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Structure Refinement of *H*-Nb_2O_5

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The crystal structure of the high-temperature modification of Nb_2O_5 (*H*-Nb_2O_5) was refined by the least-squares method based on 10140 observed intensities. The crystal data are $a=21{\cdot}153$ (7), $b=3{\cdot}8233$ (5), $c=19{\cdot}356$ (5) Å, $\beta=119{\cdot}80$ (2)°, $Z=14$, $D_x=4{\cdot}548$ g cm^{-3}. The results agree generally with those of the previous structure determination except for the position of one tetrahedrally coordinated Nb atom, which is distributed equally over 2(*i*) $0,\pm y,0$ of $P2/m$ with $y=0{\cdot}2285$ (3). The final R is 0·052. *H*-Nb_2O_5 crystallizes in the space group $P2/m$ instead of $P2$ which was assumed in the earlier work.

Introduction

H-Nb_2O_5 was first described by Brauer (1941) as the high-temperature modification of niobium pentoxide. Gatehouse & Wadsley (1964) determined its crystal structure by means of Patterson and difference syntheses using *h*0*l*, *h*1*l* and *h*2*l* intensities recorded on integrated Weissenberg photographs taken with Cu $K\alpha$ radiation; their final R was 0·118. With respect to the space group symmetry, they examined both $P2$ and $P2/m$ and chose the former. The difference between the two consists solely in the position of one tetrahedrally coordinated Nb atom. While in $P2/m$ this Nb atom must be distributed equally over two equivalent positions, in $P2$ it can occupy a definite position 1(*a*). The arrangement of the other atoms conforms to the symmetry of $P2/m$. In order to shed light on the details of the structure including the question of the space-group assignment, a least-squares refinement based on a large number of observed intensities has been carried out.

Experimental

The single-crystal samples of *H*-Nb_2O_5 were taken from the product of a crystal-growth experiment, according to Bridgman's method, performed in air using the spec-pure grade Nb_2O_5 powder of Johnson and Matthey Co. as raw material. For the X-ray measurements, which were carried out at room temperature, a spherical specimen of radius 0·171 mm was made.

The unit-cell dimensions were obtained by the least-squares method based on 2θ angles measured on a four-circle diffractometer (Rigaku) using monochromated Mo $K\alpha$ radiation ($\lambda=0{\cdot}70926$ Å). The intensities were collected on the same diffractometer. In the range of $2\theta\le 90°$, 24945 reflexions were measured of which 19278 were greater than zero. The observed intensities were reduced to a set of 10140 independent non-zero reflexions by averaging the equivalent ones, and then corrected for absorption ($\mu=56{\cdot}3$ cm^{-1}). The zero reflexions were not used for further calculations.

Structure refinement

The structure was refined by the full-matrix least-squares method with *ORFLS* (Busing, Martin & Levy, 1962). The temperature factors of the Nb atoms were assumed to be anisotropic and the extinction correction of Zachariasen (1968) was applied. The following simplified formula with $\bar{g}$ as one of the parameters to be refined was used:

$$F_o=sF_c[1+\bar{g}(\bar{T}/\sin 2\theta)\,(1+\cos^4 2\theta)\times(1+\cos^2 2\theta)^{-1}F_c^2]^{-1/4}.$$

The mean path length $\bar{T}$ weighted with the absorption term was calculated in advance as a function of $\sin\theta$ and given in the form of a table; $\bar{T}$ ranged from 0·139 to 0·229 mm. The partial polarization of the incident X-rays through the monochromator was neglected. As the capacity of the computer (FACOM 270-20) did not permit all the free parameters to be varied simultaneously, the atomic coordinates and the thermal parameters were refined alternately in separate least-squares cycles. The atomic scattering factors were taken from Hanson, Herman, Lea & Skillman (1964).

The space group was first assumed to be $P2/m$. The refinement was started with the atomic coordinates of Gatehouse & Wadsley (1964) except for those of Nb(1) which had been distributed equally over 2(i) of $P2/m$. After convergence of the least-squares refinement, the atomic coordinates and thermal parameters listed in Table 1 were obtained. The final value of the conventional R was 0·052 and $\bar{g}$ was $0{\cdot}94\times10^{-6}$. Since all the atoms but Nb(1) were confined to the mirror planes at $y=0$ and $\frac{1}{2}$ throughout the refinement cycles by the assumption of the $P2/m$ symmetry, the thermal parameter β_{22} or B of any atom whose y was in fact not exactly equal or at least not very close to those values was expected to become anomalously large to compensate for any forbidden positional shift. Examination of the thermal parameters shown in Table 1 from this point of view indicates that most of the atoms lie on the mirror planes of $P2/m$. For the large β_{22} values of Nb(2), Nb(7) and Nb(15), an equal distribution of each atom over a pair of equivalent positions on both sides of the mirror plane is one of the most probable interpretations if the symmetry of $P2/m$ is postulated. The same interpretation seems to be valid for the large B's of some O atoms. Another possible interpretation will be discussed later.

