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## The Crystal Structure of $\alpha$ -Niobium Tetraiodide

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Crystals of  $\alpha$ -NbI<sub>4</sub> are orthorhombic, space group *Cmc*2<sub>1</sub>, lattice parameters

$$a = 7.67 \pm 0.02, \quad b = 13.23 \pm 0.02, \quad c = 13.93 \pm 0.02 \text{ \AA},$$

with eight formula units in the unit cell. Final refinement by a three-dimensional anisotropic least-squares analysis resulted in an *R* value of 8.6%.

The structure of solid  $\alpha$ -NbI<sub>4</sub> is based on a distorted hexagonal close-packing of the iodine atoms. One-fourth of the available octahedral holes are occupied by niobium atoms to give infinite linear chains formed by NbI<sub>6</sub> octahedra sharing opposite edges. The niobium atoms are shifted from the centers of the octahedra toward one another in pairs to give a resulting Nb-Nb distance of 3.31 Å. Weak metal-metal interactions which couple the unpaired electrons completely explain these niobium shifts and account for the observed diamagnetism of  $\alpha$ -NbI<sub>4</sub>. The valency state of niobium in  $\alpha$ -NbI<sub>4</sub> is concluded to be IV from the observed identical environments of the niobium atoms.  $\alpha$ -NbI<sub>4</sub> and the isomorphous TaI<sub>4</sub> are the first simple metal halides which have this structure.

### Introduction

Corbett & Seabaugh (1958; Seabaugh, 1961) have synthesized and characterized by both chemical and physical means a number of new niobium iodide compounds including NbI<sub>5</sub>, NbI<sub>3</sub>, Nb<sub>3</sub>I<sub>8</sub>, and two different forms of NbI<sub>4</sub> ( $\alpha$ -NbI<sub>4</sub> and  $\beta$ -NbI<sub>4</sub>).

Complete characterization by single-crystal X-ray diffraction is needed to reveal intimate structural interrelationships among these compounds as well as to provide important fundamental knowledge concerning their nature of bonding. This investigation of the low-temperature form of NbI<sub>4</sub>,  $\alpha$ -NbI<sub>4</sub>, was undertaken with the additional object of establishing the valency state of niobium in the compound. Normally tetravalent niobium should possess an unpaired electron and hence be paramagnetic.†

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†  $\alpha$ -NbI<sub>4</sub> initially was reported to be paramagnetic (Corbett & Seabaugh, 1958), but in view of our structural results a redetermination of the magnetic susceptibility by Corbett & Seabaugh (1959) showed the compound to be diamagnetic.

Rolsten (1958) prepared the presumably isomorphous TaI<sub>4</sub> and found it to be diamagnetic. He speculated that the unpaired electron in TaI<sub>4</sub> must be paired by formation of a dimer or else solid TaI<sub>4</sub> must exist in a mixed oxidation state as Ta(III)Ta(V)I<sub>8</sub>. Mixed oxidation states (i.e., I and III) have been found for gallium and for indium dihalides (Corbett & McMullan, 1955, 1956; McMullan & Corbett, 1958; Woodward *et al.*, 1956; Garton & Powell, 1957; Corbett & Hershaff, 1958; Carlston *et al.*, 1958; Clark *et al.*, 1958).

Brauer (1948) reported NbO<sub>2</sub> to be weakly paramagnetic although much less than expected for Nb(IV) ions. Schäfer *et al.* (1961) found TaOCl<sub>2</sub> and the tantalum and niobium tetrahalides (*X* = Cl, Br, and I) to be diamagnetic and consequently suggested the presence of similar bonding conditions in niobium and tantalum compounds of the general type *MX*<sub>4</sub>, *MOX*<sub>2</sub>, and *MO*<sub>2</sub>. They also stated that no isolated Ta(IV) ions are present in TaOCl<sub>2</sub> but did not comment further on the valency state in these compounds. The structural determination of  $\alpha$ -NbI<sub>4</sub> revealed weak metal-metal bonding and thereby explained

its diamagnetism as well as that of TaI<sub>4</sub>. A preliminary report of the structure has been published (Dahl & Wampler, 1959). A structural determination (Marinder, 1960) of NbO<sub>2</sub> showed the occurrence of metal-metal doublets; presumably the compounds discussed by Schäfer *et al.* (1961) possess similar metal-metal interactions in which the unpaired electrons are coupled.

### Experimental procedure

A sample of  $\alpha$ -NbI<sub>4</sub> was kindly supplied in sealed tubes by Drs Seabaugh and Corbett. Since the compound is unstable to air and water, single crystals were loaded into glass capillaries in a dry box. Thin-walled glass capillaries were prepared with one end attached to a male-glass joint which fit an appropriate adapter with a stopcock for attachment to the vacuum line. The capillaries were evacuated and then were taken into an argon-filled dry box. Argon used for flushing was dried by cooling to -80 °C.; the box atmosphere was continuously circulated through Linde Molecular Sieve Type 4A. A thin layer of vaseline, coated on the inside capillary walls by a thin glass rod prior to insertion of several crystals into each capillary, kept the crystals oriented. The capillaries were then evacuated and hermetically sealed. This technique, although somewhat cumbersome, has worked most satisfactorily in this and other instances.

The lattice parameters *b* and *c* were determined from a back-reflection Weissenberg photograph (Buerger, 1942) with cobalt radiation; the lattice parameter *a* was determined from precession photographs in which *c* was used as an internal standard.

