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The Crystal Structure of $Nb_{12}O_{29}$(mon)

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The crystal structure of $Nb_{12}O_{29}$(mon) has been studied using single crystal X-ray methods. The unit cell has the dimensions:

$a = (31.32 \pm 0.05)$ Å
$b = (3.832 \pm 0.006)$ Å
$c = (20.72 \pm 0.04)$ Å
$\beta = (112.93 \pm 0.07)°$
$V = (2290 \pm 10)$ Å^3

and contains 4 formula units of $Nb_{12}O_{29}$. The structure proposed has the symmetry $A2/a$ and may be described in terms of NbO_6-octahedra which share edges and corners to form an infinite threedimensional framework. It is closely related to the structure proposed for $Ti_2Nb_{10}O_{29}$(mon) by Wadsley.[2]

In an earlier paper [1] in which the structure of $NbO_{2.40}$ was considered, it was shown that the $NbO_{2.40}$ sample consists of two phases and it was mentioned that all attempts to prepare the phases separately were unsuccessful. Furthermore, one of the phases was shown to be $Nb_{12}O_{29}$(o-rh), which is isostructural with $Ti_2Nb_{10}O_{29}$ (o-rh).[2] The other phase was identified by its powder pattern, and was supposed to be a monoclinic dimorph of the former, having a structure very similar to that proposed by Wadsley for $Ti_2Nb_{10}O_{29}$ (mon).[2] It was accordingly given the formula $Nb_{12}O_{29}$(mon). The present investigation shows that this assumption is correct in principle, but that the atomic arrangement has a superstructure, leading to a doubling of the a axis.

The two forms of $Nb_{12}O_{29}$ have since been prepared separately by Gruehn, Bergner and Schäfer [3] in Münster, and samples of the phases have most kindly been placed at the author's disposal.

EXPERIMENTAL

A rod-shaped single crystal of $Nb_{12}O_{29}$(mon), about 0.1 mm in length and 0.03 mm in diameter, was picked out from the same sample of $NbO_{2.40}$ as was used in the investigation of $Nb_{12}O_{29}$(o-rh).[1] Although this crystal did not give quite perfect reflexions it was

used in the investigation since no other single crystal could be found. Unfortunately all crystals found in the single phase sample mentioned above were twins.

The crystal was rotated about the rod axis (*b* axis) and both integrated and nonintegrated Weissenberg photographs *h*0*l*—*h*2*l* were taken using Cu$K\alpha$ radiation. Mo$K\alpha$ radiation was then used to obtain the nonintegrated photographs *h*3*l*—*h*4*l*. The reflexions were recorded by the multiple film technique and their relative intensities were estimated visually by comparison with an intensity scale. As the crystal investigated was so small, absorption effects were neglected. Lorenz and polarisation corrections, Fourier syntheses, stucture factors, least square refinements and interatomic distances were calculated by means of a SAAB D21 computer using a set of crystallographic programmes written by Abrahamsson *et al.*[4] The scattering factors, modified by an overall isotropic temperature factor of 0.3 Å^2, for Nb^{5+} were derived from those given by Thomas and Umeda [5] and Suzuki's [6] data for O^{2-} were used. No correction for dispersion was applied.

UNIT CELL AND SPACE GROUP

Unit cell dimensions were calculated from a powder photograph, taken with a Guinier focusing camera, KCl being used as an internal standard. In Table 1 observed and calculated powder data for $Nb_{12}O_{29}$(mon) are compared with those for $Nb_{12}O_{29}$(o-rh). In both cases the single phase samples from Münster were used. The following cell dimensions were obtained:

Table 1. Powder photographs of $Nb_{12}O_{29}$(mon) and $Nb_{12}O_{29}$(o-rh). Cu$K\alpha$ radiation. $\lambda_{CuK\alpha} = 1.5418$ Å.

$Nb_{12}O_{29}$(mon)					$Nb_{12}O_{29}$(o-rh)				
I obs	$\sin^2\theta \times 10^5$ obs	*h k l*	$\sin^2\theta \times 10^5$ calc	*I* calc	*I* obs	$\sin^2\theta \times 10^5$ obs	*h k l*	$\sin^2\theta \times 10^5$ calc	*I* calc
w	281	2 0 0	286	16	m	283	2 0 0	285	11
w	597	2 0 $\bar{2}$	602	14	vvw	553	0 0 2	555	2
vw	650	0 0 2	653	7	m	624	1 0 2	626	17
w	1139	4 0 0	1142	12	m	1141	4 0 0	1141	10
st	2227	2 0 $\bar{4}$	2224	28	vvw	1196	3 0 2	1197	2
m	2564	6 0 0	2570	23	st	2218	0 0 4	2219	19
vvst	4224	0 1 1	4212	81	vw	2285	1 0 4	2291	7
w	4335	2 1 $\bar{1}$	4329	13	st	2566	6 0 0	2567	21
vvst	4578	8 0 0	4570	92	vvst	4186	0 1 1	4184	38
vw	4670	2 1 1	4666	6	vvst	4257	1 1 1	4255	55
vvst	5009	4 0 $\bar{6}$	4998	64	vvst	4570	8 0 0	4563	100
vvw	5163	2 0 $\bar{6}$	5151	4	vw	4830	3 1 1	4826	8
m	5291	2 1 $\bar{3}$	5298	20	vvst	4995	0 0 6	4993	55
vvw	5404	6 0 $\bar{6}$	5416	3	m	5055	1 0 6	5065	25
vw	5684	4 1 1	5691	5	st	5291	0 1 3	5293	22
vvw	6275	6 1 $\bar{1}$	6278	2	vvw	5364	1 1 3	5365	1
vw	6375	10 0 $\bar{4}$	6385	3	vvw	5612	3 0 6	5635	3
vw	7123	10 0 0	7140	3	vw	5969	5 1 1	5966	5
w	7284	6 1 1	7287	13	vvw	6769	8 0 4	6782	2
vvst	7577	2 1 $\bar{5}$	7573	30	vw	7123	10 0 0	7130	5
		4 1 $\bar{5}$	7588	22	vvst	7580	1 1 5	7584	50

