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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  $Cmc2_1$ , lattice parameters

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

with eight formula units in the unit cell. Final refinement by a three-dimensional anisotropic leastsquares 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  $3\cdot31$  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. x-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.<sup>†</sup> 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 & Hershaft, 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  $MX_4$ ,  $MOX_2$ , and  $MO_2$ . 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

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 $<sup>\</sup>dagger \alpha$ -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.

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  $NbO_2$  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. Thinwalled 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  $0.8 \times 0.05 \times 0.04$  mm.) that absorption corrections were neglected. Extinction corrections were not made.

Timed-exposure precession photographs of h0l and hk0 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,

$$a = 7.67 \pm 0.02$$
,  $b = 13.23 \pm 0.02$ ,  $c = 13.93 \pm 0.02$  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  $(\lambda = 0.7107 \text{ Å}), 203 \text{ cm}.^{-1}.$ 

Systematic absences:

## hkl for h+k odd; h0l for l odd.

Space group:  $Cmc2_1(C_{2v}^{12})$ ,  $C2cm(C_{2v}^{16})$ , or  $Cmcm(D_{2h}^{17})$ . The final space group chosen,  $Cmc2_1$ , 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,  $R = (\Sigma ||F_o| - |F_c|| / \Sigma |F_o|) \times 100$ , 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  $Cmc2_1$  the niobium atoms occupy the general 8-fold set of positions (8b); the iodines occupy two sets of 8b and four sets of 4-fold special positions (4a) on mirror planes (International Tables for X-ray Crystallography, 1952). These positions are as follows:

8b  $x, y, z; \overline{x}, y, z; \overline{x}, \overline{y}, \frac{1}{2} + z; x, \overline{y}, \frac{1}{2} + z; + C$  centering. 4a 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  $Cmc2_1$  the origin is not fixed by symmetry in the c lattice-vector direction, the z parameter of one iodine,  $I_1$ , 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  $F_o \ge 4F_{\min}$ ;  $\sqrt{w} = F_o/1.6F_{\min}^2$  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		x	$\boldsymbol{y}$	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	B	$\sigma(B)$
8b	I,	0.2467	0.0061	-0.0323	0.0004	0.0003		1.25	0.07
8b	I,	0.2458	0.2334	0.2842	0.0004	0.0003	0.0003	1.33	0.07
4a	$I_{3}$	0	0.2608	0.0333	0	0.0004	0.0004	1.37	0.08
4a	I,	0.5000	0.2436	0.0440	0	0.0005	0.0004	1.45	0.08
4a	$I_5^*$	0	-0.0113	0.2096	0	0.0004	0.0004	1.39	0.08
4a	$\mathbf{I}_{6}^{\bullet}$	0.5000	0.0066	0.1999	0	0.0004	0.0004	1.51	0.08
8b	Ňb	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

$\mathbf{Position}$		$\boldsymbol{x}$	$\boldsymbol{y}$	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
8b	Ι,	0.2460	0.0065	-0.0323	0.0004	0.0002	
8b	I,	0.2451	0.2340	0.2834	0.0004	0.0003	0.0002
4a	$I_3$	0	0.2619	0.0342	0	0.0005	0.0005
4a	I	0.5000	0.2443	0.0444	0	0.0005	0.0005
4a	$I_5$	0	-0.0114	0.2102	0	0.0004	0.0005
4a	I	0.5000	0.0077	0.1999	0	0.0005	0.0005
8b	Ňb	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 iddines  $(I_1 \text{ and } I_2)$ , the bridging iodines towards which the niobium is displaced ( $I_3$  and  $I_5$ ), and the other two bridging iodines  $(I_4 \text{ and } I_6)$ . These results show the importance of the weighting scheme in least-squares refinements involving film data.



Fig. 1. Configuration of an  $(NbI_4)_2$  unit in the linear infinite chain uncorrected for thermal vibration.

To provide a better calculated model and thereby obtain more meaningful positional parameters, leastsquares 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 $Å^2 \times 10^4$

	Anisotropic												
	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	B <sub>13</sub>	$B_{23}$							
Ι,	$97 \pm 10$	$14 \pm 1$	$25\pm2$	$-1\pm 2$	$3\pm 2$	$-10\pm1$							
$\mathbf{I}_2$	$80 \pm 7$	$25 \pm 2$	$12 \pm 1$	$-8 \pm 2$	$2\pm 2$	$-3 \pm 1$							
$I_3$	$46 \pm 8$	$17 \pm 2$	$26\pm3$	0	0	$-2 \pm 2$							
I <sub>4</sub>	$54 \pm 8$	$20 \pm 2$	$12 \pm 2$	0	0	$3\pm 2$							
$I_5$	$65 \pm 9$	$17 \pm 2$	$27\pm3$	0	0	$11 \pm 2$							
I <sub>6</sub>	$59\pm9$	$18\pm2$	$33\pm3$	0	0	$-3\pm 2$							
Ńb	$25 \pm 10$	$20 \pm 1$	$12 \pm 1$	$-1 \pm 3$	$-1 \pm 4$	$-1\pm 1$							

