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The Crystal Structure of Cubic Hydrogen Tungsten Bronze

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The structure of $D_{0.53}WO_3$ has been determined by a room temperature powder neutron diffraction study. The unit cell is body centered cubic ($Im3$) and contains 8 formula weights ($a = 7.562 \pm 0.002$ Å). The average cell content was refined by a least squares method based on peak intensities. The tungsten atoms lie on the special sites of the perovskite structure and are surrounded by nearly regular octahedrons of oxygen atoms with the latter displaced from the normal perovskite positions along $\langle 110 \rangle$. The deuterium atoms constitute statistically distributed –OD bonds which are directed towards the nearest oxygen atom of a neighboring octahedron. The analogous hydrogen compound is best described as a nonstoichiometric oxide hydroxide $WO_{3-x}(OH)_x$ based on a distorted ReO_3 structure. The crystal structure is closely related to that of $In(OH)_3$ and $Sc(OH)_3$.

Introduction

The hydrogen tungsten bronzes are nonstoichiometric compounds of general formula H_xWO_3 and have been characterized in the range $0 < x < 0.6$. Their classification as bronzes is based on both electronic and structural resemblances to the sodium tungsten bronzes Na_xWO_3 $(0 < x < 1)$. Thus they exhibit metallic conductivity and weak temperature independent paramagnetism characteristic of a delocalized conduction electron band structure (*1*) and also show a similar structural progression from monoclinically distorted WO_3 to the cubic ReO_3 structure at high x values (*2*, *3*). Structurally the compounds are of interest since the nature and position of the hydrogen atoms in the lattice have not been determined.

Powder X-ray photographs showed strong lines characteristic of a simple perovskite structure but also revealed additional very weak lines which could be indexed on a cubic unit cell having double the lattice constant of this structure. Such "superlattice" reflections were more clearly shown in single crystal X-ray photographs and corresponded to a distortion of the host WO_3 framework from the ideal ReO_3 structure (*4*). A similar superstructure has been reported for the cubic sodium tungsten bronze phase (*5*). In order to deduce the hydrogen positions and also the nature of this distortion, a neutron diffraction study was made of the cubic phase. Owing to the difficulty of preparing sufficiently large single crystals, the measurements were made on powdered samples and the deuterium analogue was used in order to reduce the amount of incoherent scattering.

Sample Preparation and Analysis

Crystalline WO_3 (*6*) was refluxed with concentrated DCl in D_2O (supplied by CiBA) and zinc turnings (Analar B.D.H.) in an oxygen and water free glove box until the product was golden brown and homogeneous. The bronze was washed with D_2O and then sealed off under vacuum.

The sample was analyzed by decomposing it in vacuum where the following reaction occurs

$$D_xWO_3 \rightarrow WO_{3-y} + yD_2O + \left(\frac{x}{2} - y\right) D_2.$$

The volume of deuterium evolved was measured and the composition of the reduced tungsten oxide determined by oxidation to WO_3 on a Cahn microbalance. An x value was obtained of 0.53 ± 0.01.

A Debye–Scherrer X-ray photograph revealed a pure cubic phase of lattice constant (subcell) $a = 3.781 \pm 0.001$ Å.

Neutron Diffraction

Neutron Bragg intensities were measured at room temperature on a powder diffractometer at the reactor "Pluto", A.E.R.E. Harwell. The sample was sealed under vacuum in a quartz tube and an angular range from 5 to 90° was scanned. A neutron wavelength of 1.105 Å was obtained from the (311) planes of a copper monochromator with a takeoff angle of 60°. Absorption errors were computed to be negligible.

All the reflections observed could be indexed on a cubic unit cell of lattice constant $2a$ subject to a systematic absence when $h + k + 1 = 2n + 1$. The "superlattice" reflections were in certain cases stronger than the subcell reflections. Trial and error calculations showed that the intensity variation observed could only be accounted for by both oxygen atom displacements, represented by the special positions 24(g) of the space group $Im3$, and large deuterium atom displacements from the perovskite A interstitial sites. As $Im3$ belongs to the lower ($m3$) Laue group of the cubic class, most of the single peaks observed consisted of two or more completely superimposed reflections from independent planes in the crystal. In order to utilize all the data in refining the atomic positions, a full matrix least squares program was written in the FORTRAN language suitable for refining powder X-ray or neutron data of this type for any space group. This program minimizes the function

$$\sum_i w_i(I_{\text{obs}_i} - I_{\text{calc}_i})^2$$

The 15 strongest intensities observed were chosen for refinement and w_i was taken as $1/\sigma_i^2$ where σ_i is the standard deviation of the ith intensity as estimated from counting statistics. The neutron scattering lengths used were $b_D = 0.621 \times 10^{-12}$ cm, $b_W = 0.466 \times 10^{-12}$ cm, $b_O = 0.577 \times 10^{-12}$ cm (7).