Table 1. *Atomic coordinates and thermal parameters*

The anisotropic temperature factor is expressed as
$\exp[-(10^{-5}h^2\beta_{11}+10^{-4}k^2\beta_{22}+10^{-5}l^2\beta_{33}+2\,.\,10^{-5}hl\beta_{13})]$.

	Position	10^5x	10^4y	10^5z
Nb(1)*	2(i)	0	2285 (3)	0
Nb(2)	1(g)	50000	0	50000
Nb(3)	2(m)	16430 (3)	0	353 (3)
Nb(4)	2(m)	23623 (3)	0	23134 (3)
Nb(5)	2(m)	30284 (3)	0	45456 (3)
Nb(6)	2(m)	36087 (3)	0	4553 (3)
Nb(7)	2(m)	43325 (3)	0	27741 (4)
Nb(8)	2(m)	56270 (3)	0	9346 (3)
Nb(9)	2(m)	62943 (3)	0	32219 (3)
Nb(10)	2(n)	9353 (3)	5000	20187 (3)
Nb(11)	2(n)	15921 (3)	5000	42410 (3)
Nb(12)	2(n)	70330 (3)	5000	12414 (3)
Nb(13)	2(n)	77056 (3)	5000	35141 (3)
Nb(14)	2(n)	89895 (3)	5000	16353 (3)
Nb(15)	2(n)	96461 (3)	5000	38928 (4)

		10^4x	$10y$	10^4z	10^2B
O(1)	1(f)	0	5	5000	116 (10)
O(2)	1(h)	5000	5	5000	126 (11)
O(3)	2(m)	1180 (2)	0	2012 (2)	56 (5)
O(4)	2(m)	1867 (2)	0	4314 (2)	45 (5)
O(5)	2(m)	1931 (2)	0	1067 (3)	70 (6)
O(6)	2(m)	2639 (2)	0	3395 (3)	75 (6)
O(7)	2(m)	2619 (2)	0	139 (3)	73 (6)
O(8)	2(m)	3257 (3)	0	2417 (3)	92 (6)
O(9)	2(m)	3971 (3)	0	4790 (3)	93 (6)
O(10)	2(m)	4032 (2)	0	1497 (3)	74 (6)
O(11)	2(m)	4624 (3)	0	3833 (3)	107 (7)
O(12)	2(m)	4611 (2)	0	382 (2)	40 (5)
O(13)	2(m)	5344 (2)	0	2954 (3)	85 (6)
O(14)	2(m)	5898 (2)	0	1959 (2)	63 (5)
O(15)	2(m)	6701 (2)	0	4306 (2)	65 (6)
O(16)	2(m)	6707 (2)	0	961 (2)	36 (5)
O(17)	2(m)	7411 (2)	0	3357 (2)	46 (5)
O(18)	2(m)	8858 (2)	0	1341 (2)	49 (5)
O(19)	2(m)	9412 (2)	0	303 (2)	68 (6)
O(20)	2(m)	9638 (3)	0	3798 (3)	97 (6)
O(21)	2(n)	608 (2)	5	837 (3)	91 (6)
O(22)	2(n)	668 (2)	5	4051 (3)	89 (7)
O(23)	2(n)	1327 (2)	5	3122 (2)	67 (6)
O(24)	2(n)	2062 (2)	5	2184 (2)	45 (5)
O(25)	2(n)	2764 (2)	5	4504 (2)	44 (5)
O(26)	2(n)	3551 (2)	5	113 (2)	44 (5)
O(27)	2(n)	4275 (3)	5	2616 (3)	87 (6)
O(28)	2(n)	5855 (2)	5	884 (2)	44 (5)
O(29)	2(n)	6535 (2)	5	3176 (2)	39 (5)
O(30)	2(n)	7263 (2)	5	2257 (3)	69 (6)
O(31)	2(n)	7987 (2)	5	4577 (3)	78 (6)
O(32)	2(n)	7917 (2)	5	1318 (3)	73 (6)
O(33)	2(n)	8613 (3)	5	3614 (3)	95 (7)
O(34)	2(n)	8474 (2)	5	283 (2)	46 (5)
O(35)	2(n)	9280 (2)	5	2664 (3)	83 (6)
O(36)	2(n)	−29 (2)	5	1762 (3)	72 (6)