$Nb_{12}O_{29}$(mon)	$Nb_{12}O_{29}$(o-rh)
$a = (31.32 \pm 0.05)$ Å	$a = (28.87 \pm 0.05)$ Å
$b = (3.832 \pm 0.006)$ Å	$b = (3.833 \pm 0.006)$ Å
$c = (20.72 \pm 0.04)$ Å	$c = (20.70 \pm 0.04)$ Å
$\beta = (112.93 \pm 0.07)°$	$V = (2291 \pm 10)$ Å^3
$V = (2290 \pm 10)$ Å^3	

Assuming that there are four formula units of $Nb_{12}O_{29}$ in the elementary cell, the calculated density for $Nb_{12}O_{29}$(mon) is $d_{calc} = 4.58$ g cm^{-3} (for $Nb_{12}O_{29}$(o-rh) $d_{calc} = 4.58$ g cm^{-3} and for the sample $NbO_{2.40}$ $d_{obs} = 4.62$ g cm^{-3}).

All the lines in the powder photograph of $Nb_{12}O_{29}$(mon) could be indexed using a unit cell with $a = 15.66$ Å, but the presence of five weak reflexions observed during the examination of the Weissenberg photogram of the $h2l$ layer necessitated the doubling of the a axis, odd h indices being assigned to these reflexions. In the $h3l$ and $h4l$ layers 27 similar weak reflexions with odd h indices were found. The occurrence of these 32 reflexions could not be explained by means of twinning.

The systematically absent reflexions are:

hkl with $k + l =$ odd
$h0l$ with $h =$ odd

which is characteristic of the space groups No. 15 $A2/a$ and No. 9 Aa. All reflexions hkl with $h =$ odd are weak. It is possible that reflexions $h0l$ with $h =$ odd occur, but are so weak that they are not observable. Thus space groups No. 12 $A2/m$, No. 8 Am, and No. 5 $A2$ are also possible. Both the space groups No. 15 and No. 9 were taken into account, but since no significant difference could be found between the results obtained, the non-polar group $A2/a$ was chosen.

POSITIONS OF THE ATOMS AND REFINEMENT OF THE STRUCTURE

Preliminary atomic parameters were derived from those proposed by Wadsley for $Ti_2Nb_{10}O_{29}$ (mon).[2] The niobium atoms were therefore placed in the 8(f) positions and the oxygen atoms in the 4(a) and 8(f) positions of space group $A2/a$.

The x and z parameters were refined by least squares calculations performed on the observed 422 reflexions $h0l$—$h2l$ with even h, until all shifts were less than 1/5 of the standard deviations. During these calculations the y values were kept constant, = 0 and $\frac{1}{2}$, respectively. At this stage, the reliability index, R dropped to 11.8 %.

Attempts were also made to refine the y parameters by a least squares calculation performed on the observed 270 reflexions in $h3l$—$h4l$. The y parameters then assumed values which differed by 0—0.02 from the initial ones and the reliability index dropped from 20 to 18 %. Since the standard deviations were approximately 0.02 for the niobium positions and 0.1 for the oxygen