Refinements

All the atoms were placed initially at the perovskite special positions and assigned unit isotropic temperature factors. An R_I index, $[100 \sum_i (I_{\text{obs}_i} - I_{\text{calc}_i})]/\sum_i I_{\text{obs}_i}$, of 74% resulted.

The oxygen atoms were next displaced along $\langle 110 \rangle$ as given by the positions 24(g) $(0,y,z)$ of $Im3$ with $y + z$ constrained to equal 0.5, thus effecting the tilting of WO_6 octahedrons. An effect of this distortion is to replace the 8 equivalent A sites of the original perovskite structure by 2 sites $(000, \frac{1}{2}\frac{1}{2}\frac{1}{2})$ around which the 12 neighboring oxygen atoms have been displaced outwards and 6 sites for which the local environment is provided by 4 oxygen atoms which have been displaced inwards along the diagonals of a square with the interstitial site as center. Figure 1 shows the eight octahedrons around the $(00\frac{1}{2})$ position. When the deuterium atoms were assigned to these 6 sites, an R_I index of 29.5% was obtained.

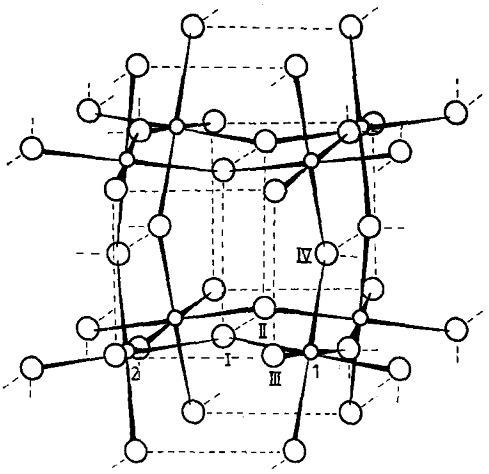

FIG. 1. The eight WO_6 octahedrons surrounding $(0,0,\frac{1}{2})$ in $D_{0.53}WO_3$: (large circles) oxygen atoms; (small circles) tungsten atoms.

The deuterium atoms were next allowed to occupy statistically 8 sites within each square array of four oxygen atoms as shown in Fig. 2. The 48 deuterium positions in the unit cell are strictly described by $24m$ D in $(0,y_1,z_1)$ and $24n$ D in $(0,y_2,z_2)$ where m and n are the occupation numbers for the two sets of positions. As the distortion found is small and in order to reduce

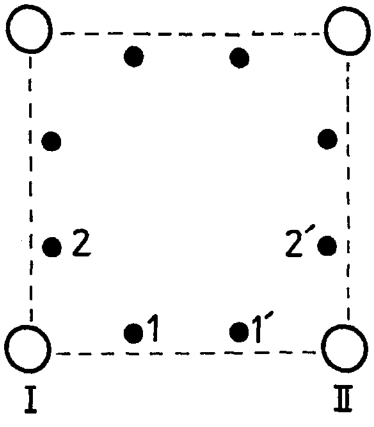

FIG. 2. The average deuterium atom distribution in $D_{0.53}WO_3$: (large circles) oxygen atoms; (small filled circles) deuterium atoms.

TABLE I

OBSERVED AND CALCULATED INTENSITIES FOR $D_{0.53}WO_3$

$h\,k\,l$	I_{calc}	I_{obs}	$\sigma(I_{obs})$
2 0 0	20.35	20.09	0.23
3 1 0 1 3 0	14.43	14.36	0.21
2 2 2	8.56	8.55	0.20
3 2 1 2 3 1	11.10	11.26	0.20
4 0 0	22.90	23.29	0.23
4 2 0 2 4 0	19.70	19.60	0.22
4 3 1 3 4 1 5 1 0 1 5 0	5.03	4.54	0.17
5 1 2 1 5 2	2.80	2.97	0.16
4 4 0	12.88	12.82	0.30
4 3 3 5 3 0 3 5 0	10.02	10.48	0.40
4 4 2 6 0 0	8.86	8.85	0.77
5 3 2 3 5 2 6 1 1	11.89	12.20	0.32
4 4 4	3.71	3.56	0.70
5 4 3 4 5 3 5 5 0 7 1 0 1 7 0	10.01	9.96	0.28
6 3 3 5 5 2 7 2 1 2 7 1	6.97	6.81	0.18

the number of variable parameters all 48 sites were assumed to be equivalent and for $D_{0.53}WO_3$ are described by 2.12D in $(0,y,z)$ and 2.12D in $(0,0.5-z,0.5-y)$. Refinement of the scale factor, three positional parameters, and three isotropic temperature factors converged to give an R_I index of 1.69%. An agreement factor, $\{[\sum_i w_i(I_{obsi} - I_{calc})]/(m-n)\}^{1/2}$, where m = number of observations (*15*), and n = number of parameters (*7*), of 1.49 resulted. The agreement between observed and calculated intensities is given in Table I, and the positional and thermal parameters, together with their estimated standard deviations, are given in Table II. The structural parameters obtained are compatible with the weakness of the reflections not included in the refinement. Further relaxation of the constraints applied to the deuterium and oxygen positions did not produce any significant improvement in the agreement or changes to the values quoted.