Table 1 (*cont.*)

	β_{11}	β_{22}	β_{33}	β_{13}
Nb(1)	37 (2)	257 (7)	52 (2)	25 (2)
Nb(2)	48 (2)	469 (8)	77 (2)	30 (2)
Nb(3)	42 (1)	105 (2)	40 (1)	19 (1)
Nb(4)	31 (1)	96 (3)	60 (1)	20 (1)
Nb(5)	37 (1)	88 (3)	79 (1)	30 (1)
Nb(6)	39 (1)	68 (2)	40 (1)	20 (1)
Nb(7)	43 (1)	471 (5)	52 (1)	23 (1)
Nb(8)	31 (1)	68 (2)	38 (1)	16 (1)
Nb(9)	37 (1)	80 (2)	55 (1)	25 (1)
Nb(10)	38 (1)	114 (3)	63 (1)	28 (1)
Nb(11)	36 (1)	85 (3)	77 (1)	29 (1)
Nb(12)	30 (1)	69 (2)	39 (1)	15 (1)
Nb(13)	33 (1)	86 (2)	52 (1)	19 (1)
Nb(14)	38 (1)	101 (3)	37 (1)	17 (1)
Nb(15)	47 (1)	541 (5)	55 (1)	27 (1)

* Occupancy parameter 0·5.

To examine the possibility of the other space group, the structure was further refined with the constraints of $P2$ symmetry. The x and z coordinates as well as the thermal parameters were changed only very slightly from their initial values taken from Table 1. The y of Nb(1) to which a definite position 1(a) had been assigned became 0·2277 (4). No attempt was made to vary the y's of the other atoms because their initial values were already good approximations and no successful refinement could be anticipated. R was 0·061 at the beginning and became 0·057 after convergence of the refinement; the latter value is still greater than that (0·052) obtained for the model with Nb(1) distributed equally over two equivalent positions.

Finally a three-dimensional F_o-F_c synthesis was carried out using each set of atomic parameters obtained by the least-squares method. For the structure in $P2/m$ the electron-density difference was within the range -7 to 5 e Å^{-3}. For the model according to $P2$, on the other hand, a distinct maximum of 21 e Å^{-3} was found at (0,0,0·7), while a broad minimum of -12 e Å^{-3} appeared in the position postulated for

Nb(1). This indicates that Nb(1) must be distributed over those two positions since the arrangement of the other atoms substantially conforms to the symmetry of *P*2/*m*.*

Discussion

Since the least-squares refinement and the subsequent difference syntheses support *P*2/*m* rather than *P*2, the former should be assigned to H-Nb_2O_5 or at least to the present sample of H-Nb_2O_5. As revealed during the refinement procedure, Nb(1) seems to be distributed over two positions even if the space group *P*2 is assumed. The question of the space group assignment really concerns the way in which the atoms, especially Nb(2), Nb(7) and Nb(15), are arranged in or over the mirror planes of *P*2/*m* rather than the location of only one atom Nb(1). It seems unlikely, though it cannot be denied absolutely, that only these three atoms are so arranged as to lower the *P*2/*m* symmetry, whereas the arrangement of the other Nb atoms conforms exactly to this symmetry as shown by the least-squares refinement. The disordered distribution of these Nb atoms might probably be realized, as is generally assumed in such cases, by the domain structure in which each domain has an ordered structure in itself and a small enough size compared with the so-called mosaic crystallite.

While the coordination octahedra of the other Nb atoms have at least two shared edges, those of Nb(2), Nb(7) and Nb(15) are connected to neighbouring octahedra only by corner sharing and form infinite straight chains parallel to **b**. It is thus also possible to consider their large β_{22}'s as being due to their thermal motions which may be somewhat different from those of the other Nb atoms.