Multiple-film equi-inclination Weissenberg photographs were obtained for nine reciprocal levels, *h*=0 to 8, with Zr-filtered Mo *K* $\alpha$  radiation. A total of 919 diffraction maxima were observed. All intensities were measured by visual comparison with a calibrated standard set of intensities and were corrected for Lorentz-polarization effects. The crystal was sufficiently small (approximate dimensions 0.8 × 0.05 × 0.04 mm.) that absorption corrections were neglected. Extinction corrections were not made.

Timed-exposure precession photographs of *h*0*l* and *hk*0 data were obtained with Mo *K* $\alpha$  radiation and were corrected for the Lorentz-polarization factor. The resulting intensities were utilized to place the Weissenberg intensity data on a common scale.

### Crystal data

$\alpha$ -NbI<sub>4</sub>; mol.wt.=600.6; phase transformation into  $\beta$ -form at 348 °C. (Seabaugh, 1961).

Orthorhombic,

*a* = 7.67 ± 0.02, *b* = 13.23 ± 0.02, *c* = 13.93 ± 0.02 Å.

Volume of unit cell = 1.414 Å<sup>3</sup>.

Density (calculated) = 5.64 g.cm.<sup>-3</sup>.

Eight formula units per unit cell; total number of electrons per unit cell, *F*(000) = 2.024.

Linear absorption coefficient for Mo *K* $\alpha$  radiation ( $\lambda$  = 0.7107 Å), 203 cm.<sup>-1</sup>.

Systematic absences:

*hkl* for *h* + *k* odd; *h*0*l* for *l* odd.

Space group: *Cmc*2<sub>1</sub>(*C*<sub>2v</sub><sup>12</sup>), *C2cm*(*C*<sub>2v</sub><sup>16</sup>), or *Cmcm*(*D*<sub>2h</sub><sup>17</sup>). The final space group chosen, *Cmc*2<sub>1</sub>, was determined by the structure ultimately found.

### Structural determination

Two-dimensional Patterson projections were calculated for the three principal zones. Interpretation of these projections and the resulting Fourier maps gave the essential features of the structure. The structure was first refined on an IBM 650 computer by an essentially diagonal least-squares method (Senko & Templeton, 1956) with individual isotropic thermal parameters and constant weighting. A final discrepancy factor,  $R = (\sum |F_o| - |F_c|) / \sum |F_o| \times 100$ , of 15.6% was obtained for the three-dimensional data. The atomic form factors for niobium and iodine used were those of Thomas & Umeda (1957). Dispersion corrections were made (Dauben & Templeton, 1955).

For the space group *Cmc*2<sub>1</sub> the niobium atoms occupy the general 8-fold set of positions (8*b*); the iodines occupy two sets of 8*b* and four sets of 4-fold special positions (4*a*) on mirror planes (*International Tables for X-ray Crystallography*, 1952). These positions are as follows:

8*b* *x*, *y*, *z*;  $\bar{x}$ , *y*, *z*;  $\bar{x}$ ,  $\bar{y}$ ,  $\frac{1}{2} + z$ ; *x*,  $\bar{y}$ ,  $\frac{1}{2} + z$ ; +*C* centering.  
4*a* 0, *y*, *z*; 0,  $\bar{y}$ ,  $\frac{1}{2} + z$ ; +*C* centering.

At this time a full matrix least-squares program for the IBM 704 (Busing & Levy, 1959) became available; further refinement was carried out with this program. Since for *Cmc*2<sub>1</sub> the origin is not fixed by symmetry in the *c* lattice-vector direction, the *z* parameter of one iodine, *I*<sub>1</sub>, was not varied. The refinement again was based on isotropic thermal parameters and constant weighting; after three cycles of refinement negligible parameter shifts were obtained. The final parameters differed from those obtained from the IBM 650 by as much as three or four standard deviations. The *R* factor decreased markedly to 10.5%. The sharp decrease in *R* is attributed to the relatively inaccurate method of obtaining trigonometric functions used in the IBM 650 program. The refinement was then repeated with weights assigned to the reflections according to the functions (Hughes, 1941; Lavine & Lipscomb, 1954)  $\sqrt{w} = 10/F_o$  if  $F_o \geq 4F_{\min}$ ;  $\sqrt{w} = F_o/1.6F_{\min}^2$  if  $F_o < 4F_{\min}$ . Although the *R* value only decreased slightly to 10.2%, the changes in the thermal parameters were as much as five times the standard deviations (constant weighting); the changes in positional parameters were as much as three times the standard deviations. The standard deviations of the parameters were slightly lowered. The resulting parameters with their

Table 1. *Final atomic parameters 704, variable weighting, isotropic*

Position		<i>x</i>	<i>y</i>	<i>z</i>	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	<i>B</i>	$\sigma(B)$
8b	I <sub>1</sub>	0.2467	0.0061	-0.0323	0.0004	0.0003	—	1.25	0.07
8b	I <sub>2</sub>	0.2458	0.2334	0.2842	0.0004	0.0003	0.0003	1.33	0.07
4a	I <sub>3</sub>	0	0.2608	0.0333	0	0.0004	0.0004	1.37	0.08
4a	I <sub>4</sub>	0.5000	0.2436	0.0440	0	0.0005	0.0004	1.45	0.08
4a	I <sub>5</sub>	0	-0.0113	0.2096	0	0.0004	0.0004	1.39	0.08
4a	I <sub>6</sub>	0.5000	0.0066	0.1999	0	0.0004	0.0004	1.51	0.08
8b	Nb	0.2171	0.1256	0.1207	0.0006	0.0003	0.0005	1.10	0.06

