.5	4	26	12	79.1	89.6	4	28	31	-	17.5	4	32	23	-	37.7
4	20	23	98.3	91.9	4	22	36	-	28.5	4	26	13	-	13.6	4	28	32	-	6.5	4	32	24	-	56.0
4	20	24	106.8	93.5	4	22	37	-	54.9	4	26	14	88.8	90.0	4	30	0	113.8	135.2	4	32	25	-	9.9
4	20	25	-	11.2	4	22	38	-	41.7	4	26	15	-	38.1	4	30	1	-	31.0	4	34	0	-	34.8
4	20	26	-	37.5	4	22	39	-	102.5	4	26	16	-	39.2	4	30	2	-	78.8	4	34	1	-	49.2
4	20	27	-	1.0	4	24	0	-	69.9	4	26	17	-	23.3	4	30	3	-	42.0	4	34	2	-	17.0
4	20	28	-	60.0	4	24	1	137.9	131.2	4	26	18	-	41.2	4	30	4	-	64.3	4	34	3	-	22.3
4	20	29	-	78.8	4	24	2	97.4	98.2	4	26	19	-	7.9	4	30	5	-	52.3	4	34	4	-	9.9
4	20	30	-	47.4	4	24	3	137.7	133.4	4	26	20	-	14.8	4	30	6	-	82.1	4	34	5	-	40.5
4	20	31	-	73.6	4	24	4	-	87.9	4	26	21	-	29.0	4	30	7	-	10.1	4	34	6	-	53.5
4	20	32	-	6.6	4	24	5	-	59.8	4	26	22	-	29.8	4	30	8	-	68.7	4	34	7	-	13.7
4	20	33	-	34.8	4	24	6	-	37.5	4	26	23	-	15.9	4	30	9	-	50.1	4	34	8	-	38.4
4	20	34	-	23.0	4	24	7	-	38.9	4	26	24	-	61.7	4	30	10	-	48.5	4	34	9	-	34.8
4	20	35	-	10.6	4	24	8	-	24.8	4	26	25	-	23.1	4	30	11	-	7.6	4	34	10	-	9.6
4	20	36	-	34.2	4	24	9	-	19.1	4	26	26	-	47.8	4	30	12	-	65.5	4	34	11	-	20.1
4	20	37	-	39.1	4	24	10	-	29.1	4	26	27	-	36.0	4	30	13	-	17.1	4	34	12	-	31.7
4	20	38	-	18.3	4	24	11	-	8.2	4	26	28	-	1.9	4	30	14	-	20.5	4	34	13	-	41.4
4	20	39	-	5.5	4	24	12	-	0.5	4	26	29	-	15.1	4	30	15	-	48.5	4	34	14	-	2.3
4	20	40	-	29.1	4	24	13	-	11.8	4	26	30	-	14.5	4	30	16	-	0.6	4	34	15	-	16.4
4	20	41	-	17.5	4	24	14	-	10.8	4	26	31	-	38.2	4	30	17	-	39.9	4	34	16	-	14.2
4	22	0	-	41.1	4	24	15	-	16.4	4	26	32	-	9.0	4	30	18	-	74.2	4	34	17	-	30.0
4	22	1	86.2	73.8	4	24	16	-	9.3	4	26	33	-	23.7	4	30	19	-	7.5	4	34	18	-	46.9
4	22	2	-	57.3	4	24	17	-	6.4	4	26	34	-	27.3	4	30	20	-	69.4	4	34	19	-	11.0
4	22	3	-	24.5	4	24	18	-	41.2	4	26	35	-	46.1	4	30	21	-	51.6	4	34	20	-	40.3
4	22	4	-	51.4	4	24	19	95.0	99.1	4	28	0	-	58.0	4	30	22	-	40.9	4	34	21	-	10.7
4	22	5	-	6.3	4	24	20	-	23.1	4	28	1	-	5.3	4	30	23	-	9.0	4	36	0	-	18.2
4	22	6	-	36.5	4	24	21	-	9.6	4	28	2	-	68.2	4	30	24	-	34.6	4	36	1	-	27.5
4	22	7	238.4	250.4	4	24	22	-	16.1	4	28	3	-	67.6	4	30	25	-	32.4	4	36	2	-	15.1
4	22	8	138.0	132.8	4	24	23	127.7	146.8	4	28	4	-	55.1	4	30	26	-	81.9	4	36	3	-	25.9
4	22	9	-	45.4	4	24	24	-	4.3	4	28	5	-	59.1	4	30	27	-	8.6	4	36	4	68.7	105.6
4	22	10	-	5.3	4	24	25	-	22.9	4	28	6	-	79.1	4	30	28	-	37.7	4	36	5	-	11.4
4	22	11	-	46.7	4	24	26	-	19.2	4	28	7	-	4.8	4	30	29	-	20.2	4	36	6	-	7.8
4	22	12	-	23.0	4	24	27	97.5	92.4	4	28	8	-	42.7	4	32	0	-	61.9	4	36	7	-	62.0
4	22	13	-	42.1	4	24	28	-	40.5	4	28	9	-	12.8	4	32	1	-	29.4	4	36	8	-	48.2
4	22	14	-	50.1	4	24	29	-	10.3	4	28	10	99.3	108.3	4	32	2	-	23.1	4	36	9	-	48.8
4	22	15	202.9	201.9	4	24	30	-	40.0	4	28	11	98.6	85.5	4	32	3	-	1.7	4	36	10	-	9.2
4	22	16	82.8	88.9	4	24	31	-	33.5	4	28	12	116.5	112.2	4	32	4	-	36.8	4	36	11	-	26.1
4	22	17	108.3	105.2	4	24	32	-	37.2	4	28	13	-	0.4	4	32	5	-	1.6	4	36	12	-	15.5
4	22	18	-	65.9	4	24	33	-	9.2	4	28	14	-	41.1	4	32	6	-	67.3	4	36	13	-	1.0
4	22	19	-	24.4	4	24	34	-	44.4	4	28	15	-	3.1	4	32	7	-	25.3	4	36	14	-	25.5