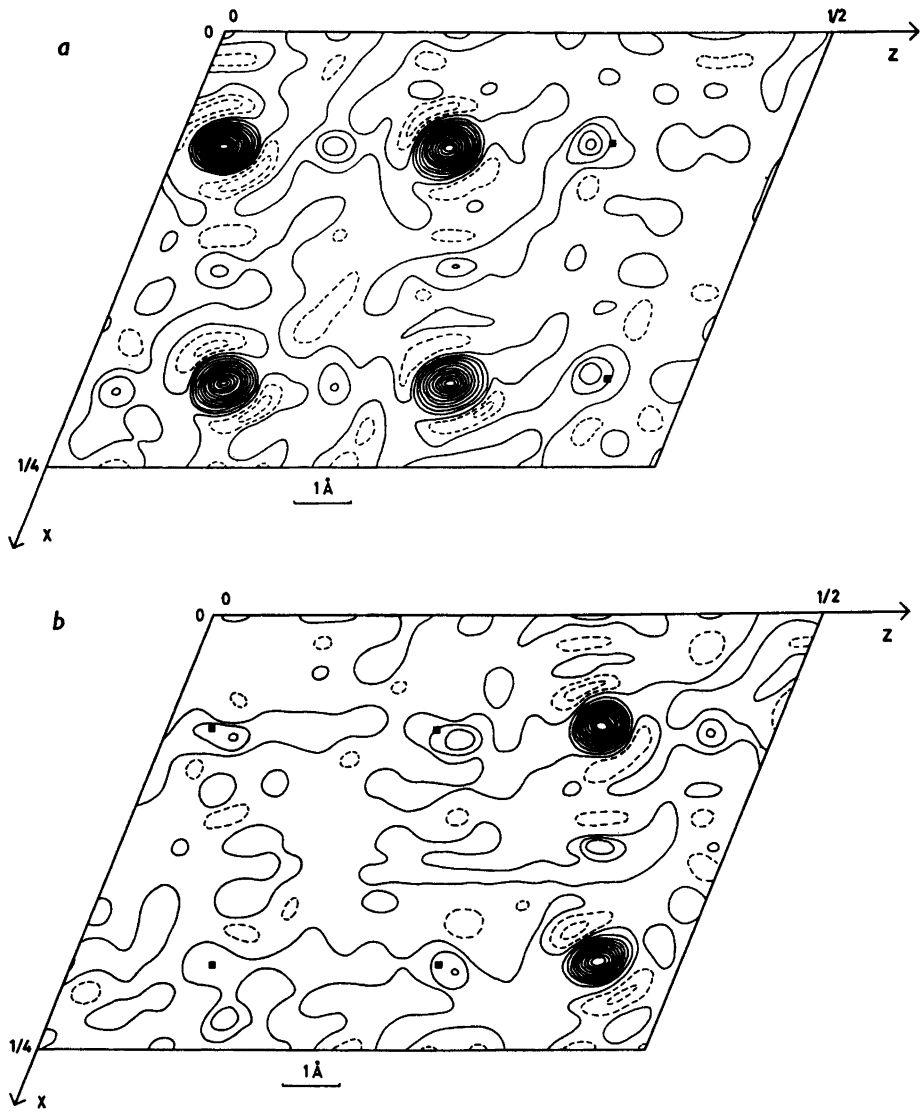

Fig. 1. Electron density sections $\varrho(x0z)$, (a), and $\varrho(x\frac{1}{2}z)$, (b). Arbitrary scale. Black squares indicate the positions of overlapping niobium atoms with $y = \frac{1}{2}$ and 0, respectively. Dashed lines indicate negative values.

positions, the changes in the y parameters could, however, not be considered to be significant. Fractional atomic parameters and their standard deviations are given in Table 2.

Table 2. Fractional atomic parameters and their standard deviations. Space group No. 15 $A2/a$.

Atom	Point position	$x \pm \sigma$	y	$z \pm \sigma$
Nb_1	8 *f*	0.0660 ± 0.0006	0.0	0.0369 ± 0.0009
Nb_2	8 *f*	0.0665 ± 0.0004	0.0	0.2239 ± 0.0006
Nb_3	8 *f*	0.0642 ± 0.0004	0.5	0.3557 ± 0.0006
Nb_4	8 *f*	0.2015 ± 0.0005	0.0	0.1190 ± 0.0007
Nb_5	8 *f*	0.2012 ± 0.0004	0.0	0.3024 ± 0.0007
Nb_6	8 *f*	0.1999 ± 0.0004	0.5	0.4329 ± 0.0006
O_1	4 *a*	0	0	0
O_2	8 *f*	0.006 ± 0.004	0.0	0.195 ± 0.005
O_3	8 *f*	0.068 ± 0.003	0.0	0.136 ± 0.005
O_4	8 *f*	0.071 ± 0.003	0.0	0.333 ± 0.005
O_5	8 *f*	0.072 ± 0.004	0.5	0.057 ± 0.005
O_6	8 *f*	0.073 ± 0.003	0.5	0.256 ± 0.005
O_7	8 *f*	0.067 ± 0.003	0.5	0.446 ± 0.005
O_8	8 *f*	0.141 ± 0.003	0.0	0.075 ± 0.005
O_9	8 *f*	0.140 ± 0.003	0.0	0.270 ± 0.005
O_{10}	8 *f*	0.141 ± 0.003	0.5	0.406 ± 0.005
O_{11}	8 *f*	0.220 ± 0.003	0.0	0.031 ± 0.005
O_{12}	8 *f*	0.208 ± 0.003	0.0	0.220 ± 0.005
O_{13}	8 *f*	0.204 ± 0.003	0.0	0.413 ± 0.005
O_{14}	8 *f*	0.223 ± 0.003	0.5	0.134 ± 0.005
O_{15}	8 *f*	0.210 ± 0.003	0.5	0.333 ± 0.005

Table 3. Niobium-niobium distances between edge-sharing octahedra. The average standard deviation is 0.025 Å.