Table 2. *Final positional parameters 704, variable weighting, anisotropic*

Position		<i>x</i>	<i>y</i>	<i>z</i>	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
8b	I <sub>1</sub>	0.2460	0.0065	-0.0323	0.0004	0.0002	—
8b	I <sub>2</sub>	0.2451	0.2340	0.2834	0.0004	0.0003	0.0002
4a	I <sub>3</sub>	0	0.2619	0.0342	0	0.0005	0.0005
4a	I <sub>4</sub>	0.5000	0.2443	0.0444	0	0.0005	0.0005
4a	I <sub>5</sub>	0	-0.0114	0.2102	0	0.0004	0.0005
4a	I <sub>6</sub>	0.5000	0.0077	0.1999	0	0.0005	0.0005
8b	Nb	0.2157	0.1252	0.1202	0.0005	0.0003	0.0006

standard deviations are listed in Table 1. The thermal parameters after this refinement showed much more internal consistency than those obtained from the constant weighting refinements. The thermal parameters are approximately the same in each of the following pairs of similar atoms (see Fig. 1 for atom designation); the apical iodines (I<sub>1</sub> and I<sub>2</sub>), the bridging iodines towards which the niobium is displaced (I<sub>3</sub> and I<sub>5</sub>), and the other two bridging iodines (I<sub>4</sub> and I<sub>6</sub>). These results show the importance of the weighting scheme in least-squares refinements involving film data.

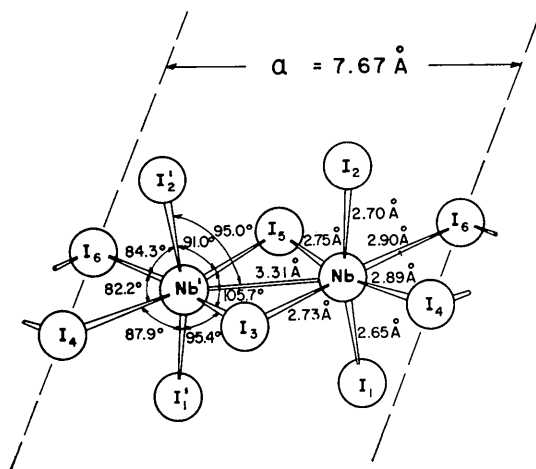


Fig. 1. Configuration of an  $(\text{NbI}_4)_2$  unit in the linear infinite chain uncorrected for thermal vibration.

To provide a better calculated model and thereby obtain more meaningful positional parameters, least-squares refinement was continued. Individual atom temperature factors expressed in the form

$$\exp\{-[B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl]\}$$

were used. For the iodine atoms in special positions (set 4a) on mirror planes, the thermal coefficients

$B_{12}$  and  $B_{13}$  are required by symmetry to be zero (Levy, 1956). The final  $R$  value from the anisotropic refinement is 8.6%. The final positional parameters are listed in Table 2; the thermal parameters, in Table 3; and the final values for scaled  $F_o$  and  $F_c$ , in Table 4.

Table 3. *Final thermal parameters in  $\text{Å}^2 \times 10^4$* 

	Anisotropic					
	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
I <sub>1</sub>	97 ± 10	14 ± 1	25 ± 2	-1 ± 2	3 ± 2	-10 ± 1
I <sub>2</sub>	80 ± 7	25 ± 2	12 ± 1	-8 ± 2	2 ± 2	-3 ± 1
I <sub>3</sub>	46 ± 8	17 ± 2	26 ± 3	0	0	-2 ± 2
I <sub>4</sub>	54 ± 8	20 ± 2	12 ± 2	0	0	3 ± 2
I <sub>5</sub>	65 ± 9	17 ± 2	27 ± 3	0	0	11 ± 2
I <sub>6</sub>	59 ± 9	18 ± 2	33 ± 3	0	0	-3 ± 2
Nb	25 ± 10	20 ± 1	12 ± 1	-1 ± 3	-1 ± 4	-1 ± 1

The bond lengths and angles for an  $\text{NbI}_4$  unit and their standard deviations which were computed from the final parameters of the anisotropic refinement are given in Table 5. Intra- and interchain distances between non-bonding atoms are listed in Table 6. The letters  $A$  and  $B$  before an atom designation denote different symmetry-related atoms. A Function and Error Program was kindly furnished by Busing & Levy for our calculations on the IBM 704 (Busing & Levy, 1959).

