

## Location of Deuterium Sites in the Defect Pyrochlore DTaWO<sub>6</sub> from Neutron Powder Diffraction Data

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### Abstract

Time-of-flight neutron powder spectra were taken of the defect pyrochlore DTaWO<sub>6</sub> at 12 and 300 K on the high-resolution powder diffractometer at Argonne's ZING-P' pulsed neutron source. The powder data in the range  $0.52 \text{ \AA} \leq d \leq 2.42 \text{ \AA}$ , which represent 243 allowed Bragg reflections at both temperatures, were fit using a Rietveld-analysis code modified for time-of-flight data. From a difference Fourier synthesis of the 12 K powder data based solely on the positions of the refined metal and O positions, D was located in partially occupied 48(*f*) sites of space group  $Fd\bar{3}m$  ( $O_h^7$ , No. 227; origin at  $\bar{3}m$ ). Further Rietveld refinement of the 12 K [ $R_{F^2} = 8.08\%$ ,  $R_{wp} = 5.64\%$ ,  $a = 10.4269$  (1)  $\text{\AA}$ ] and 300 K [ $R_{F^2} = 8.32\%$ ,  $R_{wp} = 4.68\%$ ,  $a = 10.4281$  (1)  $\text{\AA}$ ] data indicated that the D sites are 1.024 (9)  $\text{\AA}$  at 300 K [1.021 (10)  $\text{\AA}$  at 12 K] from each O position. The D sites form spiral chains in interconnecting open channels along  $\langle 110 \rangle$  directions. The distance from a deuteron to its nearest-neighbor D site is 2.653 (2)  $\text{\AA}$  at 300 K [2.652 (2)  $\text{\AA}$  at 12 K]. These results are not inconsistent with a tunneling mechanism of deuteron transport between neighboring sites of these spiral chains.

### Introduction

Solids that possess defect-pyrochlore structures have shown promise as alkali-metal (Goodenough, Hong & Kafalas, 1976) and hydrogen (Butler & Biefeld, 1979; Biefeld, Butler & Azevedo, 1981) fast-ion conductors. The cubic ( $Fd\bar{3}m$ ; origin at  $\bar{3}m$ ) pyrochlore structure ( $A_2B_2X_6X'$ ), viewed down the  $[110]$  crystallographic direction, is shown in Fig. 1. This structure can be described as a framework of  $B_2X_6$  corner-shared

octahedra, with  $B$  ions in 16(*c*) positions and  $X$  ions occupying 48(*f*) positions, that form channels parallel to all  $\langle 110 \rangle$  directions in the crystal;  $A_2X'$  units of an interpenetrating subarray, with  $A$  and  $X'$  ions occupying 16(*d*) and 8(*b*) sites respectively, reside in these channels. Defect pyrochlores arise when the  $A_2X'$  subarray is removed and monovalent cations either occupy the 8(*b*) sites or partially occupy symmetry-related sites within the  $\langle 110 \rangle$  channels. The latter is indeed the situation in DTaWO<sub>6</sub> and, most probably, its proton analogue (see below).

Biefeld, Butler and Azevedo (Butler & Biefeld, 1979; Biefeld, Butler & Azevedo, 1981) have looked at HTaWO<sub>6</sub> and DTaWO<sub>6</sub> with pulsed <sup>1</sup>H NMR spectrometry as a function of temperature in an attempt to characterize the mode of proton (deuteron) conduction in these defect pyrochlores. The structural features associated with the TaWO<sub>6</sub> framework are well known from previous work on related defect pyrochlores (Hervieu, Michel & Raveau, 1971; Groult, Michel & Raveau, 1973), but the positions of H (D) were not known. In modeling the NMR relaxation data, the eight protons (deuterons) in the unit cell were assumed to

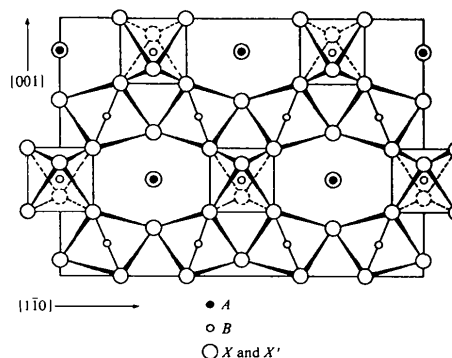


Fig. 1. The  $[110]$  projection of a typical cubic pyrochlore  $A_2B_2X_6X'$  showing the ( $B_2X_6$ ) skeleton of corner-shared octahedra and the  $A-X'-A$  channels parallel to  $[110]$  (after Goodenough, Hong & Kafalas, 1976).