Fig. 1 shows the projection of the structure along **b**. The interatomic distances were calculated by means of *ORFFE* (Busing, Martin & Levy, 1964) and are summarized in Tables 2 and 3. Each Nb atom except for Nb(1) is surrounded octahedrally by six, and Nb(1) tetrahedrally by four O atoms. The distance between O atoms forming an unshared edge of an octahedron ranges from 2·706 (6) to 3·152 (6); the mean distance is 2·845 Å. The minimum, maximum and mean lengths of the shared edges of the octahedra are 2·562 (4), 2·707 (6) and 2·611 Å respectively. The range of O–O distances is much narrower than that reported by Gatehouse & Wadsley. The distance between two Nb atoms whose coordination octahedra are joined by a common corner varies from 3·773 (1) to 3·957 (2); the mean is 3·833 Å. The Nb–Nb distances between two edge-shared octahedra are within the limits of 3·254 (1) and 3·765 (2); the mean is 3·424 Å. The distances from Nb(1) to the next Nb neighbours, 3·551 (1) and 3·546 (1) Å, lie between the two kinds of Nb–Nb distances mentioned above. The bond angles at Nb(1) range from 105·4 (2) to 123·2 (2)°. Throughout the paper, estimated

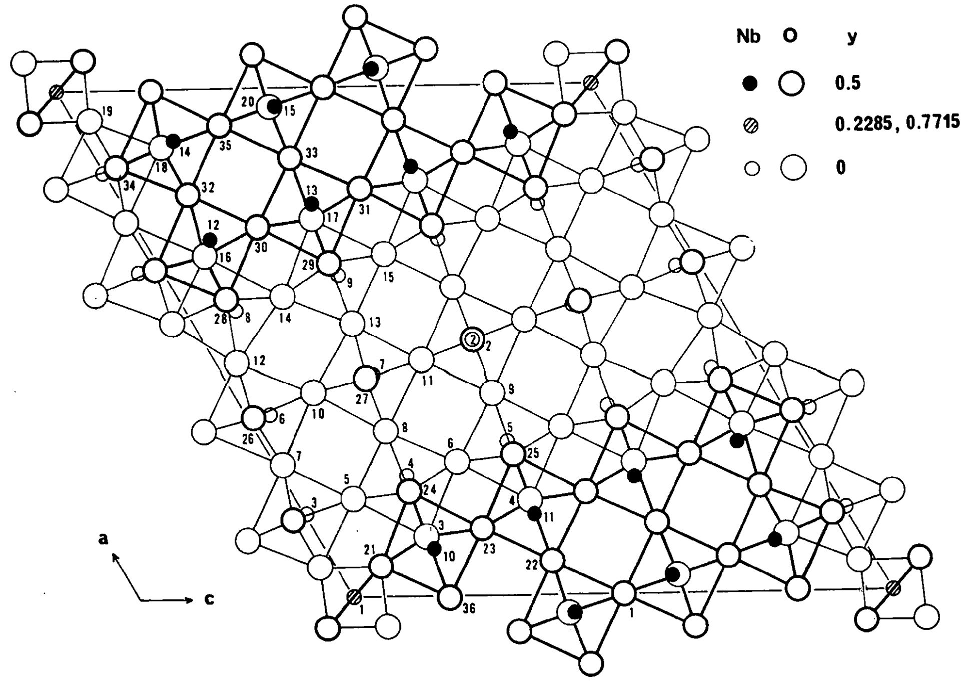

Fig. 1. Projection of the structure along **b**. Atoms are denoted by numbers only.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31270 (52 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Nb–O *interatomic distances* (Å)