The bond lengths and angles for an NbI<sub>4</sub> 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 rth principal axis (r=1, 2, or 3), and the angles  $\varphi(r, i)$ , made by the rth principal axis with the *i*th crystallographic axis. Examination of the displacements shows all the atoms to have anisotropic character. The restrictions on the temperaturefactor coefficients of the bridging iodines which lie Table 4. Observed and calculated structure factors

h	k	1	<b>r</b> o	r <sub>e</sub>	Åe	Be	h	k	1	7,	rq	A <sub>c</sub>	Bc	h	k	1	z <sub>o</sub>	Fc.	Ac	B <sub>C</sub>	h	k	1 <b>F</b> o	<b>7</b> c	A <sub>c</sub>	Bc
0	0	4 68 9 4 6 <b>7</b>	503 245 158 158 158 158 157 26 157 26 157 26 157	553 1078 1777 260 154	57% 988 557 -76 - 24 55	27 -232 18 120 -331 -81 -77	0	12	01274567	927 29 9988 66 89 11 19	85998 8798 1088 10 10 10 10 10 10 10 10	205 195 101 -98 145 718 145 718	0 15 19 19 19 19 19 19 19 19 19 19 19 19 19	1	7	0-274568	142 142 122 117 115 06	135 135 116 118 111 102 55	1327 11 74 58 42 94 5	°\$883885	2	2	3 167 4 116 5 239 6 212 7 8 92 9 4 9 9 12 9 9 12 9 9	136 929 174 207 111 50	107 -1072 -1772 -1748 -1755 -1755 -1755 -1755 -1755 -1755 -1755 -1755 -1755 -1755 -1755 -1755 -1755 -1755 -1755 -1755 -1755 -1757 -1	848849874
0	2	54 56 78 910 11	223321686777775	18599127737 309127737 3010 510 3010 510 510 510 510 510 510 510 510 510 510	-13957307208952559	-122 -1098 -269 -1 177 -930 97 -54 -51			8 10 11 12 13 16 17 18	208 195 159 164 149 230 146 118	211 178 167 145 218 145 120	-206 -63 104 -163 -140 -217 -128 -60	-44 -167 -130 -798 14 -67 -104	1	y	9101112151617 0	1988 25675 20	105 1310 130 562 867 91	7948594 9	-9174-259 -14-259 -1-4-259 			11 178 182 214 182 18 17 16 17 18 17 18 19 10 10 10 10	176 264 485 126 485 126 170 101	167-1-8182-57-1-9-59-59	55548888888
		12 13 14 15 16 17 18 19 20	258 4 4 556 150	21760 2000 21260 2000 2000 2000 2000 2000 2	10 84 838 888 10 84 838 888	-219 -15井 -25井 -15井 -215 -25 -25 -25 -25 -25 -25 -25 -25 -25 -2	0	14	N-489101150	29922884 202824 202824 20284 20292 20284 20292 20284 20292 2028 20292 2028 20292 2028 20292 2020 200 2020 2020 2000 200 200 2000 2000 2000 200 2000 2	508162289898 76228998	24757 165 588 24 54	188 -276 -276 -255 -74 -79 -79 -0			127456780	106 57 89 11 75 75 75 75 75 75 75 75 75 75 75 75 75	105 106 102 87 118 143 160 137 04	8 22 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	-26 -46 81 -60 -108 -129 141 -110 17	2	4	0 296 1 160 2 756 4 301 5 162 6 678 7 146 7 146	2435767651289	2423 -123 -305 -100 -53 -100 -53	0 -57 19 -110 782 126
C	) 4	012045	245 9254 5874 9254 5874	10 11 12 12 9 9 5 15	104 1141 141 141 141 141 141 141 141 141	199 087 199 1985 199 199			1 2 5 11 21 31 417	180 156 161 191 142 145 125	19969444481 19691444814 19691444481	135 114 118 779 -179 -113 -104	32229455	1	11	12 13 14 0 1 2 3	8975 8971759	70877 788130 1140	19.24 CT (8.81)	-00 X 000 78	2	6	11 12 12 17 14 17 14 17 16 22 18 187 22 58 10 10 10 10 10 10 10 10 10 10 10 10 10	115 177 187 162 196 196 78	-148 -1413 -1124 -15 20	8888858589
		678011215146	2797751391058	8889785984 8889785984	10 5 8 5 7 5 9 8 1	2002	0	18 20	1457833	156 158 160 171 145 156 125	1223 1435 1622 1243 1431 131	-91 79 105 147 17 70 80	81 -119 -123 106 -123 -123			+ 5678 910 11 15	£19888951988	12886668187	2009 27 6988	3595968693		1	2 597 125 127 1276 197	919191928892268 2199228	-910 -313 -147 -137 -157 -157 -157 -157	8884449888