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occupy randomly 48 of the 96(*g*) sites available, at a distance of  $\sim 1.0$  Å from the nearest 48(*f*) O position. From these NMR data, the site-to-site proton (deuteron) attempt frequency was found to be abnormally small ( $\sim 3 \times 10^{10} \text{ s}^{-1}$ ), as was the activation energy ( $\sim 0.3$  eV), which suggested that proton (deuteron) conduction occurs within these solids *via* a phonon-assisted tunneling mechanism. It was desired that the actual positions of the H (D) be located in HTaWO<sub>6</sub> and DTaWO<sub>6</sub> to verify this interpretation of the NMR data. However, single crystals of DTaWO<sub>6</sub> and HTaWO<sub>6</sub> have not been obtained to date, which has rendered the usual techniques of structure solution impossible.

In the present work, the structure of DTaWO<sub>6</sub>, including the location of D, has been elucidated from high-resolution time-of-flight neutron powder diffraction data by using a combination of Rietveld refinement and Fourier synthesis techniques. This method has been successful previously in locating D sites in deuterium  $\beta$ -alumina from neutron powder diffraction data (Tofield, Jacobson, England, Clarke & Thomas, 1979).

### Experimental

A powder sample of DTaWO<sub>6</sub> was prepared by ion exchange of KTaWO<sub>6</sub> with DCl in D<sub>2</sub>O and subsequent dehydration as described previously (Biefeld, Butler & Azevedo, 1981). Preliminary X-ray powder spectra indicated that the sample was single phase with approximate cell parameter  $a = 10.33$  Å; mass spectral analysis showed that deuterium substitution was  $97 \pm 2\%$  complete.

Approximately 15 g of DTaWO<sub>6</sub> were sealed in a thin-walled vanadium can (1.1 cm diameter by 5 cm long) and placed in the sample position of the high-resolution time-of-flight powder diffractometer (HRPD) at Argonne's ZING-P' pulsed spallation neutron source. The design and operation of the HRPD has been described elsewhere (Jorgensen & Rotella, 1982). Data were collected in an ambient environment ( $T = 300$  K) with the back-scattering detector banks ( $2\theta = \pm 160^\circ$ ) for  $\sim 33$  h (4.0  $\mu\text{A}$ ; 132  $\mu\text{A h}$ ). The time-averaged thermal neutron flux (Jorgensen & Rotella, 1982) on the sample was  $2.9 \times 10^4 \text{ n cm}^{-2} \text{ s}^{-1}$  for this data set. A second set of powder data were collected in the back-scattering detectors for  $\sim 45$  h (5.6  $\mu\text{A}$ ; 252  $\mu\text{A h}$ ) with the same sample cooled by a closed-cycle DISPLEX refrigerator (Air Products, Inc.) to 12 K, with a time-averaged thermal neutron flux on the sample of  $4.1 \times 10^4 \text{ n cm}^{-2} \text{ s}^{-1}$ .