Neighbouring atoms	Distance in Å
Nb_2—Nb_3	3.36
Nb_4—Nb_5	3.43
Nb_4—Nb_6	3.65
Nb_5—Nb_6	3.33
Nb_6—Nb_6	3.29

Electron density sections $\varrho(x0z)$ and $\varrho(x\frac{1}{2}z)$ calculated from the $h0l$—$h2l$ data are shown in Fig. 1. These data are of course too limited to give the correct three-dimensional electron density, but the sections give a fairly satisfactory picture of the structure. The structure of $Nb_{12}O_{29}$(mon) is illustrated by an idealized picture of regular octahedra in Fig. 2, and a projection of the real structure on the xz plane is given in Fig. 3. The niobium-niobium distances between atoms in edge-sharing octahedra are given in Table 3, and the niobium-oxygen distances within the octahedra in Table 4. The distances between adjacent oxygen atoms varies within the range 2.5—3.1 Å with an average standard deviation of 0.2 Å. A comparison between observed and calculated structure factors is given in Table 5.

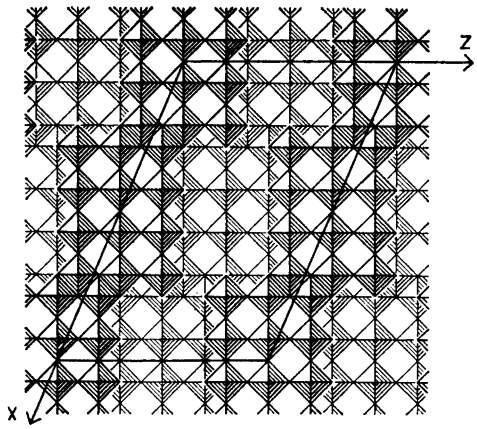

Fig. 2. Idealized structure of $Nb_{12}O_{29}$(mon) with one unit cell indicated.

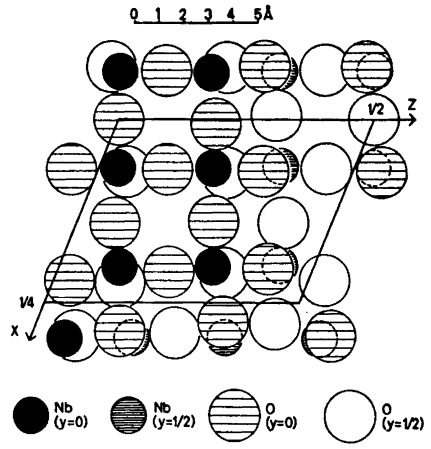

Fig. 3. Projection on the xz plane of the structure of $Nb_{12}O_{29}$(mon). Dashed circles indicate the positions of niobium atoms at $y = 0.5$ overlapped by oxygen atoms at $y = 0.0$.

Table 4. Distances between central niobium atoms and coordinating oxygen atoms within the octahedra. The average standard deviation is 0.1 Å.

Central atom	Ligand	Distance in Å	Central atom	Ligand	Distance in Å
Nb_1	O_1	1.90	Nb_4	O_8	1.74
	O_3	2.02		O_{11}	2.13
	$2 \times O_5$	1.96		O_{12}	2.01
	O_7	1.91		$2 \times O_{14}$	2.01
	O_8	2.18		O_{15}	2.54
Nb_2	O_2	1.76	Nb_5	O_9	1.76
	O_3	1.85		O_{12}	1.81
	O_4	2.21		O_{13}	2.25
	$2 \times O_6$	2.01		O_{14}	2.23
	O_9	2.13		$2 \times O_{15}$	2.00
Nb_3	O_2	2.02	Nb_6	O_{10}	1.70
	$2 \times O_4$	2.01		$O_{11}(1)$	1.87
	O_6	2.19		$O_{11}(2)$	2.32
	O_7	1.83		$2 \times O_{13}$	1.98
	O_{10}	2.22		O_{15}	2.23

DISCUSSION

Monoclinic $Nb_{12}O_{29}$ is a member of the general oxide group $B_2C_{m,n}$($m = 3$ and $n = 4$) and can thus be described by a structural symbol (Fig. 4) of the type introduced by Andersson [7] to describe relations between transition metal oxides.

Table 5. Comparison between calculated and observed structure factors from Weissenberg photographs of $Nb_{12}O_{29}$(mon). Cu$K\alpha$ radiation has been used to obtain the $h0l-h2l$ data and Mo$K\alpha$ radiation for the $h3l-h4l$ data.