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		<b>7</b> 4 568	\$\$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$	442 818 94 166 742	5 -95 160 -19	274 -818 11 -43 -742	1	1	9 567	157 44 86 108	146 42 80 111	92 41 40 50	-113 -10 -49 105			1 2 10 4 5	12878	146 125 100 87	1999998	ት ଜୁድ ଜୁ ଜୁ ଜୁ ଜୁ	2	8	16 123 17 109 18 141 0 162	121 105 139	29 -59 131 -125	118 85 44
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		4 56 7 8 11	229 157 129 74 171	128 128 129 66	140 29 31 -33 101	-91 172 -125 -125 -57 -122			790 11	9.588 50	89 49 51 75 90	-571998	81 -11 -46 -56 -66	1	17	10 11 0 1	85 55	12 97 97 986	198 - 984	97 -26 -39	2	10	1 55 59 12 12 12 12 12 12 12 12 12 12 12 12 12	575 124 112	24 57 24 79 79 79	- 192 49 - 492 - 799 - 169
		12 13 14 16 17	486 142 263 174 131	527 152 274 175 126	-524 -148 -89 -161 -111	80.84			134 156 17	2888351	554979	82869	-75 -13 -13 -13 -13 -13 -13 -13 -13 -13 -13			174 56 70	177878148	70 71 105 115 114	545556	2012/02			7 240 10 12 140 13 20 14	270	-158 277 192 172 172	-185 27 38 137 176 176
•	0 10	1 74 5	204 95 496 317	262 96 517 311	-20 75 15 15 15	125 44 -514 -281	1	5	012	131 142 135	120 132 127	-120 118 -81	0 -58 -58	1	19	3 4	96 91	94	ッ -17 55	71 76			16 10 18 12 19 14	107 5 107 5 147	43 102 128	98 B 18 72
			120       120       100       100       100       112       12 <td>111 121 121 132 133 139 139 139 139 139 139 139</td> <td>114 229 -7 67 110 -113 -9 136 -114 -136 -114 -136 -20</td> <td>ኯ፝፝፝፝፝ ጞ፟፟፟፟፟ጟ፝፟፝<sup>5</sup>፟ኯ፟፝<sup>5</sup>፟፟፟<sup>5</sup> ኯ፟፝፟፟፟፟፟ ኯ፟፟፟፟፟ ኯ፟፟፟፟ ኯ፟፟፟፟ ኯ፟፟፟፟ ኯ፟፟፟ ኯ፟፟፟ ኯ፟፟፟ ኯ፟፟፟ ኯ፟፟፟ ኯ፟፟፟ ኯ፟፟ ኯ</td> <td></td> <td></td> <td>34 5678 91121345</td> <td>12×82298851198</td> <td>287 FB 56 58 8 55</td> <td>27553655977</td> <td>15134199-19758849</td> <td>1</td> <td>21 0</td> <td>0 1 4 6 80 12 12 12 12 12 12 12 12 12 12 12 12 12</td> <td>8985 1572 574 119 20 12 1772 574 119 20 12 1772 574 119 20 12</td> <td>87 91 1204 1052 1052 1052 1052 1052 1052 1052 1052</td> <td>-87 78 108 10 4 55 986 57 -9764 55 986 57</td> <td>0 -56 1301 405 -784 -119</td> <td>2</td> <td>12</td> <td>0 20 1 18 2 4 16 5 29 7 20 7 9 11 18 12 14 12</td> <td>167 177 161 161 161 161 161 161 161 161</td> <td>1674 -1955 -1955 -1955 -1999 -1999 -1100</td> <td>0 7904 50 791 - 92 198 - 190 1791 - 92 198</td>	111 121 121 132 133 139 139 139 139 139 139 139	114 229 -7 67 110 -113 -9 136 -114 -136 -114 -136 -20	ኯ፝፝፝፝፝ ጞ፟፟፟፟፟ጟ፝፟፝ <sup>5</sup> ፟ኯ፟፝ <sup>5</sup> ፟፟፟ <sup>5</sup> ኯ፟፝፟፟፟፟፟ ኯ፟፟፟፟፟ ኯ፟፟፟፟ ኯ፟፟፟፟ ኯ፟፟፟፟ ኯ፟፟፟ ኯ፟፟፟ ኯ፟፟፟ ኯ፟፟፟ ኯ፟፟፟ ኯ፟፟፟ ኯ፟፟ ኯ			34 5678 91121345	12×82298851198	287 FB 56 58 8 55	27553655977	15134199-19758849	1	21 0	0 1 4 6 80 12 12 12 12 12 12 12 12 12 12 12 12 12	8985 1572 574 119 20 12 1772 574 119 20 12 1772 574 119 20 12	87 91 1204 1052 1052 1052 1052 1052 1052 1052 1052	-87 78 108 10 4 55 986 57 -9764 55 986 57	0 -56 1301 405 -784 -119	2	12	0 20 1 18 2 4 16 5 29 7 20 7 9 11 18 12 14 12	167 177 161 161 161 161 161 161 161 161	1674 -1955 -1955 -1955 -1999 -1999 -1100	0 7904 50 791 - 92 198 - 190 1791 - 92 198

on mirror planes correspond to fixing the direction of one principal axis of displacement for each atom normal to the mirror plane as seen in Table 7.