The diffraction data for DTaWO<sub>6</sub> at 300 K and 12 K were fit using Rietveld's (1969) method, modified for time-of-flight neutron powder data (Jorgensen & Rotella, 1982; Von Dreele, Jorgensen & Windsor, 1982). Discrepancy indices used below have been

defined elsewhere (Jorgensen & Rotella, 1982). The coherent neutron scattering lengths (in fm) used in the analysis are as follows:  $b(\text{D}) = 6.672$ ,  $b(\text{O}) = 5.803$ ,  $b(\text{Ta}) = 6.91$  and  $b(\text{W}) = 4.77$ . Background was fit using a refinable three-parameter analytical function. The six refinable peak-shape parameters of the resolution function (Carpenter *et al.*, 1975) were determined previously for the HRPD from a Si powder pattern; however, the DTaWO<sub>6</sub> Bragg peaks were broadened relative to the instrumental resolution and the Gaussian component of the resolution function was varied during the refinement. The data at both temperatures were fit over the range of  $d$  spacings from 0.52 to 2.42 Å which included 3641 consecutive 5  $\mu\text{s}$ -wide time channels and 243 allowed Bragg reflections.

The metal and O positions (Groult, Michel & Raveau, 1973) were refined with anisotropic thermal parameters to convergence with discrepancy indices of  $R_F = 11.01\%$ ,  $R_p = 3.76\%$  and  $R_{wp} = 5.76\%$  for the data at 300 K and  $R_F = 11.03\%$ ,  $R_p = 4.52\%$  and  $R_{wp} = 6.70\%$  for those at 12 K. The 'observed' and calculated structure factors for the 243 contributory reflections were determined from the 12 K data (Rietveld, 1969; Cheetham & Taylor, 1977) and were used as input for a difference Fourier synthesis from a locally modified version of the Canterbury Fourier computer program of R. J. Dellaca and W. T. Robinson. The 12 K data were chosen for the Fourier analysis because it was thought that the low temperature would tend to minimize the thermal vibration of the D, thus localizing it for easier identification in the difference density maps. A difference Fourier synthesis was calculated from these reflections, from which the D atoms were unambiguously located in 48(*f*) sites ( $0.41, \frac{1}{8}, \frac{1}{8}$ ), approximately 1.04 Å from each O position. Fig. 2 is the  $z = \frac{1}{8}$  section of the difference map, contoured to indicate a pair of symmetry-related D sites; the residual neutron density around the O positions is probably due to a systematic error in the model (*e.g.*,

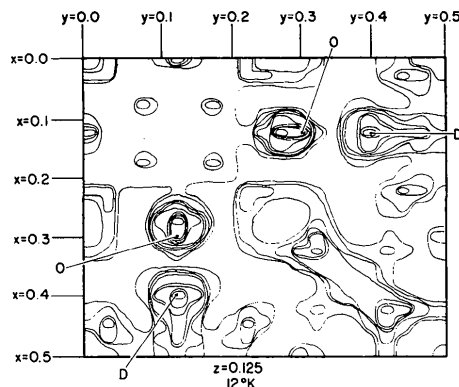


Fig. 2. The  $z = \frac{1}{8}$  section of the difference Fourier neutron density map based solely on the Ta/W and O positions from the 12 K powder data. The positions of symmetry-related D sites are clearly shown  $\sim 1$  Å from the labeled O positions.

Table 1. Models for D sites in DTaWO<sub>6</sub> and refined D parameters

Model	Variables	300 K		12 K	
		Degrees of freedom	$R_{wp}$ (%)	Degrees of freedom	$R_{wp}$ (%)
A: D in 48( <i>f</i> ) site (isotropic)	15	2161	4.7792	2209	5.8781
B: D in 48( <i>f</i> ) site (anisotropic)	17	2159	4.6822	2207	5.6443
C: D in 96( <i>g</i> ) site (isotropic)	16	2160	4.6816	2208	5.6420
D: D in 96( <i>g</i> ) site (anisotropic)	19	2157	4.6765	2205	5.6345

Refined D parameters [see footnote (a) in Table 2; deuterium stoichiometry fixed at 1.0]