#### Analysis of anisotropic thermal motion

The three orthogonal principal axes of the ellipsoid of thermal vibration were computed from the anisotropic temperature coefficients  $B_{ij}$  in Table 3 by the method of Busing & Levy (1958). Table 7 contains  $u(r)$ , the root-mean-square component of thermal displacement of the atom along the  $r$ th principal axis ( $r=1, 2, \text{ or } 3$ ), and the angles  $\varphi(r, i)$ , made by the  $r$ th principal axis with the  $i$ th crystallographic axis. Examination of the displacements shows all the atoms to have anisotropic character. The restrictions on the temperature-factor coefficients of the bridging iodines which lie

Table 4. Observed and calculated structure factors

h	k	l	F <sub>o</sub>	F <sub>c</sub>	A <sub>c</sub>	B <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	A <sub>c</sub>	B <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	A <sub>c</sub>	B <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	A <sub>c</sub>	B <sub>c</sub>
0	0	4	503	559	559	27	0	12	0	392	395	395	0	1	7	0	142	133	133	0	2	2	3	167	136	107	82
0	0	6	267	233	233	-230	0	1	1	142	133	133	0	2	2	1	142	133	133	0	2	2	4	239	229	229	202
0	0	8	158	100	100	120	0	2	2	120	116	116	116	2	2	2	120	116	116	116	2	2	5	167	136	107	82
0	0	10	628	778	778	120	0	3	3	120	116	116	116	2	2	3	120	116	116	116	2	2	6	212	174	172	24
0	0	12	236	233	233	-230	0	4	4	206	220	220	143	2	3	4	117	111	111	111	2	2	7	226	229	229	149
0	0	14	261	260	260	81	0	5	5	189	184	184	167	2	4	5	113	102	102	102	2	2	8	124	111	111	24
0	0	16	153	154	153	-77	0	6	6	111	110	110	106	2	6	6	69	63	63	63	2	2	9	499	530	525	47
0	2	3	222	185	-139	-122	0	8	8	208	211	-206	-44	2	8	8	64	55	55	55	2	2	10	178	176	167	55
0	2	4	803	1099	-35	-1098	0	10	10	195	178	-163	-167	2	10	10	113	105	105	105	2	2	11	214	225	225	117
0	2	5	301	312	158	-269	0	11	11	159	167	104	-130	2	11	11	122	130	130	130	2	2	12	182	164	-81	142
0	2	6	216	237	237	-1	0	12	12	164	177	-165	-170	2	12	12	112	112	112	112	2	2	13	473	483	482	-18
0	2	7	286	293	280	177	0	13	13	149	145	-140	-36	2	13	13	94	84	84	84	2	2	14	176	157	-54	118
0	2	8	137	110	110	-97	0	14	14	230	218	-217	-14	2	14	14	169	168	168	168	2	2	15	157	149	14	120
0	2	9	157	145	134	-54	0	15	15	146	145	-144	-57	2	15	15	173	173	173	173	2	2	16	154	149	149	188
0	2	10	111	105	-158	-51	0	16	16	118	120	-120	-104	2	16	16	100	91	91	91	2	2	17	103	170	159	60
0	2	11	175	166	-158	-51	0	17	17	227	227	-219	-154	2	17	17	106	105	105	105	2	2	18	173	171	95	75
0	2	12	230	227	227	-219	0	18	18	188	188	-188	-16	2	18	18	106	106	106	106	2	2	19	103	170	159	60
0	2	13	188	177	177	-154	0	19	19	299	309	245	188	2	19	19	106	106	106	106	2	2	20	296	248	248	0
0	2	14	94	96	96	-89	0	20	20	283	276	-276	-276	2	20	20	106	106	106	106	2	2	21	160	136	-123	-54
0	2	15	253	228	228	-213	0	21	21	284	284	-284	-284	2	21	21	106	106	106	106	2	2	22	736	737	737	767
0	2	16	136	118	118	-117	0	22	22	281	281	-281	-281	2	22	22	106	106	106	106	2	2	23	301	306	-305	3
0	2	17	180	182	182	-182	0	23	23	121	121	-121	-121	2	23	23	106	106	106	106	2	2	24	151	161	-108	-116
0	2	18	131	112	112	-105	0	24	24	133	138	-138	-59	2	24	24	106	106	106	106	2	2	25	678	782	782	0
0	2	19	250	233	233	-230	0	25	25	378	345	345	0	2	25	25	106	106	106	106	2	2	26	146	139	153	188