In order more easily to visualize the thermal motions of individual atoms with respect to the infinite molecular chains, the r.m.s. component of thermal displacement of each atom along a set of molecular axes was computed. The natural choice of molecular axes is given by

$$X_1 \propto V, X_2 \propto V \times W, X_3 \propto X_1 \times X_2,$$

where V is the Nb-Nb direction and W is the  $I_1-I_2$ direction. With this choice of axes,  $X_2$  approximately coincides with the  $I_3-I_5$  direction and  $X_3$  with the

ь	k	1	¥0	r <sub>c</sub>	<b>▲</b> _c	Be	ь	k	1	T <sub>o</sub>	r <sub>c</sub>	Ac.	ве	ь	k	1	¥0	<b>7</b> _c	Ac	Вс	ь	k	1	ro	r <sub>c</sub>	A <sub>c</sub>	вс
2	12	14 16	102 1 <b>3</b> 4	71 118	-5 111	-71 -41	3	9	012	205 186 137	206 200 153	-206 176 -97	0 -95 -118	4	6	12 15 16	165 118 151	147 125 149	28 -116 40	-144 -45 143	5	5	9 10 11	91 87 99	80 86 91	-8 -16 54	-80 -84 75
2	14	2345	X 21 87 98	517 518 104 84	-230 -79 76	クタ -219 -68 -万			246 7	15	15956	-19 -18 -19 -19 -19	-58 -11 67	4	8	20 20 18	156 165 830	124 164 807	-123 1 807	7 164 0			12 13 14 15	95 106 103 115	106 113 113 127	70 -81 74 -115	478. 17
		6 9 10 12	78 189 157	103 207 193	-61 -105 139	85 178 67			8 9 11	84 72 85 15	81 64 90	88 <sup>4</sup> -	-80 -26 -29 -76			1234	242 197 95	205 179 97	9854	122 165 1	5	7	16 0	92 207	85 180	-78 180	<del>بر</del> م
_		14 15	161 180	161 203	138	33 76	_		13 14	123 100	143	-108 89	94 73			567	181 181 17 95	175 51 100	106 29 19	197 -41 -98			234	163 116 76	152 152 104 66	105 -10 -25	-// 112 104 61
2	16	1456	198 198	129 94 161 275	-108 64 -126 -31	-70 68 -100 275	3	11	123	168 174 123 127	148 139 120 130	148 121 82 -40	188- 1889 0			8 11 12 13	97 126 502 114	126 407 125	885 895 895 895	-31 -98 31			7 8 9	12,00,02	66 94 112 147	-40 95 4	-52 -10 -112
		7 8 11	159 159 148	168 180 152	-100 -141 -88	194 112 123			L≢ LN00 0	127 107 92	123	17 -57 60 30	12/5/9/1	ĥ	10	14 16	183 155	202 159	-64 -153	-192 -44 67	E	•	11 12	144 109	155	154 -116	-21 -8
2	18	125	175 164 93	176 147 64	117 -142 -31	-131 가 50			10 11 12	121 123 93	136 118 95	-45 118 -95	129 -1 7	7		1045	118 421 219	102 416 216	28788	55 -414 -199	2	9	1345	88 110 162	85 104 160	586	19 55 -43 -14
		7 11 13	192 123 132	198 101 198	-108 88 -72	-84 50 118	3	13	0 1 2	101 85 90	91 87 80	-91 86 -80	0 -16 -7			ь 789	104 226 370 108	111 226 395 121	357 -5 70	-67 163 -394 -99			6 7 8 9	192 195 151 102	188 192 151 100	-55 116 114 -90	-180 152 -100
2	20	2 8 10	103 114 118	118 66 100	-80 - <b>1</b> 19	8688			<b>N</b> 4 54	99 110 121	101 117 131	-95 -10599	31 -50 -117			10 12 13	122 118 140	120 110 159	99 -5 103	-67 -110 -121	5	11	1 2	88 131	72 117	52 105	49 -51
2	22	3	123	144	-98	-106			7 8 9	15121 95	143 132 100	-265 55 -992	116 -94 40	4	12	0 1 4	374 205 305	346 200 316	<b>746</b> 154 309	0 128 •64			74 56	152 152 142 128	146 141 135	136 48 10	-192 -192 -193
3	1	54 56	105 102 127 105	105 107 124 108	66 107 -23 -39	82 7 122 101	3	15	234	90 118 128	77 122 141	75 -107 100	-14 59 99			56810	175 156 169 156	176 133 151 116	113 53 -146 -45	155 122 -38 -107			7 8 9	59994	101 71 81 90	80.00	58 48 -1 17