these alternatives would involve a careful analysis of three complete refinements, for instance by applying Hamilton's test procedure.[6] Hamilton's test gives valid results only for data free from systematic errors. The visual intensity estimation procedure may well suffer from systematic errors, which are very difficult to remove. Furthermore, the structure factors should be corrected for anisotropic thermal vibrations. In the present case, an anisotropic refinement would hardly provide reliable results in view of the uncertainties in the interlayer scaling, and the limitation of the *h* values to a maximum of four. In spite of the restrictions mentioned, attempts were, however, made to refine the structure, assuming lower symmetries but neglecting anisotropic thermal vibrations.

The $Cmc2_1$ refinement converged slowly to an *R* value of 0.097. The maximum displacement of the atoms from the centrosymmetric positions was up to four times larger than the standard deviations calculated.

In the $C2cm$ refinement, the origin and the direction of the *a* axis were chosen at the beginning of the refinement by fixing the *x* coordinate for one of the eightfold niobium positions arbitrarily at zero, and shifting the initial *x* parameter for another eightfold niobium position to a value slightly different from zero. The refinement converged extremely slowly, and even after ten cycles, the shifts in the *x* parameters were nearly of the same order of magnitude as the calculated standard deviations. The minimum in the least squares calculation is evidently very shallow, and there is obviously a great danger that the refinement might slip into a false minimum. In fact, a second refinement with different initial parameter values converged towards a set of coordinates which appeared to be significantly different from those of the first refinement.

The Hamilton tests for the $Cmc2_1$ and the $C2cm$ refinements indicated in both cases highly significant deviations from $Cmcm$ symmetry. However, as is evident from the previous discussion, the validity of the Hamilton test is uncertain in the present case. It seems that much more accurate intensity measurements are necessary to settle the space group problem. From the

Table 4. Interatomic distances and standard deviations for Nb_4As_3 (in Ångström units). Distances less than 4.2 Å are listed.