Discussion

Some important bond angles and distances in the structure are given in Table III. It must be emphasized that for a defect compound such values refer to the contents of the average unit cell of the crystal.

The tungsten atoms are arranged on a primitive cubic lattice and are surrounded by almost regular octahedrons of oxygen atoms linked together by corner sharing. The octahedrons are tilted 11° from the -W-W- direction producing an O-O distance between adjacent octahedrons of 3.264 Å. The deuterium atoms are statistically attached to all the oxygen atoms as deuteroxyl bonds 1.10 Å long and displaced 11.8° off the line to the neighboring oxygen atom. The deviation from a normal O-H bond length of 1 Å may be significant since it is quite feasible that the oxygen atoms are relaxed from their average positions whenever a deuterium atom is attached. Thus the O-D and O-D-O distances must be regarded as upper limits to the actual values. This relaxation of the oxygen atoms cannot be

TABLE II

ATOMIC PARAMETERS FOR $D_{0.53}WO_3$[a]

Atom	Position	x	y	z	B (Å^2)	Atoms/ unit cell
D(1)	24(g)	0.0	0.073(5)	0.314(4)	5.0(1.0)	2.12
D(2)	24(g)	0.0	0.186(4)	0.427(5)	5.0(1.0)	2.12
O	24(g)	0.0	0.2158(4)	0.2842(4)	1.0(0.1)	24.0
W	8(c)	0.25	0.25	0.25	0.7(0.2)	8.0

[a] Estimated standard deviations in parentheses.

TABLE III

Bond distances (Å)		Bond angles (°)	
W1–W2	3.781(1)	OI–W1–OIII	89.0
W1–OI	1.926(1)	OI–W1–OIV	89.0
OI–OII	3.264(2)	OIII–W1–OIV	91.0
OI–OIII	2.698(1)	W1–W2–OI	11.0
OIII–OIV	2.748(1)	D1–OI–OII	11.8
OI–D1	1.10(1)	W1–OI–W2	158.1
D1–OII	2.20(1)	W1–OI–D1	99.1
D1–D1′	1.10(2)		
D1–D2	1.21(2)		
D1–D2′	2.34(1)		

large as the oxygen temperature factor is not abnormally high (*8*) and the actual O–D–O distance is almost certainly too large for hydrogen bonding to occur. With the limited data available a complete treatment of the thermal motion was not possible but the large isotropic temperature factor obtained for the deuterium atoms is most probably due to librational motion [c.f. $Ca(OH)_2$ (*9*)].

The crystal structure shows that the hydrogen tungsten bronze is an oxide hydroxide $WO_{3-x}(OH)_x$ with the tungsten atoms in an average oxidation state of $(6 - x)$. In the limiting case $x = 3$, a hydroxide $M(OH)_3$ would result and the hydrogen tungsten bronze structure reported here is indeed found for the trivalent hydroxides $In(OH)_3$ and $Sc(OH)_3$ (*10*, *11*). For In $(OH)_3$ the distortion of the ReO_3 type framework is much larger than found here, there being sufficient hydrogen atoms to hydrogen bond all the oxygen atoms present (O–D–O = 2.82 Å).

In the case of the hydrogen bronze there are 4.24 hydrogen atoms distributed among 48 positions in the unit cell. When averaged over the whole crystal these positions have equal fractional occupancy. The coherent neutron diffraction affords no direct information about the local distribution of hydrogen atoms among the available crystallographic sites but certain arrangements can be eliminated for purely chemical reasons since they would give rise to impossibly short interatomic distances. Thus two hydrogen atoms would not occupy adjacent sites 1 and 1′ (1.10 Å), nor be attached to the same oxygen atom as in arrangement 12(1.21 Å). In order to proceed further it is necessary to utilize experimental techniques which are sensitive to the local atom environments in crystals.

Structure investigations are at present in progress on the tetragonal (T_A) hydrogen bronze phase and also on the cubic lithium and sodium tungsten bronzes all of which show marked similarities to the cubic hydrogen bronze structure.

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