		7 11 12	7965 9 27	288.84	12878	0 5%1-77			5678	<u>3</u> 98825	130 104 956	0 4 4-0 26	-130 104 82			11 12 13	112 159 118	174 166 123	85 -158 -118 -118	-105 -49 -33			11 15 16	90 108 109	85 54 94 92	¥9,8,≩	-72 -18 -5
		14 15 16	12 981	110 99 72	76 -90 -71	79 -41 16	3	17	9	100 146	93 148	-84 -148	-58 	4	14	17 2	130 224	120 224	-107	-55 以	5	13	012	135 147 144	136 149 144	-136 124 -72	0 -81 -123
3	3	17 18 0	84 82 154	88 55 133	-40 19 133	-78 -52 0	4	0	1 2 4	152 96 451	140 99 456	118 -63 456	-75 -76 19			4 8 9	2 <b>34</b> 214 197	222 228 28	60 5 126	-225 -227 -190			5 6 7 10	113 86 94 4	119 60 68 88	27 -29 7 11	115 -55 67 -87
-	-	123	141 121 118	129 113 105	888	-98 112 98			68 12	95 156 506	97 35 1554 554	-128 -128 -581	-9.58	4	16	0152	258 169 121	265 159 139	265 111 94	0 113 101			11 12 13	95 98 101	89988	79 78 -70	41 -60 69
		567	101 71 60	91 63 61	4 54	-7.25	4	2	ĩć Z	234 93	235 70	-228 -51	-57 -47	4	18	57	136 130	120 136	78 110	-91 80	5	15	0	122 123	118 126	118 122	-32
		9 10 12	115 157 140 84	109 155 149 88	19 57 7 7	-148 149 -13			4567	189	195 174 151 165	-282 151 125	-155 -155 107	5	1	4 56	79 111 142	80 117 148	-80 65 -55	-2 -97 -137			2048	106 76 81	109 70 58	い7 -列 51	103 70 27
		13 16 17	67 76 85	58 39 71	36 -13 69	46 -37 16			8 10 11	604 126 101 185	201755	-21 120 -91	-719 -43 -22			78910	166 145 111 95	171 151 120 108	96 27 20 29	141 -81 95 108			9 10 11	98 106 114	90 116 105	-29 -52 103	-85 103 -16
3	5	1 2 3	90 110 129	62 94 118	47 -79 -118	41 49 0			151618	108 209 140	110 194 149	58 72 -149	-95 180 -1			11 12 13	123 50 50 50	126 99 67	-126 -95 -13	13 -25 -66	5	17	5678	111 120 120	119 137 127	57,67	-105 -155 94
		7 56 7	129	119 134 155	-192	-86 -114 125		4	0	826 179	197 850 137	850 113	190 17	5	3	0 1 2	66 110 152	61 83 134	-61 -14 50	0 81 -123	6	0	68	516 169	90 709 176	43 -174	708 28
		9 10 11	151 151 151 151 151 151 151 151 151 151	599.647	-109 -109 -17	-91 105 88			2 10-4 5	995 610 196	67 68 692 116	କ୍ଷ୍ୟୁକ୍ଷ ଜ୍ୟୁକ୍ଷ	-64 -55 -2595			56	192 191 151	170 171 147 122	-154 171 75	-15 -127 122			10 16 18	201 85 188	79 208	-29 76 -54	22 -201
-	7	12	67 78	46 76	-15 -76	_43 _4			678	168 81 909	168 67 721	72 10 -314	809 PM			78910	89856	997168 <b>7</b>	87158	10 0 44	6	2	2456	67595917	8875	84,48	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2
2	1	545	90 137 190 204	129 176 190	-127 147 15	1469			11 12 13	97 50 20	85 59 77	-3876	-6 11 -11			11 12 13	102 77 81	19/62	00 27 49 27 49	-94-1-52			7 10 12	74 318 144	50 51 14	489	4982
		6789	152 112 82 81	155 117 87 81	-16 84 -41 -71	15-51 77 -78			14 16 17	116 289 106	98 316 67	-316 -59	-9/ -92			14 15 16 17	101 113 117 94	90 190 198 91	129 -106 -106	80 18 20 91			14 16 18	99 108	950 95 116	990 11 106	-198,49
		10	81 71 60	2883	5777	89°	4	6	1946	87 9956 j	962 868 89	-7 222 -1	-92 172 -629	5	5	012	189 167 190	142 153 160	-142 115 -40	0 -100 -162	6	4	0 1 2 4	128 101 425 67	101 75 768 79	101 -69 11 -79	0 -28 768 0
		15 16 17	19959	5898 10	1998 -98 -94				8 9 10 11	58835	888899	15128158	-545			3478	19888 19888	174 22 74 77	99 195 145	14 5 5 5 6			5678	107 516 103 103	85975	-61 17 -54 -92	-65 565 80 17