Nb atom	Surrounding oxygens and distances to them				Mean Nb–O distance
Nb(1)	O(19$^{\mathrm{iv}}$)	1·838 (5)	O(19$^{\mathrm{ii}}$)	1·838 (5)	1·826
	O(21)	1·813 (4)	O(21$^{\mathrm{viii}}$)	1·813 (4)	
Nb(2)	O(2)	1·9116 (2)	O(2$^{\mathrm{ii}}$)	1·9116 (2)	1·968
	O(9)	2·005 (5)	O(9$^{\mathrm{v}}$)	2·005 (5)	
	O(11)	1·986 (5)	O(11$^{\mathrm{v}}$)	1·986 (5)	
Nb(3)	O(5)	1·775 (4)	O(7)	1·973 (5)	2·006
	O(18$^{\mathrm{iv}}$)	2·327 (3)	O(19$^{\mathrm{iv}}$)	1·989 (6)	
	O(34$^{\mathrm{iii}}$)	1·986 (1)	O(34$^{\mathrm{iv}}$)	1·986 (1)	
Nb(4)	O(3)	2·267 (4)	O(5)	2·112 (4)	2·006
	O(6)	1·872 (4)	O(8)	1·801 (5)	
	O(24)	1·991 (1)	O(24$^{\mathrm{ii}}$)	1·991 (1)	
Nb(5)	O(4)	2·269 (4)	O(6)	1·954 (4)	1·999
	O(9)	1·807 (5)	O(15$^{\mathrm{v}}$)	2·001 (3)	
	O(25)	1·982 (1)	O(25$^{\mathrm{ii}}$)	1·982 (1)	
Nb(6)	O(7)	1·866 (5)	O(10)	1·753 (4)	2·051
	O(12)	2·194 (4)	O(16$^{\mathrm{iv}}$)	2·479 (3)	
	O(26)	2·007 (1)	O(26$^{\mathrm{ii}}$)	2·007 (1)	
Nb(7)	O(8)	2·023 (5)	O(10)	2·226 (4)	1·987
	O(11)	1·824 (5)	O(13)	1·991 (5)	
	O(27)	1·930 (1)	O(27$^{\mathrm{ii}}$)	1·930 (1)	
Nb(8)	O(12)	1·865 (4)	O(12$^{\mathrm{iv}}$)	2·340 (3)	2·034
	O(14)	1·769 (4)	O(16)	2·258 (4)	
	O(28)	1·986 (1)	O(28$^{\mathrm{ii}}$)	1·986 (1)	
Nb(9)	O(13)	1·808 (5)	O(14)	2·154 (4)	2·003
	O(15)	1·830 (4)	O(17)	2·243 (4)	
	O(29)	1·992 (1)	O(29$^{\mathrm{ii}}$)	1·992 (1)	
Nb(10)	O(3)	1·983 (1)	O(3$^{\mathrm{i}}$)	1·983 (1)	1·992
	O(21)	2·034 (5)	O(23)	1·868 (4)	
	O(24)	2·242 (4)	O(36)	1·843 (5)	
Nb(11)	O(4)	1·982 (1)	O(4$^{\mathrm{i}}$)	1·982 (1)	1·997
	O(22)	1·801 (5)	O(23)	1·949 (4)	
	O(25)	2·269 (4)	O(31$^{\mathrm{v}}$)	2·000 (5)	
Nb(12)	O(16)	2·013 (1)	O(16$^{\mathrm{i}}$)	2·013 (1)	2·018
	O(26$^{\mathrm{iv}}$)	2·276 (4)	O(28)	2·230 (4)	
	O(30)	1·774 (4)	O(32)	1·801 (4)	
Nb(13)	O(17)	1·987 (1)	O(17$^{\mathrm{i}}$)	1·987 (1)	1·999
	O(29)	2·225 (4)	O(30)	2·130 (4)	
	O(31)	1·836 (4)	O(33)	1·831 (5)	
Nb(14)	O(18)	1·974 (1)	O(18$^{\mathrm{i}}$)	1·974 (1)	2·000
	O(32)	2·034 (4)	O(34)	2·281 (4)	
	O(35)	1·769 (4)	O(36$^{\mathrm{vi}}$)	1·966 (5)	
Nb(15)	O(1$^{\mathrm{v}}$)	1·887 (1)	O(20)	1·920 (1)	1·972
	O(20$^{\mathrm{i}}$)	1·920 (1)	O(22$^{\mathrm{vi}}$)	2·027 (5)	
	O(33)	1·974 (5)	O(35)	2·103 (4)	

Symmetry code

(i) $x, 1+y, z$; (ii) $x, -1+y, z$
(iii) $1-x, -1+y, -z$; (iv) $1-x, y, -z$
(v) $1-x, y, 1-z$; (vi) $1+x, y, z$
(vii) $-1+x, y, z$; (viii) $-x, y, -z$

Table 3. O–O *distances* (Å) *within each coordination polyhedron*

Central atom	Minimum	Maximum	Mean
Nb(1)	2·904 (4)	3·235 (10)	2·976
Nb(2)	2·757 (4)	2·839 (6)	2·783
Nb(3)	2·742 (4)	3·014 (6)	2·807
Nb(4)	2·574 (4)	3·019 (5)	2·811
Nb(5)	2·588 (4)	3·014 (5)	2·805
Nb(6)	2·674 (3)	3·097 (6)	2·843
Nb(7)	2·740 (4)	2·960 (6)	2·801
Nb(8)	2·579 (4)	3·152 (6)	2·829
Nb(9)	2·562 (4)	3·017 (5)	2·809
Nb(10)	2·574 (4)	3·033 (5)	2·796
Nb(11)	2·588 (4)	3·010 (5)	2·801
Nb(12)	2·579 (4)	2·989 (5)	2·803
Nb(13)	2·562 (4)	3·018 (5)	2·801
Nb(14)	2·618 (4)	3·036 (6)	2·803
Nb(15)	2·718 (4)	2·827 (6)	2·784

standard deviations are given in parentheses in units of the last quoted decimal place.

Apart from the space group assignment and the details of the structure, the results of the present work generally agree well with those of Gatehouse & Wadsley.

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