Model	Temperature (K)	Temperature									
		<i>x</i>	<i>y</i>	<i>z</i>	$B_{iso}$ (Å <sup>2</sup> )	$\beta_{11}^*$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
A	300	0.4051 (11)	$\frac{1}{8}$	= <i>y</i>	4.91 (24)						
	12	0.4049 (11)	$\frac{1}{8}$	= <i>y</i>	5.10 (22)						
B	300	0.4083 (9)	$\frac{1}{8}$	= <i>y</i>		46 (7)	160 (12)	= $\beta_{22}$	0	0	101 (15)
	12	0.4080 (10)	$\frac{1}{8}$	= <i>y</i>		63 (9)	166 (14)	= $\beta_{22}$	0	0	114 (17)
C	300	0.4085 (10)	0.1066 (8)	= <i>y</i>	2.65 (20)						
	12	0.4086 (10)	0.1061 (8)	= <i>y</i>	2.89 (21)						
D	300	0.4076 (10)	0.1068 (11)	= <i>y</i>		48 (7)	74 (12)	= $\beta_{22}$	10 (6)	= $\beta_{12}$	12 (14)
	12	0.4089 (13)	0.1061 (11)	= <i>y</i>		68 (9)	75 (14)	= $\beta_{22}$	-2 (7)	= $\beta_{12}$	26 (15)

\*  $\beta_{ij}$  are  $\times 10^4$ .

problems in fitting background or problems associated with the measurement of the incident neutron spectrum). The located D position with anisotropic thermal parameters was added to the model, and the refinement converged to  $R_F = 8.32\%$ ,  $R_p = 3.26\%$  and  $R_{wp} = 4.68\%$  for the 300 K data, and  $R_F = 8.08\%$ ,  $R_p = 3.91\%$  and  $R_{wp} = 5.64\%$  for the 12 K data.

The thermal-vibration ellipsoids of D were relatively large ( $\langle U_{max} \rangle = 0.362$  Å for 300 K data and 0.378 Å for 12 K data), and the long direction pointed toward possible 96(*g*) sites separated by  $\sim 0.6$  Å. Since the NMR analysis is based upon a model of deuterons at 96(*g*) sites,  $\sim 1.0$  Å from O atoms (Biefeld, Butler & Azevedo, 1981), we felt it necessary to test whether this model represented a significant improvement over a model with D in 48(*f*) sites. Therefore, refinements were effected for D in a 96(*g*) site at a starting position of (0.41, 0.1, 0.1), first with an isotropic thermal parameter for D, and secondly assuming anisotropic D thermal motion. The results of these refinements at both temperatures, along with the analogous refinements for D in a 48(*f*) site, are summarized in Table 1. The refinement of D in a 96(*g*) site with an isotropic thermal parameter (model C in Table 1 with 16 variables) converged to  $R_{wp} = 5.6420\%$  at 12 K and  $R_{wp} = 4.6816\%$  at 300 K; this model represents a disordering of D into sites displaced by  $\sim 0.3$  Å across the mirror plane containing the 48(*f*) site. D in the 48(*f*) site with anisotropic thermal parameters (model B in Table 1 with 17 variables) refined to convergence with  $R_{wp} = 5.6443\%$  at 12 K and  $R_{wp} = 4.6822\%$  at 300 K. Since the fits to models B and C were virtually identical, the significance of the addition of anisotropic thermal

vibration to the model of D in a 96(*g*) site (model D in Table 1 with 19 variables) was assessed. These refinements converged to  $R_{wp} = 5.6345\%$  at 12 K and  $R_{wp} = 4.6765\%$  at 300 K. The Hamilton *R*-factor ratio indicated that for model D to be statistically preferred over model B at a 99.5% confidence level,  $R_{wp}$  must be lowered by at least a factor of ( $\mathcal{H}_{b=2, N=2207, \alpha=0.005}$ ) 1.0024 (*International Tables for X-ray Crystallography*, 1974; see Table 4.2, pp. 288–292). The observed *R*-factor ratios were 1.0017 and 1.0012 for the 12 and 300 K data respectively, indicating that model D was

Table 2. Results of Rietveld analysis of DTaWO<sub>6</sub> at 300 and 12 K (model B)