 $I_1-I_2$  direction. The amplitudes of thermal vibration, u(m), along  $X_1, X_2$ , and  $X_3$  are given in Table 8.

The unusual sensitivity of thermal parameters to systematic error makes it difficult to attach definite physical significance to the calculated amplitudes of thermal motion. It should be noted, however, that for the niobium atom and apical iodines  $(I_1 \text{ and } I_2)$  the indicated r.m.s. displacements normal to the bonding directions are greater than the displacements along the bonds.

Corrections in the bond lengths to allow for this thermal effect are of the order of 0.01 Å and are

Table 4. (cont.)

h	k	1	70	7c	<b>A</b> 2	3 <sub>c</sub>	h	k	1	7 <sub>0</sub>	X.	۸c	B <sub>C</sub>	h	k	1	¥0	<b>7</b> c	<b>▲</b> c	3,	h	k	1	70	Y <sub>c</sub>	Ac	Bc
6	4	10 11 12	310 80 78	357 74 83	နာင်္န အီနိုင်	<b>3</b> 57 564 49	6	14	14 15	114 112	112 118	110 110	22 44	7	7	16 17	9 <b>3</b> 96	88 96	-88 79	2 90	8	4	1 2 4	88 90 266	68 75 254	55 13 254	39 74 6
,	~	16 18	101 163	106 152	106 -20	-6 -150	6	<b>1</b> 6	125	81 76 114	85 85 110	-7-5-82	ያ መቆ ያ	7	9	0 1 2	213 196 143	188 172 126	-188 148 -66	-88 -107			58 12	63 56 250	57 112 283	33 -107 -281	47 31 32
0	0	234	576 188	557 178 178	-57 -130	-11 -12 -121 -82			789	120 93 77	105 116 101 63	-67	94 70			2 11 12 13	84 114 123	90 123 131	84 106 -90	80 55 -61 95	8	6	14 16 1	108 139 71	143	-16 -141	-110 -20
		6 9 10	115 120 275	83 116 287	-87-1-785	-1 102 -27			10 11	95 106	74 107	-65	74 85	7	11	14 0	103 140	104 131	72 131	74 0	•	-	234	56 79 350	好のあり	\$ <b>4</b> ₽ ₽ ₽	-1 34 -343
		12 14 15	130 256 110	120 276 110	12 276 104 21	119 -4 34 88	6 7	18 1	1	101 78	95 91 100	59 100	-71 69			1234	122 105 112 106	117 101 103	89 45 4	-75 91 103			6 7 8	75 86 306	65 84 326	61 50 -8	-15 67 - <b>32</b> 6
6	8	18 1	106 132	96 114	-106	35 -43			7 56 7	119 105 88	130 116 93	-34 -17 -85	125 115 -78			589	94 86 114	77 87 110	-65 68 -11	-41 54 -109	8	6	9 10 12	71 86 99	71 89 82	37 83 25	-60 -32 -78
		2 567	237 153 430	204 196 483 1	-28 -95 11	2027			11 12 13	84 94 102	8788	56 79 -94 6	39928			10 11 12	108 103 95	115 100 91	-17 98 -88	20 22	9	Q	16 20	98 102	99 100	30 1	94 100
		8 9 10	140 76 227	150 150 75 222	-138 -26 -10	57 -70 22	7	3	15 0	89 119	88 114	-79 114	- <b>3</b> 9	7	13	234	59 102 112	59 96 114	-52 -96 -109	27 -3 -33	0	0	1 2 4	123 59 233	107 107 45 226	87 87 31 225	65 8 2 1 8 6
ć	10	11 18	118 141	118 140	-76 -18	-138 -138			123	113 118 122	117 116 119	63 2 75 T	-99 116 92			5679	114 109 108	110 106 113	578726	-95.86			5600	96 86 117	92 79 106	52 27 -106	76 74 6
0	10	234	105 361 155 95	1257	-578 -95 -49	-01 20 -97 -74			<b>7</b> 567	ይ. ይ. ይ. <u>የ</u>	888 8	-77 -86 -47 -61	0 -50 -33	7	15	9 3	95 100	-112 98 92	-78 -89	-72 59 25			12 14 16	177 79 121	191 75 127	- 191 -21 -127	-70 -72 -10
		6790	70 109 78	70 110 71	-62 -57 -카	84 - 84 - 84 - 84 - 84 - 84 - 84 - 84 -			8 9 10	108 140 127	110 148 137	110 46 13	-141 136			4 56	112 109 109	121 113 93	94 6 -1	76 -113 93	8	10	347	127 248 70	114 237	94 11	65 -256
		10 11 12 13	87 93 105	96 94 113	-76 -74	5 87 84	7	5	1 2	84 111	62 94	10 -50	51 80	7	17	0 1 2	124 114 98	137 121 82	-137 98 -44	0 -70 -69			8 9 10	204 117 83	230	68 74	-230 -101 -37
_		14 16	192 95	191 83	190 30	11 77			345	136 127 122	127 124 108	-121 -124 79	-90-75	8	С	460	284 75	<b>2</b> 0 20 20 20 20 20 20 20 20 20 20 20 20 20	320 30	11 76	8	12	12 0	83 281	57 257	2 257	-57 0
¢	12	1 2 5	114 118 209 149	111 181 178	-100 -52 -103	-47 173 -92			789	115 130 136	120 135 149	1052	-100 -61 -115			10 12 14	69 244 81	78 280 91	-17+ 14 -278 _4	-77 -77 -91			245	-150 -150 92	71 125 95	0,28 13 13 13 13 13 13 13 13 13 13 13 13 13	787475
		6 7 8	262 138 74	256 140 85	-21 -69 -59	255 122 58	7	7	10 0	99 60 71	106 49	98 -49	99 0 87	8	2	16 3	165 65	178 52	-177 41 28	-14 31	8	14	12 3	131 75	138 78	-137 67	-12 40
		11 12	120 83	105 127 81	-78 8 9 7 8	100 43			12174	72 105 158	52 74 99 147	-70 18 -99 130	-72 -7 69			6 8 10	79 740	72 791 92	-20 72 -10 89	-391 -25			5 7 8	1253 89 139	178 88 178 179	2553 °	-190 -70 -62 -133
6	14	123	89 25 28 25 28	85 217 172	71 -216 -121	-46 26 -122			56 7	161 137 122	165 140 121	276	-163 140 85			12 16 18	110 125 39	98 124 85	90 20 20 20 20	-90 113 1	8	16	9 0	87 129	93 118	54 118	-76 0
		4 9 10	91 95	51 103 112	-50 103	-59 43			9 15	998 99	90 61 79	-61 -61 78	10 10	8	4	20 0	582	122 526	( 526	0			4 5	3885	91 97 90	82 49	-28
													•			•					8	18	3 4	85 87	72 70	61 개	78 -63