h	k	l	|F| obs	F calc	h	k	l	|F| obs	F calc	h	k	l	|F| obs	F calc	h	k	l	|F| obs	F calc	h	k	l	|F| obs	F calc
0	0	2	127	-140	14	0	22	594	533	2	1	21	221	186	24	1	17	554	556	10	2	0	275	296
0	0	4	129	-109	14	0	16	333	331	2	1	17	789	-681	24	1	5	92	-30	10	2	6	272	293
0	0	6	213	-200	14	0	12	562	-527	2	1	11	334	347	24	1	3	209	235	10	2	8	390	-381
0	0	8	167	-137	14	0	10	867	-827	2	1	5	902	-813	24	1	1	424	-469	10	2	10	485	518
0	0	10	306	-232	14	0	6	230	197	2	1	3	531	-558	24	1	5	353	-349	10	2	16	198	246
0	0	12	570	-524	14	0	0	1185	1405	2	1	1	351	406	24	1	11	574	653	12	2	22	498	519
0	0	14	142	260	14	0	2	278	-309	2	1	1	216	-274	26	1	21	288	307	12	2	16	221	-229
2	0	16	946	-837	14	0	4	123	117	2	1	5	349	358	26	1	15	357	-344	12	2	10	346	-307
2	0	12	124	128	14	0	6	300	-264	2	1	11	755	-778	26	1	17	508	459	12	2	8	320	315
2	0	10	153	102	14	0	10	243	230	2	1	21	786	698	26	1	11	333	376	12	2	6	574	-596
2	0	8	185	196	14	0	12	111	-122	2	1	23	203	253	26	1	5	656	-697	12	2	0	346	-411
2	0	6	334	350	14	0	14	183	210	4	1	21	503	-501	26	1	3	562	491	12	2	4	316	404
2	0	4	576	588	14	0	16	509	-527	4	1	19	392	335	28	1	23	245	321	12	2	6	676	773
2	0	2	164	-196	16	0	26	235	205	4	1	11	387	-327	28	1	21	450	519	12	2	10	121	-127
2	0	0	162	-146	16	0	22	175	-169	4	1	7	335	304	28	1	17	126	-160	12	2	16	276	-305
2	0	2	65	79	16	0	16	584	-524	4	1	5	808	693	28	1	11	471	-578	14	2	22	440	482
2	0	4	148	135	16	0	14	142	210	4	1	1	132	-158	28	1	5	136	162	14	2	16	243	289
2	0	6	135	126	16	0	12	263	-217	4	1	1	255	283	28	1	1	212	-185	14	2	12	493	-456
2	0	8	267	266	16	0	10	325	232	4	1	5	655	-626	28	1	3	196	-214	14	2	10	672	-681
2	0	10	974	-961	16	0	6	294	-317	4	1	7	143	-199	28	1	5	466	477	14	2	6	174	173
2	0	22	881	769	16	0	4	134	169	4	1	11	287	210	30	1	17	265	257	14	2	0	829	1079
4	0	22	286	-209	16	0	2	158	-159	4	1	17	520	479	30	1	11	420	-524	14	2	2	247	-245
4	0	16	183	167	16	0	0	825	850	4	1	19	321	-282	30	1	5	388	-341	14	2	4	252	-220
4	0	12	192	-160	16	0	6	335	294	4	1	21	154	222	30	1	1	624	590	14	2	10	220	205
4	0	8	438	-425	16	0	10	700	-673	6	1	23	273	-304	30	1	1	270	301	14	2	16	382	-484
4	0	4	1216	1380	16	0	12	344	-292	6	1	21	364	-383	32	1	17	531	-627	16	2	22	180	-153
4	0	2	99	108	16	0	16	202	134	6	1	11	1339	1411	32	1	5	559	468	16	2	16	485	-473
4	0	2	73	79	18	0	22	245	240	6	1	9	142	-146	32	1	3	227	-266	16	2	14	259	191
4	0	0	276	268	18	0	16	445	-449	6	1	5	356	-304	32	1	1	182	207	16	2	10	220	196
4	0	4	226	-264	18	0	10	387	-320	6	1	1	149	171	32	1	5	558	564	16	2	6	243	-272
4	0	6	861	-1006	18	0	8	1004	1158	6	1	1	418	-527	34	1	15	213	234	16	2	0	595	706
4	0	8	261	268	18	0	4	189	229	6	1	3	352	356	34	1	5	355	330	16	2	6	240	258
4	0	10	273	284	18	0	0	254	-214	6	1	5	367	-366	34	1	1	189	180	16	2	10	584	-602
4	0	12	137	-99	18	0	6	438	-424	6	1	11	356	-326	36	1	11	705	797	16	2	12	228	-267
4	0	16	222	175	18	0	8	349	361	6	1	15	431	391	36	1	5	411	330	18	2	22	209	217
6	0	24	258	188	18	0	10	292	-206	6	1	17	524	429	0	2	2	156	-99	18	2	16	407	-402
6	0	22	791	-702	18	0	16	258	-268	8	1	15	283	255	0	2	4	111	-84	18	2	10	272	-267
6	0	16	148	-158	20	0	22	877	-725	8	1	13	305	-271	0	2	6	139	-136	18	2	8	792	962
6	0	12	450	412	20	0	10	861	845	8	1	11	399	390	0	2	12	438	-450	18	2	0	206	-181
6	0	10	1416	1438	20	0	8	465	-468	8	1	5	382	307	0	2	14	260	222	18	2	6	350	-384
6	0	8	290	-281	20	0	6	224	286	8	1	1	175	172	1	2	4	128	0	18	2	8	282	322
6	0	6	320	-323	20	0	0	335	335	8	1	1	672	-824	1	2	2	211	0	18	2	10	142	-187
6	0	0	516	-559	20	0	4	411	-348	8	1	1	314	-430	2	2	16	797	-751	20	2	22	554	-660