Unit-cell and discrepancy-index information						
		300 K		12 K		
Crystal system		Cubic				
Space group		<i>Fd3m</i> (Origin at $\bar{3}m$ )				
<i>a</i> (Å)		10.4281 (1)		10.4269 (1)		
<i>V</i> (Å <sup>3</sup> )		1134.01 (4)		1133.62 (4)		
<i>Z</i>			8			
Formula weight			462.81			
$\rho_{calc}$ (g cm <sup>-3</sup> )		5.421		5.423		
Number of observations		2176		2224		
Number of reflections			243			
Number of variables			18			
$R_F$ (%)		8.32		8.08		
$R_p$ (%)		3.26		3.91		
$R_{wp}$ (%)		4.68		5.64		
$R_{exp}$ (%)		2.42		2.25		
Positional parameters						
Site	Sym.	Stoichio-	<i>x</i>	<i>y</i>	<i>z</i>	Tempera-
		metry				ture (K)
Ta/W	16( <i>c</i> )	$\bar{3}m$	0	0	0	300
			0	0	0	12
O	48( <i>f</i> )	<i>mm</i>	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	300
			$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	12
D	48( <i>f</i> )	<i>mm</i>	0.92 (8)	0.4083 (9)	$\frac{1}{2}$	300
			0.98 (8)	0.4081 (10)	$\frac{1}{2}$	12

Table 2 (cont.)

Anisotropic thermal parameters ( $\beta_{ii}$  are  $\times 10^4$ )

	$\beta_{11}^{(a)}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	$\langle U_{\max} \rangle^{(b)}$	Temperature (K)
Ta/W	38.1 (9)	$=\beta_{11}$	$=\beta_{11}$	-19.1 (8)	$=\beta_{12}$	$\beta_{12}$	0.178	300
	40.6 (9)	$=\beta_{11}$	$=\beta_{11}$	-20.1 (7)	$=\beta_{12}$	$\beta_{12}$	0.183	12
O	20.8 (11)	14.4 (6)	$=\beta_{22}$	0	0	12.7 (8)	0.122	300
	19.4 (10)	12.2 (5)	$=\beta_{22}$	0	0	8.9 (7)	0.108	12
D	38 (9)	146 (17)	$=\beta_{22}$	0	0	92 (17)	0.362	300
	60 (11)	162 (21)	$=\beta_{22}$	0	0	113 (20)	0.389	12

(a) The anisotropic thermal parameters enter the calculated structure factor expression in the form:  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ .

(b) These values represent the root-mean-square amplitudes of vibration (in Å) along the major axis of the vibration ellipsoids of the corresponding atom.