## Table 5. Bond lengths and angles with standard deviations

Bond	Length (uncorrected)	Length (corrected for thermal vibration)	Bond angles (uncorrected)	
$\begin{array}{c} \mathrm{Nb-I_1}\\ \mathrm{Nb-I_2}\\ \mathrm{Nb-I_3}\\ \mathrm{Nb-I_5}\\ \mathrm{Nb-I_6}\\ \mathrm{Nb-Nb} \end{array}$	$\begin{array}{c} 2{\cdot}652\pm0{\cdot}007\ \text{\AA}\\ 2{\cdot}700\pm0{\cdot}007\\ 2{\cdot}728\pm0{\cdot}008\\ 2{\cdot}890\pm0{\cdot}007\\ 2{\cdot}753\pm0{\cdot}007\\ 2{\cdot}753\pm0{\cdot}007\\ 2{\cdot}899\pm0{\cdot}007\\ 3{\cdot}308\pm0{\cdot}009 \end{array}$	$\begin{array}{c} 2{\cdot}667\pm 0{\cdot}007 \ \text{\AA} \\ 2{\cdot}713\pm 0{\cdot}007 \\ 2{\cdot}739\pm 0{\cdot}007 \\ 2{\cdot}900\pm 0{\cdot}007 \\ 2{\cdot}900\pm 0{\cdot}007 \\ 2{\cdot}766\pm 0{\cdot}007 \\ 2{\cdot}911\pm 0{\cdot}007 \end{array}$	$\begin{array}{c} I_1-Nb-I_2\\ I_1-Nb-I_3\\ I_1-Nb-I_4\\ I_1-Nb-I_6\\ I_2-Nb-I_6\\ I_2-Nb-I_4\\ I_2-Nb-I_6\\ I_2-Nb-I_6\\ I_3-Nb-I_6\\ I_3-Nb-I_6\\ I_3-Nb-I_6\\ I_4-Nb-I_5\\ I_4-Nb-I_5\\ I_4-Nb-I_6\\ I_5-Nb-I_6\\ Nb-I_3-Nb\\ Nb-I_3-Nb\\ Nb-I_4-Nb\\ $	$\begin{array}{c} 169\cdot 3\pm 0\cdot 1^{\circ}\\ 95\cdot 4\pm 0\cdot 2\\ 87\cdot 9\pm 0\cdot 2\\ 91\cdot 6\pm 0\cdot 2\\ 87\cdot 9\pm 0\cdot 2\\ 91\cdot 6\pm 0\cdot 2\\ 87\cdot 9\pm 0\cdot 2\\ 87\cdot 4\pm 0\cdot 2\\ 87\cdot 4\pm 0\cdot 2\\ 87\cdot 4\pm 0\cdot 2\\ 84\cdot 3\pm 0\cdot 2\\ 86\cdot 3\pm 0\cdot 3\\ 105\cdot 7\pm 0\cdot 2\\ 168\cdot 4\pm 0\cdot 2\\ 167\cdot 9\pm 0\cdot 2\\ 82\cdot 2\pm 0\cdot 2\\ 85\cdot 7\pm 0\cdot 2\\ 74\cdot 6\pm 0\cdot 2\\ 74\cdot 6\pm 0\cdot 2\\ 74\cdot 0\pm 0\cdot 2\end{array}$

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

Intrachain	
$I_1 - I_3 = 3.980 \pm 0.008$	Å
$-1_4$ 3.852 $\pm$ 0.008	
$-1_5$ $3.877 \pm 0.008$	
$-I_6 \qquad 3.775 \pm 0.008$	
$-I_1'$ 3.774 $\pm$ 0.012	
$-AI_1$ $3.896 \pm 0.012$	
$I_{9}-I_{3}$ 3.965 + 0.008 A	Å
$-I_4^{\circ}$ 3.864 + 0.007	
$-I_5^*$ 3.888 + 0.008	
$-I_6 = 3.760 + 0.008$	
$-I_{0}'$ $3.760 + 0.012$	
$-\tilde{AI}_{2}$ $3.910 + 0.012$	
$I_3 - I_4$ 3.845 $\pm 0.010$ A	Å
$-I_5$ $4 \cdot 370 + 0 \cdot 009$	
$I_{4} - I_{6}$ 3.806 + 0.009 A	Å
$I_5 - I_6 = 3.846 \pm 0.010 A$	Į
Interchain	
$I_1 - BI_2$ $3.889 + 0.008$	ł
$I_{0}-BI_{0}$ 3.987 + 0.007	
$I_{-BI} = 3.079 \pm 0.007$	