0	2	20	145	106	106	-40	0	26	26	150	193	136	139	2	26	26	106	106	106	106	2	2	27	574	641	641	34
0	4	0	912	1104	1104	108	0	27	27	180	193	136	139	2	27	27	106	106	106	106	2	2	28	128	115	-74	88
0	4	1	236	194	161	-137	0	28	28	161	169	118	121	2	28	28	106	106	106	106	2	2	29	173	187	-113	-148
0	4	2	24	189	24	-137	0	29	29	191	184	-179	-11	2	29	29	106	106	106	106	2	2	30	223	224	224	0
0	4	3	823	95	95	-6	0	30	30	142	124	-119	-11	2	30	30	106	106	106	106	2	2	31	157	162	162	-162
0	4	4	27	94	94	-82	0	31	31	144	124	-119	-11	2	31	31	106	106	106	106	2	2	32	187	182	182	0
0	4	5	267	266	266	-266	0	32	32	125	117	-104	-53	2	32	32	106	106	106	106	2	2	33	810	78	26	73
0	4	6	137	115	115	-105	0	33	33	136	122	-91	81	2	33	33	106	106	106	106	2	2	34	810	911	-910	26
0	4	7	437	460	460	-460	0	34	34	138	143	-119	-119	2	34	34	106	106	106	106	2	2	35	397	419	-313	-279
0	4	8	351	383	383	-383	0	35	35	160	162	-162	-162	2	35	35	106	106	106	106	2	2	36	123	107	-62	-87
0	4	9	118	108	108	-108	0	36	36	171	171	-171	-171	2	36	36	106	106	106	106	2	2	37	176	162	144	-74
0	4	10	308	425	425	-425	0	37	37	143	143	-143	-143	2	37	37	106	106	106	106	2	2	38	182	182	-137	16
0	4	11	106	93	93	-82	0	38	38	156	143	-123	-123	2	38	38	106	106	106	106	2	2	39	75	96	93	63
0	4	12	308	425	425	-425	0	39	39	123	113	-103	-53	2	39	39	106	106	106	106	2	2	40	75	75	-39	-23
0	4	13	106	93	93	-82	0	40	40	123	113	-103	-53	2	40	40	106	106	106	106	2	2	41	462	476	-476	246
0	4	14	308	425	425	-425	0	41	41	123	113	-103	-53	2	41	41	106	106	106	106	2	2	42	171	171	-21	-68
0	4	15	106	93	93	-82	0	42	42	123	113	-103	-53	2	42	42	106	106	106	106	2	2	43	192	185	18	154
0	4	16	308	425	425	-425	0	43	43	123	113	-103	-53	2	43	43	106	106	106	106	2	2	44	360	401	401	0
0	4	17	106	93	93	-82	0	44	44	123	113	-103	-53	2	44	44	106	106	106	106	2	2	45	209	220	208	208
0	6	1	181	173	166	-169	0	28	28	134	131	106	106	2	28	28	106	106	106	106	2	2	46	123	121	29	118
0	6	2	458	442	442	-442	0	29	29	157	146	-123	-113	2	29	29	106	106	106	106	2	2	47	109	103	-59	-59
0	6	3	750	818	818	-818	0	30	30	157	146	-123	-113	2	30	30	106	106	106	106	2	2	48	141	139	131	131
0	6	4	98	94	94	-93	0	31	31	157	146	-123	-113	2	31	31	106	106	106	106	2	2	49	109	103	-59	-59
0	6	5	175	166	166	-169	0	32	32	157	146	-123	-113	2	32	32	106	106	106	106	2	2	50	141	139	131	131
0	6	6	670	742	742	-742	0	33	33	157	146	-123	-113	2	33	33	106	106	106	106	2	2	51	162	125	-125	-81
0	6	7	352	354	354	-354	0	34	34	157	146	-123	-113	2	34	34	106	106	106	106	2	2	52	237	217	-68	206
0	6	8	151	149	149	-149	0	35	35	157	146	-123	-113	2	35	35	106	106	106	106	2	2	53	137	99	97	19
0	6	9	111	105	105	-105	0	36	36	157	146	-123	-113	2	36	36	106	106	106	106	2	2	54	226	216	-152	-153
0	6	10	203	182	182	-182	0	37	37	157	146	-123	-113	2	37	37	106	106	106	106	2	2	55	749	829	829	829
0	6	11	174	185	185	-185	0	38	38	157	146	-123	-113	2	38	38	106	106	106	106	2	2	56	212	213	-228	168
0	6	12	196	172	172	-172	0	39	39	157	146	-123	-113	2	39	39	106	106	106	106	2	2	57	269	322	-228	168
0	6	13	149	152	152	-152	0	40	40	157	146	-123	-113	2	40	40	106	106	106	106	2	2	58	96	113	-39	-106
0	6	14	208	195	195	-195	0	41	41	157	146	-123	-113	2	41	41	106	106	106	106	2	2	59	212	213	-228	168
0	6	15	145	141	141	-141	0	42	42	157	146	-123	-113	2	42	42	106	106	106	106							