Nb1 –	As1	2.545 (2)		As1 –	Nb1	2.545 (2)
2	As3	2.627 (1)			Nb5	2.574 (1)
2	As2	2.644 (1)		2	Nb2	2.615 (1)
	As4	2.752 (2)		2	Nb3	2.641 (1)
	Nb2	3.089 (2)			Nb4	2.645 (1)
	Nb1	3.321 (3)		2	As3	3.345 (1)
2	Nb3	3.361 (1)		2	As1	3.516 (0)
	Nb5	3.487 (2)			As2	3.776 (2)
2	Nb1	3.516 (0)			As2	3.829 (2)
	Nb3	3.724 (2)		2	As2	4.059 (2)
				2	As4	4.089 (2)
Nb2 –	As4	2.573 (1)		As2 – 2	Nb1	2.644 (1)
2	As1	2.615 (1)		2	Nb2	2.652 (1)
2	As2	2.652 (1)		2	Nb3	2.660 (1)
2	Nb4	2.905 (1)			Nb3	2.711 (2)
	Nb1	3.089 (2)			Nb4	2.732 (1)
2	Nb5	3.273 (1)		2	As2	3.516 (0)
	Nb3	3.419 (2)			As1	3.776 (2)
	Nb3	3.426 (2)			As1	3.829 (2)
2	Nb2	3.516 (0)		2	As4	3.836 (1)
	As3	4.122 (2)			As3	3.925 (2)
				2	As1	4.059 (2)
Nb3 – 2	As1	2.641 (1)		As3 – 4	Nb1	2.627 (1)
2	As2	2.660 (1)		2	Nb5	2.693 (2)
	As2	2.711 (2)		4	As1	3.345 (1)
2	Nb4	3.075 (1)		2	As3	3.516 (0)
2	Nb3	3.160 (2)		2	As4	3.669 (3)
2	Nb1	3.361 (1)		2	As2	3.925 (2)
	Nb2	3.419 (2)			As4	4.109 (3)
	Nb2	3.426 (2)		2	Nb2	4.122 (2)
2	Nb3	3.516 (0)		2	Nb3	4.186 (1)
	Nb1	3.724 (2)				
	As3	4.186 (1)				
Nb4 – 2	As1	2.645 (1)		As4 – 2	Nb2	2.573 (1)
2	As2	2.732 (1)		2	Nb5	2.715 (2)
4	Nb2	2.905 (1)		2	Nb1	2.752 (2)
4	Nb3	3.075 (1)		2	As4	3.516 (0)
2	Nb4	3.516 (0)		2	As3	3.669 (3)
				4	As2	3.836 (1)
				4	As1	4.089 (2)
Nb5 – 2	As1	2.574 (1)			As3	4.109 (3)
2	As3	2.693 (2)				
2	As4	2.715 (2)				
4	Nb2	3.273 (1)				
2	Nb1	3.487 (2)				
2	Nb5	3.516 (0)				

crystal chemical point of view there is no obvious reason to expect any deviation from *Cmcm* symmetry for the Nb_4As_3 structure. Since neither the *Cmcm* least squares refinement nor the final difference synthesis showed any abnormal features, it appears that the structure model given in Table 2 represents the most reasonable approximation to the correct structure that can be derived from the present experimental data.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Interatomic distances in Nb_4As_3 are listed in Table 4. A projection of the structure along the *a* axis is illustrated in Fig. 1.
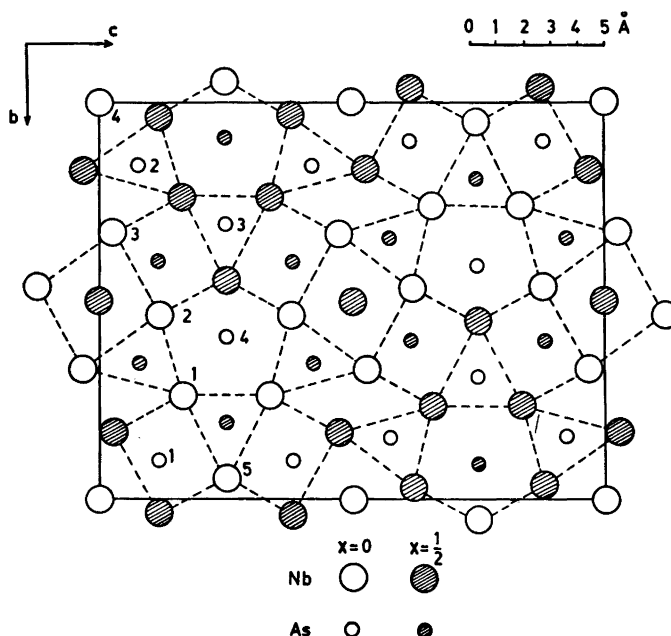