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 $u(1)$	Along $I_3-I_5$ direction $u(2)$	Along $I_1 - I_2$ direction $u(3)$
$I_1$	0·170 Å	0·158 Å	0·110 Å
$I_2$	0.124	0.148	0.111
$I_3$	0.112	0.135	0.140
I <sub>4</sub>	0.127	0.116	0.127
$I_5$	0.139	0.095	0.180
$I_6$	0.133	0.155	0.157
Ňb	0.086	0.131	0.110

an (NbI4)2 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  $\pm 0.007$ ) for Nb–I<sub>3</sub> and Nb–I<sub>5</sub>; 2.90 and 2.91 Å (both  $\pm 0.007$ ) 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

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Atom	r	u(r)	$\varphi(r, a)$	$\varphi(r, b)$	$\varphi(r, c)$
I1	1	$0.084 \pm 0.007$ Å	$91 \cdot 2 \pm 2 \cdot 2^{\circ}$	$27.9 + 2.7^{\circ}$	$62 \cdot 1 + 2 \cdot 7^{\circ}$
	<b>2</b>	$0.167 \pm 0.006$	$37 \cdot 6 + 31 \cdot 2$	72.5 + 11.9	$122 \cdot 1 + 26 \cdot 1$
	3	$0{\cdot}176\pm0{\cdot}006$	$52 \cdot 4 \pm 31 \cdot 2$	$111 \cdot 1 + 10 \cdot 1$	$45 \cdot 1 \pm 23 \cdot 6$
$I_2$	1	$0.106 \pm 0.006$	$89.3 \pm 5.3$	73.8 + 6.3	16.2 + 6.5
-	<b>2</b>	$0.139 \pm 0.004$	$132 \cdot 2 \pm 9 \cdot 8$	$135 \cdot 1 + 9 \cdot 5$	77.6 + 7.4
	3	$0.166 \pm 0.006$	$137.7 \pm 9.8$	$49.6 \pm 9.3$	$100.3 \pm 4.2$
$I_3$	1	$0.161 \pm 0.009$	90.0	97.6 + 6.5	7.6 + 6.5
-	<b>2</b>	$0.117 \pm 0.010$	180.0	90.0	90.0
	3	$0.109 \pm 0.010$	90.0	$7.6 \pm 6.5$	$82.4 \pm 6.5$
$\mathbf{I_4}$ .	1	$0.102 \pm 0.012$	90.0	110.0 + 11.9	20.0 + 11.9
	<b>2</b>	$0.127 \pm 0.009$	180.0	90.0	90.0
	3	$0.138\pm0.007$	90.0	$20.0 \pm 11.9$	$70.0 \pm 11.9$
$I_5$	1	$0.181 \pm 0.008$	90.0	60.3 + 4.1	29.7 + 4.1
	<b>2</b>	$0.139 \pm 0.010$	180.0	90.0	90.0
	3	$0.094 \pm 0.011$	90.0	$29.7 \pm 4.1$	$119.7 \pm 4.1$
$I_6$	1	$0.182 \pm 0.009$	90.0	$99.9 \pm 6.5$	$9.9 \pm 6.5$
	<b>2</b>	$0.133 \pm 0.010$	180.0	90.0	90.0
	3	$0.124 \pm 0.008$	90.0	$9.9 \pm 6.5$	$80.1 \pm 6.5$
Nb	1	$0.135 \pm 0.004$	$92 \cdot 2 \pm 10 \cdot 6$	$14.3 \pm 6.5$	$104 \cdot 1 + 6 \cdot 4$
	<b>2</b>	$0.106 \pm 0.005$	$84 \cdot 1 \pm 33 \cdot 3$	$103.8 \pm 7.0$	$164.9 \pm 12.3$
	3	$0.086 \pm 0.018$	$6\cdot 3\pm 30\cdot 7$	$86 \cdot 5 \pm 11 \cdot 9$	84.8 + 32.9



Fig. 2. [100] 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 unocucpied. 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  $3\cdot31$  Å is the longest distance known which definitely involves a pairing of electrons. Much shorter Nb-Nb bonds are found in the ion [Nb<sub>6</sub>Cl<sub>12</sub>]<sup>2+</sup> (2\cdot85 Å) (Vaughan *et al.*, 1950) and in niobium metal (2·86 Å) (Sutton, 1958). Since all the niobium atoms in  $\alpha$ -NbI<sub>4</sub> have identical environments, it can be



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



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  $\alpha$ -NbL<sub>4</sub> 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,  $(NbI_4)_2$ , (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**

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.

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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

### (Received 18 January 1962 and in revised form 15 March 1962)

 $\alpha$ -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

$$a = 8 \cdot 84 \pm 0.03, \ b = 5 \cdot 10 \pm 0.02, \ c = 9 \cdot 69 \pm 0.03 \text{ Å};$$
  
$$\beta = 98 \cdot 25 \pm 0.25^{\circ}.$$

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.