6	0	2	180	171	20	0	6	491	-487	8	1	11	1065	1186	2	2	8	159	159	20	2	10	662	693
6	0	4	210	-240	20	0	16	416	605	8	1	17	199	-167	2	2	6	250	276	20	2	8	389	-388
6	0	8	114	-120	22	0	22	190	-171	10	1	17	932	882	2	2	4	392	427	20	2	6	208	245
6	0	10	315	-282	22	0	16	221	-275	10	1	5	695	-644	2	2	2	216	-140	20	2	0	320	291
6	0	14	109	-142	22	0	12	591	628	10	1	3	279	277	2	2	0	155	-107	20	2	4	289	-309
6	0	16	886	824	22	0	10	452	362	10	1	1	158	-198	2	2	6	80	90	20	2	6	401	-432
8	0	22	265	218	22	0	0	980	-1069	12	1	21	742	791	2	2	8	223	238	22	2	12	470	548
8	0	16	361	304	22	0	2	214	206	12	1	13	360	-333	2	2	10	820	-797	22	2	10	286	312
8	0	14	329	-266	22	0	12	268	212	12	1	7	336	-288	3	2	4	151	0	22	2	0	716	-927
8	0	12	496	481	22	0	14	174	-168	12	1	5	293	-243	4	2	22	189	-192	22	2	12	175	197
8	0	10	238	-170	24	0	16	859	854	12	1	1	239	-233	4	2	8	414	-340	24	2	16	609	769
8	0	8	94	56	24	0	14	220	-246	12	1	3	241	-177	4	2	6	880	1091	24	2	14	257	-219
8	0	6	351	356	24	0	0	242	-266	12	1	5	1148	1140	4	2	0	220	199	24	2	6	140	150
8	0	2	101	105	24	0	6	242	-227	12	1	17	705	-560	4	2	4	158	-212	24	2	0	241	-233
8	0	0	1125	-1577	24	0	10	670	687	12	1	19	266	228	4	2	6	770	-887	24	2	6	269	-207
8	0	4	94	151	26	0	8	765	-879	14	1	23	350	298	4	2	8	213	216	24	2	10	770	635
8	0	6	240	-192	26	0	6	704	625	14	1	11	1178	-1207	4	2	10	200	228	26	2	10	98	144
8	0	8	85	87	26	0	8	240	-206	14	1	1	249	253	5	2	8	171	0	26	2	6	624	-782
8	0	10	789	762	28	0	22	760	796	14	1	1	668	826	5	2	4	140	0	26	2	6	549	567
8	0	12	574	482	28	0	10	496	-648	14	1	3	284	-279	6	2	22	654	-639	26	2	8	153	-190
8	0	14	110	-128	28	0	4	285	294	14	1	15	346	318	6	2	12	396	344	28	2	10	506	-579
8	0	16	154	-185	28	0	10	147	141	16	1	9	186	-134	6	2	10	1054	1115	28	2	8	214	218
10	0	22	320	-253	30	0	12	488	-493	16	1	3	318	-343	6	2	8	243	-216	28	2	4	193	266
10	0	16	960	899	30	0	6	191	-200	16	1	1	693	865	6	2	6	288	-262	30	2	12	325	-447
10	0	12	192	-168	30	0	0	1045	944	16	1	11	905	-947	6	2	0	368	-410	30	2	6	200	-182
10	0	10	317	286	32	0	22	192	200	18	1	17	789	-701	6	2	2	179	149	30	2	0	876	855
10	0	8	97	-98	32	0	16	682	-693	18	1	7	254	-227	6	2	4	161	-216	32	2	16	421	-633
10	0	6	592	-592	32	0	6	259	267	18	1	5	246	240	6	2	10	271	-239	32	2	6	180	241
10	0	4	309	-354	32	0	6	121	146	18	1	5	934	1042	6	2	16	741	745	34	2	8	220	-211
10	0	0	362	371	34	0	8	171	-233	18	1	3	173	-207	8	2	22	190	198	34	2	6	585	620
10	0	6	366	356	34	0	6	673	680	20	1	21	640	-677	8	2	16	262	267	36	2	12	259	287
10	0	8	447	-455	34	0	0	257	228	20	1	13	364	437	8	2	14	278	-232	36	2	10	450	472
10	0	10	587	603	34	0	4	139	-175	20	1	3	83	-30	8	2	12	396	401					
12	0	16	260	271	36	0	16	199	-217	20	1	1	271	289	8	2	10	179	-138					
12	0	22	644	574	36	0	12	271	309	20	1	5	931	-823	8	2	6	340	293					
12	0	16	296	-260	36	0	10	478	510	20	1	11	270	-240	8	2	0	915	-1243					
12	0	12	248	168	36	0	0	194	-211	22	1	25	223	204	8	2	8	63	73					
12	0	10	389	-381	38	0	16	185	224	22	1	17	304	-233	8	2	10	660	623					
12	0	8	383	359	38	0	14	210	-202	22	1	11	880	1046	8	2	12	414	423					
12	0	6	638	-689	38	0	12	317	359	22	1	5	152	212	8	2	16	195	-168					
12	0	0	428	-511	38	0	6	303	332	22	1	3	89	-86	10	2	22	214	-228					
12	0	4	506	504	0	1	1	613	1005	22	1	1	340	-351	10	2	16	798	786					
12	0	6	814	913	0	1	5	355	-265	22	1	1	418	-551	10	2	10	258	217					
12	0	12	110	109	0	1	11	687	-735	22	1	5	96	136	10	2	6	502	-536					
12	0	16	318	-333	0	1	21	178	-218	22	1	11	374	322	10	2	4	238	-295					