Table 4. (cont.)

h	k	l	$V_0$	$V_c$	$A_c$	$B_c$	h	k	l	$V_0$	$V_c$	$A_c$	$B_c$	h	k	l	$V_0$	$V_c$	$A_c$	$B_c$	h	k	l	$V_0$	$V_c$	$A_c$	$B_c$
6	4	10	310	357	40	357	6	14	14	114	112	110	22	7	7	16	93	88	-88	2	8	4	1	88	68	55	39
		11	80	74	-108	46			15	112	118	110	44			17	96	96	32	90		2	2	90	75	13	74
		12	78	83	-108	46																4	2	88	68	55	39
		13	101	106	-106	-6																6	2	90	75	13	74
		14	163	152	-153	-153																8	2	88	68	55	39
		15																				10	2	90	75	13	74
		16																				12	2	88	68	55	39
		17																				14	2	90	75	13	74
		18																				16	2	88	68	55	39
		19																				18	2	90	75	13	74
		20																				20	2	88	68	55	39
		21																				22	2	90	75	13	74
		22																				24	2	88	68	55	39
		23																				26	2	90	75	13	74
		24																				28	2	88	68	55	39
		25																				30	2	90	75	13	74
		26																				32	2	88	68	55	39
		27																				34	2	90	75	13	74
		28																				36	2	88	68	55	39
		29																				38	2	90	75	13	74
		30																				40	2	88	68	55	39
		31																				42	2	90	75	13	74
		32																				44	2	88	68	55	39
		33																				46	2	90	75	13	74
		34																				48	2	88	68	55	39
		35																				50	2	90	75	13	74
		36																				52	2	88	68	55	39
		37																				54	2	90	75	13	74
		38																				56	2	88	68	55	39
		39																				58	2	90	75	13	74
		40																				60	2	88	68	55	39
		41																				62	2	90	75	13	74
		42																				64	2	88	68	55	39
		43																				66	2	90	75	13	74
		44																				68	2	88	68	55	39
		45																				70	2	90	75	13	74
		46																				72	2	88	68	55	39
		47																				74	2	90	75	13	74
		48																				76	2	88	68	55	39
		49																				78	2	90	75	13	74
		50																				80	2	88	68	55	39
		51																				82	2	90	75	13	74
		52																				84	2	88	68	55	39
		53																				86	2	90	75	13	74
		54																				88	2	88	68	55	39
		55																				90	2	90	75	13	74
		56																				92	2	88	68	55	39
		57																				94	2	90	75	13	74
		58																				96	2	88	68	55	39
		59																				98	2	90	75	13	74
		60																				100	2	88	68	55	39
		61																				102	2	90	75	13	74
		62																				104	2	88	68	55	39
		63																				106	2	90	75	13	74
		64																				108	2	88	68	55	39
		65																				110	2	90	75	13	74
		66																				112	2	88	68	55	39
		67																				114	2	90	75	13	74
		68																				116	2	88	68	55	39
		69																				118	2	90	75	13	74
		70																				120	2	88	68	55	39
		71																				122	2	90	75	13	74
		72																				124	2	88	68	55	39
		73																				126	2	90	75	13	74
		74																				128	2	88	68	55	39
		75																				130	2	90	75	13	74
		76																				132	2	88	68	55	39
		77																				134	2	90	75	13	74
		78																				136	2	88	68	55	39
		79																				138	2	90	75	13	74
		80																				140	2	88	68	55	39
		81																				142	2	90	75	13	74
		82																				144	2	88	68	55	39
		83																				146	2	90	75	13	74
		84																				148	2	88	68	55	39
		85																				150	2	90	75	13	74
		86																				152	2	88	68	55	39
		87																				154	2	90	75	13	74
		88																				156	2	88	68	55	39
		89																				158	2	90	75	13	74
		90																				160	2	88	68	55	39
		91																				162	2	90	75	13	74
		92																				164	2	88	68	55	39
		93																				166	2	90	75	13	74
		94																				168	2	88	68	55	39
		95																				170	2	90	75	13	74
		96																									

Table 6. Nearest neighbor I-I distances in NbI<sub>4</sub>

Intrachain	
I <sub>1</sub> -I <sub>3</sub>	3.980 ± 0.008 Å
-I <sub>4</sub>	3.852 ± 0.008
-I <sub>5</sub>	3.877 ± 0.008
-I <sub>6</sub>	3.775 ± 0.008
-I <sub>1</sub> '	3.774 ± 0.012
-AI <sub>1</sub>	3.896 ± 0.012
I <sub>2</sub> -I <sub>3</sub>	3.965 ± 0.008 Å
-I <sub>4</sub>	3.864 ± 0.007
-I <sub>5</sub>	3.888 ± 0.008
-I <sub>6</sub>	3.760 ± 0.008
-I <sub>2</sub> '	3.760 ± 0.012
-AI <sub>2</sub>	3.910 ± 0.012
I <sub>3</sub> -I <sub>4</sub>	3.845 ± 0.010 Å
-I <sub>5</sub>	4.370 ± 0.009
I <sub>4</sub> -I <sub>6</sub>	3.806 ± 0.009 Å
I <sub>5</sub> -I <sub>6</sub>	3.846 ± 0.010 Å
Interchain	
I <sub>1</sub> -BI <sub>3</sub>	3.889 ± 0.008 Å
I <sub>3</sub> -BI <sub>6</sub>	3.987 ± 0.007
I <sub>4</sub> -BI <sub>5</sub>	3.972 ± 0.007

Atoms related by a mirror and *C*-centering are designated by *A* and *B* respectively.

listed in Table 5. These corrections in bond lengths due to thermal vibrations are less than twice the standard deviations of the uncorrected bond lengths.

### Discussion of the structure

Solid  $\alpha$ -NbI<sub>4</sub> consists of infinite chains parallel to the *a* axis formed by NbI<sub>6</sub> octahedra sharing two opposite edges. The niobium atoms are each shifted 0.26 Å from the centers of the octahedra of iodine atoms toward one another in pairs to give a resulting Nb-Nb distance of 3.31 Å. Fig. 1 shows the configuration of

Table 8. *R.m.s.* displacements along molecular chain axes

Atom	Along Nb-Nb direction <i>u</i> (1)	Along I <sub>3</sub> -I <sub>5</sub> direction <i>u</i> (2)	Along I <sub>1</sub> -I <sub>2</sub> direction <i>u</i> (3)
I <sub>1</sub>	0.170 Å	0.158 Å	0.110 Å
I <sub>2</sub>	0.154	0.148	0.111
I <sub>3</sub>	0.117	0.135	0.140
I <sub>4</sub>	0.127	0.116	0.127
I <sub>5</sub>	0.139	0.095	0.180
I <sub>6</sub>	0.133	0.155	0.157
Nb	0.086	0.131	0.110

an (NbI<sub>4</sub>)<sub>2</sub> unit in the infinite linear chain corresponding to one unit cell in periodicity (i.e., of length  $a=7.67$  Å). With respect to an origin chosen at the center of the localized unit, the approximate point group symmetry is  $D_{2h}-mmm$ ; the required crystallographic symmetry through this point is  $C_s-m$ . The two Nb-I distances (corrected for thermal motion) for each of the two pairs of similar bridge bonds do not differ significantly, 2.74 and 2.77 Å (both ± 0.007) for Nb-I<sub>3</sub> and Nb-I<sub>5</sub>; 2.90 and 2.91 Å (both ± 0.007) for Nb-I<sub>4</sub> and Nb-I<sub>6</sub>. The difference between the two apical Nb-I distances, 2.67 and 2.71 Å (both ± 0.007 Å) is possibly significant. The mean of the two apical Nb-I bond lengths, 2.69 Å, is considerably shorter than the mean bridge Nb-I length, 2.83 Å. This smaller distance is consistent with a higher bond order for the terminal (apical) Nb-I bonds.