Fig. 1. The crystal structure of Nb_4As_3 projected on (100).

The three arsenic atoms As1, As2 and As3 are surrounded by six niobium atoms in a triangular prismatic coordination. As1 has one additional niobium neighbour outside one of the quadrilateral faces of the prism, and As2 has two additional niobium neighbours. The Nb_4As_3 structure can be described as an array of interconnected Nb_6As triangular prisms, with one additional niobium atom, Nb4, and one additional arsenic atom, As4, inserted in the holes between the prisms. Nb4 is surrounded by eight niobium atoms situated at the corners of a slightly distorted cube. A similar structural feature occurs in several phosphide, arsenide, sulfide, and selenide representatives of the Ta_2P, $Nb_{21}S_8$, Nb_7P_4, and Nb_5P_3 types, and the significance of this particular

coordination has been discussed by Franzen *et al.*[4] and by Hassler.[5] As4 is surrounded by six niobium neighbours in a rather irregular arrangement. Four niobium atoms lie in the same plane as As4, while the two remaining niobium atoms lie at a distance of $a/2$ from this plane, one above and the other below the plane. The As−Nb distances range between 2.55 and 2.75 Å, and are on an average 2.611 Å for As1, 2.670 Å for As2, 2.649 Å for As3, and 2.680 Å for As4. As far as the interatomic distances are concerned, the coordination about As4 is thus not very different from the coordination about the other three types of arsenic atom. The average of all As−Nb distances in the structure is 2.652 Å, which corresponds closely to the sum of the Goldschmidt 12-coordination radius for niobium, 1.47 Å, and the tetrahedral covalent radius for arsenic, 1.18 Å. All As−As distances are larger than 3.3 Å. The niobium atoms have rather high coordination numbers. If distances shorter than 3.75 Å are taken into account (further Nb−Nb distances are longer than 4.2 Å), the niobium atoms have 4−6 arsenic neighbours and 8−11 niobium neighbours. The coordination number for Nb3 is 16, for the remaining niobium atoms it is 14. The average of the nonequivalent Nb−Nb distances in the structure is 3.274 Å, which exceeds the Goldschmidt diameter for 12-coordination by 11 %.

The main structural features of Nb_4As_3 are closely similar to those normally displayed by metal-rich compounds between transition metals and elements with unfilled p levels. In these compounds, the p element atoms are generally surrounded by transition metal atoms in a triangular prismatic arrangement. This type of coordination occurs for three of the four non-equivalent types of arsenic atom in Nb_4As_3. The irregular six-coordination of niobium atoms about As4 might appear somewhat anomalous. However, arsenic atoms in irregular six-coordination also occur in the Ti_5Te_4-type structures of Ta_5As_4 and Mo_5As_4.[1]

REFERENCES

1. Rundqvist, S., Carlsson, B. and Pontchour, C.-O. *Acta Chem. Scand.* **23** (1969) 2188.
2. Rundqvist, S. *Acta Chem. Scand.* **20** (1966) 2427.
3. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III.
4. Franzen, H. F., Smeggil, J. and Conard, B. R. *Mater. Res. Bull.* **2** (1967) 1087.
5. Hassler, E. *Acta Chem. Scand.* **25** (1971) 129.
6. Hamilton, W. *Acta Cryst.* **18** (1965) 502.

Received October 10, 1970.