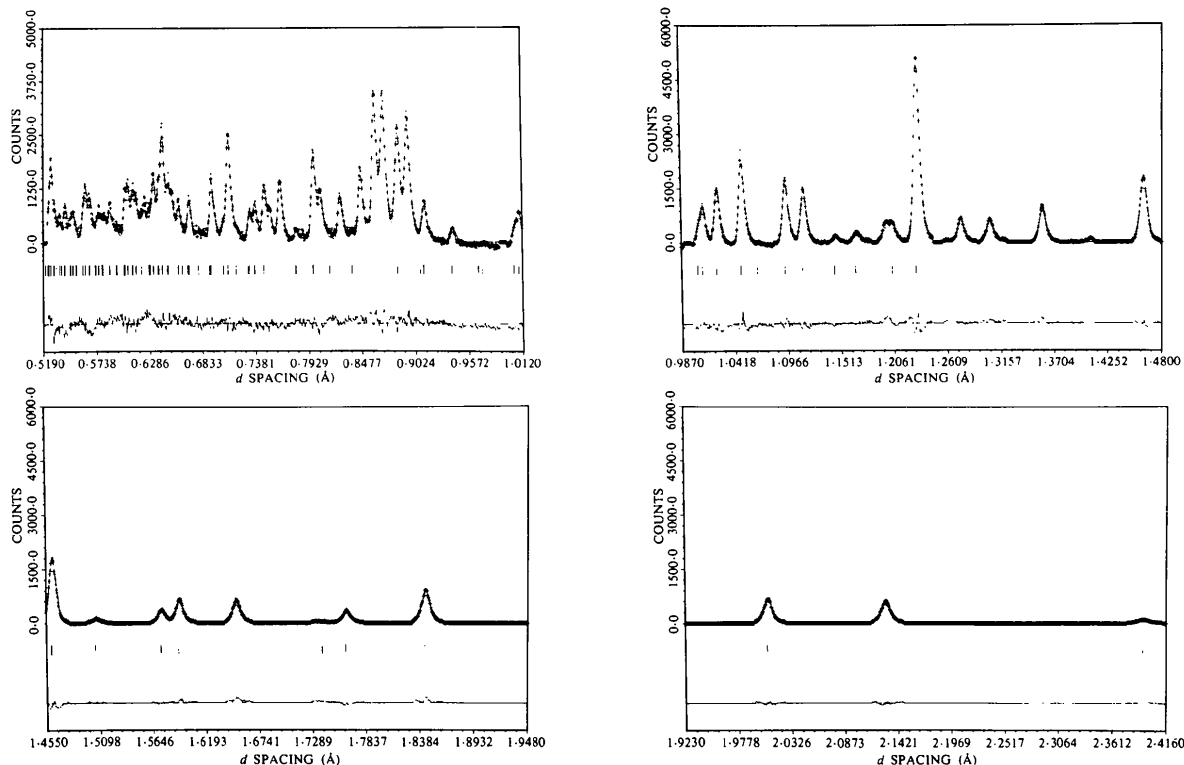


Fig. 3. Final refinement profile for DTaWO<sub>6</sub> at 300 K [cubic,  $Fd\bar{3}m$  (No. 227, origin at  $\bar{3}m$ , D at 0.408, 0.125, 0.125)]. The plus signs (+) are the raw-data points; the solid line is the best-fit profile. A difference (observed - calculated) curve appears at the bottom of the figure. Tick marks below the profile indicate the positions of the Bragg reflections included in the calculation. Background has been removed prior to plotting. The straight-line segments at zero counts are regions of the spectrum which have been excluded from the calculation.

preferred at a 90–95% confidence level. A similar comparison of model *D* with model *C* ( $\chi^2/b = 3$ ,  $N = 2207$ ,  $\alpha = 0.005 = 1.0029$ ; observed *R*-factor ratios of 1.0017 and 1.0011 at 12 and 300 K, respectively) showed that model *D* was preferred at an 80–90% confidence level. From the above comparisons, we felt that we could not distinguish among models *B*, *C* and *D* from our diffraction data; we continued the analysis assuming model *B* [anisotropic thermal vibration for deuterium in a 48(*f*) site].

To test if all of the D had been located, the amount of D was now included as a variable in the refinements at 300 and 12 K. At both temperatures, the stoichiometry of D was within one estimated standard deviation of 1.0 – at 300 K, the stoichiometry of D was

0.92 (8), and at 12 K, 0.98 (8). This, coupled with the fact that difference Fourier maps based on the final structural parameters at both temperatures did not show any other structural features above noise, indicated that our analysis was complete.

Table 2 lists the final structural parameters and discrepancy indices for the Rietveld analyses at 300 and 12 K. Figs. 3 and 4 are the final refinement profiles of DTaWO<sub>6</sub> at 300 and 12 K, respectively.\*

\* The numerical intensities for the measured points of the diffraction profiles (Figs. 3 and 4) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36646 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