Table 5. (Continued).

h	k	l	|F| obs	F calc	h	k	l	|F| obs	F calc	h	k	l	|F| obs	F calc	h	k	l	|F| obs	F calc	h	k	l	|F| obs	F calc
0	3	5	229	-208	9	3	3	122	0	24	3	5	385	-283	4	4	0	640	712	13	4	2	119	0
0	3	11	492	-554	9	3	1	123	0	24	3	11	381	555	4	4	0	127	124	13	4	6	97	0
0	3	13	221	168	10	3	17	604	706	26	3	21	150	262	4	4	6	542	-625	14	4	22	240	375
0	3	27	350	390	10	3	5	589	-594	26	3	19	288	-285	4	4	8	199	148	14	4	16	183	215
1	3	3	122	0	10	3	3	311	217	26	3	17	339	383	4	4	10	220	159	14	4	12	278	-334
2	3	17	510	-555	10	3	1	112	77	26	3	11	254	298	5	4	8	180	0	14	4	10	584	-476
2	3	11	278	255	10	3	5	133	-136	26	3	5	394	-567	5	4	2	80	0	14	4	6	136	125
2	3	5	570	597	10	3	11	169	204	26	3	5	450	408	5	4	8	54	0	14	4	0	699	707
2	3	3	416	-357	10	3	21	517	-554	26	3	11	228	-99	6	4	22	498	-502	14	4	2	329	-166
2	3	1	142	-179	11	3	3	135	0	28	3	21	374	440	6	4	10	836	733	14	4	6	205	-156
2	3	5	244	259	12	3	21	771	657	28	3	17	142	-135	6	4	8	215	-141	14	4	10	135	159
2	3	11	506	-590	12	3	19	264	-267	28	3	11	417	-477	6	4	6	218	-173	14	4	16	320	-385
2	3	21	604	590	12	3	7	211	-203	28	3	5	226	138	6	4	0	221	-255	15	4	14	103	0
3	3	13	133	0	12	3	5	201	-175	28	3	3	203	-177	6	4	2	177	102	16	4	16	262	-360
3	3	5	111	0	12	3	1	245	-162	28	3	5	419	399	6	4	8	66	-72	16	4	14	175	146
3	3	3	151	0	12	3	9	227	-128	30	3	27	245	416	6	4	10	198	-171	16	4	10	156	141
4	3	21	408	419	12	3	5	774	862	30	3	17	207	209	6	4	16	455	573	16	4	6	229	-193
4	3	19	331	274	12	3	17	520	-468	30	3	11	275	-433	7	4	12	91	0	16	4	0	637	497
4	3	11	273	-241	13	3	3	168	0	30	3	5	335	-274	7	4	2	129	0	16	4	6	125	189
4	3	7	151	206	14	3	11	789	-916	30	3	1	447	487	8	4	22	156	160	16	4	10	396	-458
4	3	5	451	511	14	3	1	562	585	32	3	27	175	280	8	4	14	237	-173	18	4	16	231	-305
4	3	1	166	190	14	3	3	344	-207	32	3	21	225	178	8	4	12	377	283	18	4	10	199	-191
4	3	5	536	-578	17	3	27	467	477	32	3	17	520	-531	8	4	10	140	-94	18	4	8	754	681
4	3	11	214	168	16	3	27	909	609	32	3	11	142	83	8	4	6	228	-196	18	4	0	113	-133
4	3	17	428	390	16	3	17	126	-154	32	3	5	403	385	8	4	0	660	-812	18	4	6	185	-292
4	3	19	289	-233	16	3	5	298	-245	32	3	3	289	-220	8	4	2	81	32	18	4	8	338	247
5	3	9	75	0	16	3	1	682	626	32	3	5	320	308	8	4	10	377	438	20	4	22	445	-519
5	3	7	93	0	16	3	5	112	152	34	3	11	209	-185	8	4	12	364	318	20	4	10	448	491
5	3	5	80	0	16	3	11	736	-784	34	3	7	295	204	8	4	16	256	-130	20	4	8	436	-278
6	3	11	856	1011	17	3	3	171	0	34	3	5	257	276	9	4	10	84	0	20	4	0	241	215
6	3	9	122	-89	18	3	19	381	207	34	3	5	525	-478	9	4	4	65	0	20	4	6	237	-333
6	3	5	230	-217	18	3	17	570	-571	36	3	11	684	676	10	4	22	220	-179	20	4	16	347	440
6	3	3	203	-92	18	3	11	218	-170	38	3	27	445	-469	10	4	16	479	584	22	4	12	363	412
6	3	1	139	101	18	3	5	839	788	38	3	5	393	276	10	4	10	119	144	22	4	10	125	231
6	3	1	306	-391	20	3	21	498	-567	38	3	1	573	-441	10	4	6	434	-381	22	4	0	762	-693
6	3	3	430	269	20	3	17	130	150	40	3	17	474	528	10	4	0	262	198	22	4	16	251	151
6	3	5	251	-268	20	3	11	319	331	40	3	5	470	-424	10	4	6	150	202	24	4	16	493	589
6	3	11	221	-251	20	3	7	310	215	44	3	11	550	-563	10	4	8	325	-271	24	4	14	194	-167
6	3	15	259	325	20	3	3	237	132	0	4	2	110	-60	10	4	10	304	383	24	4	0	189	-179
6	3	17	340	357	20	3	5	680	-670	0	4	12	228	-328	11	4	10	66	0	24	4	10	458	498
6	3	27	422	-436	20	3	17	411	442	0	4	14	176	165	11	4	4	100	0	26	4	6	463	-598
7	3	13	130	0	22	33	17	187	-187	1	4	2	126	0	11	4	10	107	0	26	4	6	380	440
7	3	1	117	0	22	3	11	813	815	2	4	16	417	-570	12	4	22	268	410	28	4	22	523	584
8	3	27	673	-532	22	3	5	195	161	2	4	4	230	266	12	4	16	129	-174	28	4	10	315	-445
8	3	15	114	209	22	3	1	232	-279	2	4	2	153	-86	12	4	10	122	-208	30	4	14	151	86
8	3	13	298	-195	22	3	1	339	-441	2	4	8	213	171	12	4	8	333	226	30	4	12	296	-345
8	3	11	136	273	22	3	11	150	275	2	4	10	637	-559	12	4	6	444	-419	30	4	0	530	669
8	3	5	447	225	24	3	27	583	-458	2	4	22	523	567	12	4	4	88	31	32	4	16	448	-498
8	3	3	208	121	24	3	17	383	460	3	4	2	80	0	12	4	0	341	-274	34	4	6	447	491
8	3	1	561	-609	24	3	11	173	-187	3	4	8	82	0	12	4	4	294	279	34	4	4	435	-414
8	3	1	246	-311	24	3	3	240	195	4	4	22	100	-154	12	4	6	549	555	36	4	22	434	-430
8	3	11	891	912	24	3	1	425	-375	4	4	8	372	-229	12	4	10	183	-101	36	4	10	398	370