The arrangement of the chains in the unit cell are given in Figs. 2-4. The [100] unit cell projection (Fig. 2) clearly shows the packing of the infinite linear chains normal to the chain length. An informative way of viewing the  $\alpha$ -NbI<sub>4</sub> structure is to consider the iodine atoms as being in hexagonal close-packed array. This hexagonal close-packing is evident in the projection of the structure along the [010] direction

Table 7. The principal axes *r.m.s.* displacements and orientations with crystallographic axes

Atom	<i>r</i>	<i>u</i> ( <i>r</i> )	$\varphi$ ( <i>r</i> , <i>a</i> )	$\varphi$ ( <i>r</i> , <i>b</i> )	$\varphi$ ( <i>r</i> , <i>c</i> )
I <sub>1</sub>	1	0.084 ± 0.007 Å	91.2 ± 2.2°	27.9 ± 2.7°	62.1 ± 2.7°
	2	0.167 ± 0.006	37.6 ± 31.2	72.5 ± 11.9	122.1 ± 26.1
	3	0.176 ± 0.006	52.4 ± 31.2	111.1 ± 10.1	45.1 ± 23.6
I <sub>2</sub>	1	0.106 ± 0.006	89.3 ± 5.3	73.8 ± 6.3	16.2 ± 6.5
	2	0.139 ± 0.004	132.2 ± 9.8	135.1 ± 9.5	77.6 ± 7.4
	3	0.166 ± 0.006	137.7 ± 9.8	49.6 ± 9.3	100.3 ± 4.2
I <sub>3</sub>	1	0.161 ± 0.009	90.0	97.6 ± 6.5	7.6 ± 6.5
	2	0.117 ± 0.010	180.0	90.0	90.0
	3	0.109 ± 0.010	90.0	7.6 ± 6.5	82.4 ± 6.5
I <sub>4</sub>	1	0.102 ± 0.012	90.0	110.0 ± 11.9	20.0 ± 11.9
	2	0.127 ± 0.009	180.0	90.0	90.0
	3	0.138 ± 0.007	90.0	20.0 ± 11.9	70.0 ± 11.9
I <sub>5</sub>	1	0.181 ± 0.008	90.0	60.3 ± 4.1	29.7 ± 4.1
	2	0.139 ± 0.010	180.0	90.0	90.0
	3	0.094 ± 0.011	90.0	29.7 ± 4.1	119.7 ± 4.1
I <sub>6</sub>	1	0.182 ± 0.009	90.0	99.9 ± 6.5	9.9 ± 6.5
	2	0.133 ± 0.010	180.0	90.0	90.0
	3	0.124 ± 0.008	90.0	9.9 ± 6.5	80.1 ± 6.5
Nb	1	0.135 ± 0.004	92.2 ± 10.6	14.3 ± 6.5	104.1 ± 6.4
	2	0.106 ± 0.005	84.1 ± 33.3	103.8 ± 7.0	164.9 ± 12.3
	3	0.086 ± 0.018	6.3 ± 30.7	86.5 ± 11.9	84.8 ± 32.9

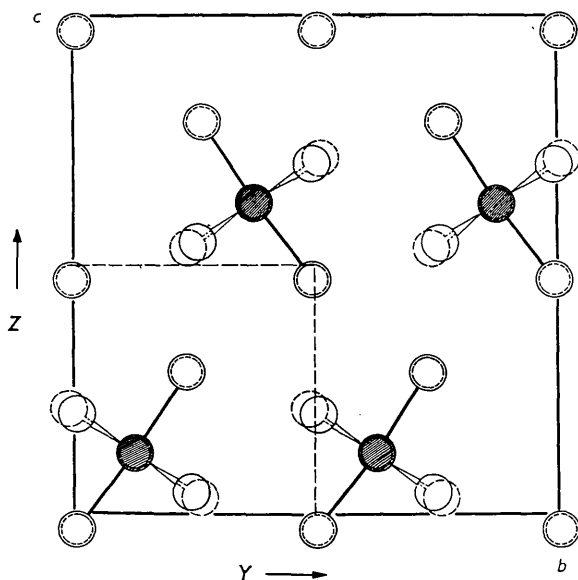


Fig. 2. [100] projection of the unit cell. The asymmetric part is outlined by dashed lines.

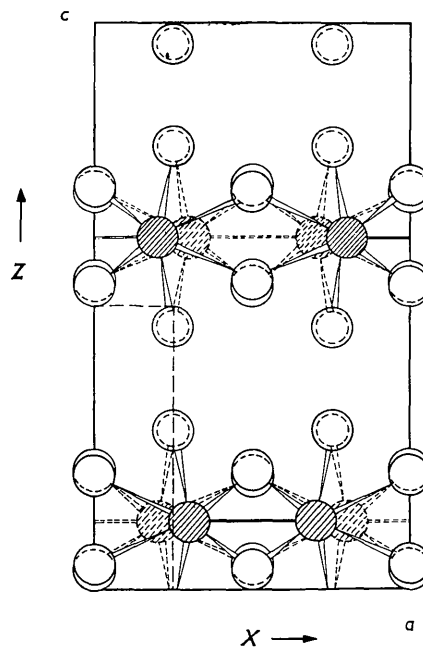


Fig. 3. [010] projection of the unit cell. The asymmetric part is outlined by dashed lines.