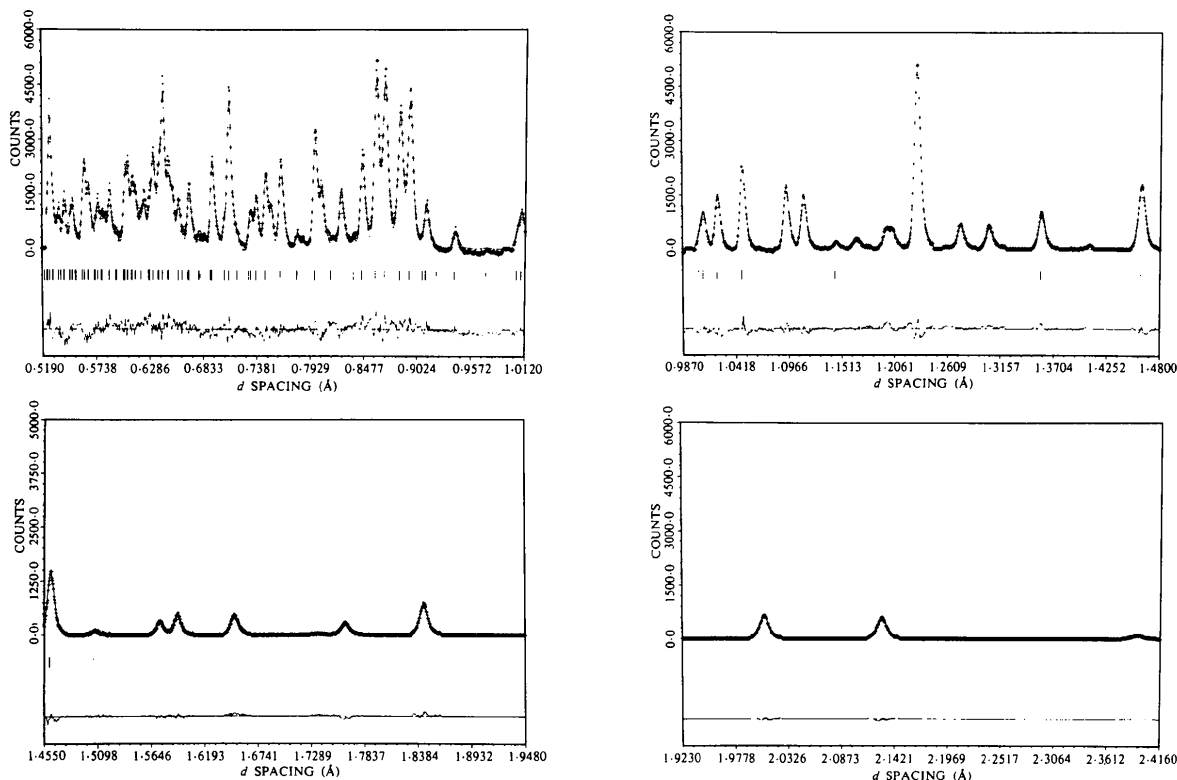


Fig. 4. Final refinement profile for DTaWO<sub>6</sub> at 12 K. The format is the same as in Fig. 3.

### Discussion

Selected interatomic distances are collected in Table 3. These distances have not been corrected for librational effects, and this raises an interesting point about the relative magnitudes of the anisotropic thermal parameters at 300 and 12 K. A perusal of the thermal parameters in Table 2 indicates that the vibration ellipsoids of the metal and D atoms become slightly larger as the temperature is decreased from 300 to 12 K, and that the O thermal ellipsoids decrease by only a small amount over this temperature range. These variations could be indicative of real static positional differences among equivalent sites that really cannot be locally identical, since some O atoms have Ta neighbors, some have W neighbors and one-sixth have D neighbors. This sort of behavior for the thermal parameters as a function of temperature could also arise from unaccounted-for systematic errors in the characterization of the incident spectrum of neutron wavelengths, and the fitting of background- and/or wavelength-dependent effects on intensities such as absorption or extinction, which all may affect the values of the thermal parameters (Jorgensen & Rotella, 1982). Systematic errors of these types seem to exhibit little effect on the values of positional parameters, however (Lager, Ross, Rotella & Jorgensen, 1981).

Table 3. Selected interatomic distances (Å) for DTaWO<sub>6</sub> at 300 and 12 K

	300 K	12 K
Ta/W—O	1.9470 (3)	1.9469 (3)
O—O	2.7295 (13)	2.7296 (12)
O—D	1.024 (9)	1.021 (10)
D—D (nearest neighbor)	2.653 (2)	2.652 (2)
D—D (second neighbor)	3.196 (3)	3.198 (3)

Fig. 5 is an ORTEP-II diagram (Johnson, 1976) with 50% equiprobability thermal ellipsoids showing the structure of DTaWO<sub>6</sub> at 300 K projected down the [110] direction. A comparison of the structural parameters of the 12 K analysis with those at 300 K (Table 2) clearly indicates that a similar projection of the structure at 12 K would be virtually identical to Fig. 5.