In his studies on various molybdenum and tungsten oxides Magnéli [8] has found several phases which are built up of major structural units or blocks formed by metal-oxygen octahedra joined by the sharing of corners in the same way as in the ReO_3-type structure. These blocks extend infinitely in two dimensions but comprise a finite number of octahedra in the third direction. Adjacent blocks are joined by octahedra sharing edges. In the family of oxides including the dimorphs of $Nb_{12}O_{29}$ the structures likewise contain structural units of ReO_3-type. Here, however, the blocks extend over a finite

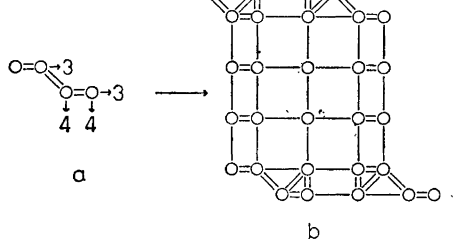

Fig. 4. General formula representing the oxides of the group $B_2\bar{C}_{m,n,(a)}$. With $m = 3$ and $n = 4$ this formula gives the structure for $Nb_{12}O_{29}$(mon), (*b*). These structural symbols are introduced by Andersson.[7]

number of octahedra in two dimensions but have an infinite length in the third direction, the mutual coupling of adjacent blocks being by octahedra sharing edges. The description of structures in terms of such units has been successfully applied by Wadsley and Roth [2,9-11] to the mixed niobium-titanium and niobium-tungsten oxide systems and the concept may also be helpful in further studies on binary niobium oxides.

Results of phase analysis studies on slightly reduced Nb_2O_5 performed by the author [12] are still not conclusive concerning the number and compositions of phases existing in this region. The general appearance of the powder patterns of the various niobium oxides rich in oxygen makes it, however, possible that further phases exist with structures similar to the one described in this article or related to the structures of high-temperature Nb_2O_5[13] and $TiNb_{24}O_{62}$.[10] A characteristic feature of the latter compounds is the presence of metal atoms in a tetrahedral environment of oxygen atoms. The role played in all these structures by the ReO_3-type blocks is, however, a dominating one, which is also reflected in the similarities between their X-ray patterns and in particular their powder patterns. Thus the latter are of limited value in establishing the structural type of such phases.

The doubling of the unit cell of $Nb_{12}O_{29}$(mon) may possibly be due to deviations of the y parameters from the values 0 and $\frac{1}{2}$, giving rise to a slight puckering of the atomic sheets parallel to the xz plane. The scattering effects from this kind of deformation should be more easily observable in the layer lines with high k values. A structure built up of puckered planes cannot be described in terms of mirror planes, thus the space groups No. 12 $A2/m$ and No. 8 Am were not considered, and since it was possible to explain the structure using the concept of a glide-planes, the space group No. 5 $A2$ was not taken into account. Accordingly No. 15 $A2/a$ probably is the correct space group.

The octahedra sheets building up $Nb_{12}O_{29}$(o-rh) [1] may be puckered in a way similar to that in $Nb_{12}O_{29}$(mon), which may also be the case in other phases in this oxide system. As the a axis of $Nb_{12}O_{29}$(o-rh) already extends over two blocks of ReO_3-type structure according to the zig-zag-arrangement of the blocks in this structure, it is not probable that deviations from $y = 0$ and $\frac{1}{2}$ will lead to a larger unit cell.

The observed data in this investigation seems to be insufficient for an accurate determination of the y parameters. It is hoped that a single crystal goniostat will be available at this department during the coming year, in which case a reinvestigation of this compound is planned, or, alternatively, an investigation of a related compound using complete three-dimensional data, corrected for absorption.

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