(Fig. 3). The niobium atoms occupy 1/4 of the available octahedral holes to form linear chains by filling every other row of octahedral holes in every other layer. To a first approximation the iodine atoms lie in four layers at  $y=0, 1/4, 1/2,$  and  $3/4$ ; the niobium atoms fill 1/2 the octahedral holes at  $y=1/8$  and  $5/8$ ; the holes at  $3/8$  and  $7/8$  are unoccupied. The small but significant directional shifts of the iodine atoms from regular hexagonal close-packed positions (observed in Figs. 3 and 4) can be readily explained from the niobium positions. For instance, the bridge iodines toward which the niobium atoms have shifted are further apart than are the bridge iodines away from which the niobium atoms have shifted (4.37 versus 3.81 Å). The distances of the nearest of the twelve iodine neighbors are given in Table 6 for each iodine in the asymmetric unit. As expected, the shorter iodine-iodine contacts result from iodine atoms bonded to niobiums in the same chain. These intrachain contacts with the exception of the bridge iodine distance mentioned above vary from 3.76 to 4.0 Å. The iodine-iodine contacts between chains range from 3.9 to 4.3 Å; surprisingly, most interchain distances are shorter than the normal van der Waals distance of 4.3 Å (Pauling, 1960).

Structural calculations of X-ray data showed the tetraiodides of Nb and Ta to be isomorphous (Dahl & Wampler, 1959). These are the first simple metal halides which have this structure; the metal-metal distance of 3.31 Å is the longest distance known which definitely involves a pairing of electrons. Much shorter Nb-Nb bonds are found in the ion  $[\text{Nb}_6\text{Cl}_{12}]^{2+}$  (2.85 Å) (Vaughan *et al.*, 1950) and in niobium metal (2.86 Å) (Sutton, 1958). Since all the niobium atoms in  $\alpha\text{-NbI}_4$  have identical environments, it can be

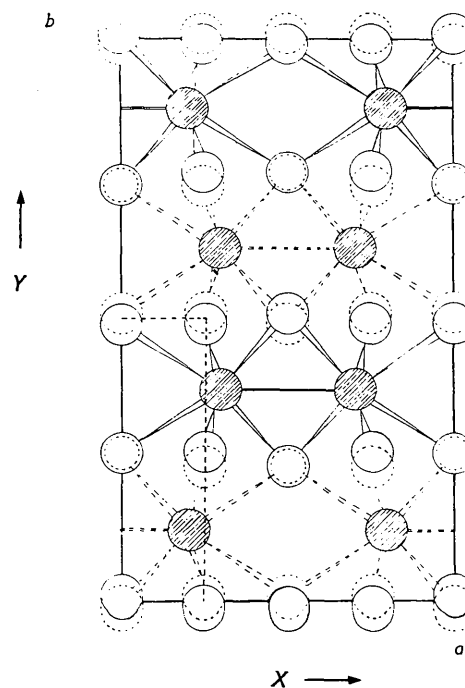


Fig. 4. [001] projection of the unit cell. The asymmetric part is outlined by dashed lines.

concluded that the valency state for Nb is IV and not a mixture of III and V states.

A qualitative description of the nature of bonding of  $\alpha\text{-NbI}_4$  has been outlined in terms of simple M.O. theory based on assumed octahedral symmetry about



each niobium atom (Dahl & Wampler, 1959). M.O. symmetry arguments based on a model of idealized  $D_{2h}$  symmetry for the localized structural unit,  $(\text{NbI}_4)_2$ , (not given here to conserve space) are consistent with our proposal of weak metal-metal interaction involving the direct overlap of pairs of  $d_{xy}$  niobium orbitals.

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### Short Communications

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*Acta Cryst.* (1962). **15**, 911

**A preliminary investigation of the crystal and molecular structure of  $\alpha$ -D-glucose monohydrate.** By R. C. G. KILLEAN, W. G. FERRIER and D. W. YOUNG, *Carnegie Laboratory of Physics, Queen's College, Dundee, Scotland*

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$\alpha$ -D-Glucose (1 $\alpha$ -D-glucopyranose) is easily crystallized as a monohydrate. The needle crystals are monoclinic and the cell dimensions obtained from Weissenberg photographs are

$$a = 8.84 \pm 0.03, \quad b = 5.10 \pm 0.02, \quad c = 9.69 \pm 0.03 \text{ \AA};$$

$$\beta = 98.25 \pm 0.25^\circ.$$

The density is  $1.512 \pm 0.005$  g.cm.<sup>-3</sup>, indicating that

there are two molecules per unit cell. The only systematic absences observed were  $0k0$  for  $k$  odd, and the space group is thus  $P2_1$ .

Equi-inclination Weissenberg photographs were taken with Cu radiation, a multi-film technique being used, and the intensities were estimated visually for some thousand reflections. Several small crystal specimens were employed and no absorption corrections have been applied.