At 300 and 12 K, DTaWO<sub>6</sub> possesses a defect-pyrochlore structure. The eight Ta and eight W atoms are assumed to be randomly distributed over the 16(c) sites in an *Fd3m* unit cell, and the O atoms have unit occupation in 48(*f*) sites. The TaWO<sub>6</sub> moiety forms an octahedron of precise *O<sub>h</sub>* point symmetry with metal(Ta/W)—O distances of 1.9470 (3) Å at 300 K and 1.9469 (3) Å at 12 K, and O—O distances of 2.7295 (13) Å at 300 K and 2.7296 (12) Å at 12 K.

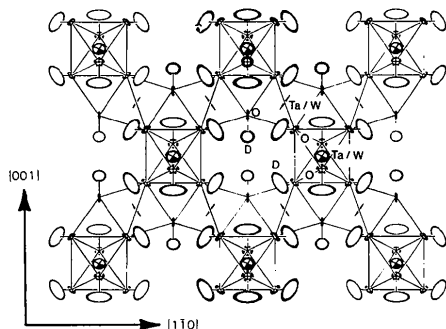


Fig. 5. The crystal structure of DTaWO<sub>6</sub> at 300 K projected down [110]. Note that the D sites lie within open channels parallel to  $\langle 110 \rangle$  directions, at 1.024 (9) Å from the nearest O position. The distance between nearest-neighbor D sites is 2.653 (2) Å. These D sites form spirals parallel to  $\langle 110 \rangle$  within these channels. (ORTEP-II drawing; 50% equiprobability thermal ellipsoids.)

Each octahedron is linked to six other TaWO<sub>6</sub> octahedra by corner-sharing its O atoms. In three dimensions, the corner-shared octahedra form a framework with interconnecting open channels parallel to all  $\langle 110 \rangle$  directions. The six O atoms, which comprise the 'walls' of these channels, possess  $C_{2h}$  point symmetry with four O atoms forming a plane perpendicular to a particular  $\langle 110 \rangle$  direction and the other two O atoms below this imaginary plane (see Figs. 1 and 5). Within the open channels, the eight deuterons in the unit cell are randomly distributed over 48(*f*) sites which lie 1.024 (9) Å at 300 K and 1.021 (10) Å at 12 K from each of the O positions. The D sites form spirals running along the 'walls' of the channels, with nearest-neighbor D sites lying 2.653 (2) Å at 300 K and 2.652 (2) Å at 12 K from each other. There are no other sites that are occupied in the  $\langle 110 \rangle$  channels.

In defect pyrochlores that contain alkali-metal ions and water of hydration, the water molecules have been postulated to reside in either 8(*b*) or 32(*e*) ( $\frac{3}{8} < x_{H_2O} < \frac{1}{2}$ , where  $x_{H_2O}$  is the *x* coordinate of the O position of the water) sites depending on the nature of the alkali-metal ion, and the alkali-metal ions are said to occupy 16(*d*) sites (Goodenough, Hong & Kafalas, 1976; Michel, Groult & Raveau, 1975). In HTaWO<sub>6</sub>·H<sub>2</sub>O (DTaWO<sub>6</sub>·D<sub>2</sub>O), there are no alkali-metal ions at the 16(*d*) positions, and the H<sub>2</sub>O (D<sub>2</sub>O) molecules are assumed to exist in either 8(*b*) [Hervieu, Michel & Raveau (1971); 8(*a*) with origin at  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ] or 16(*d*) (Butler & Biefeld, 1979) sites. The eight protons (deuterons) could very well occupy half of the 96(*g*) sites available (Butler & Biefeld, 1979), since this would tend to minimize any H–H<sub>2</sub>O (D–D<sub>2</sub>O) stereochemical interactions introduced by the presence of H<sub>2</sub>O (D<sub>2</sub>O) in the channels. Upon dehydration to HTaWO<sub>6</sub> (DTaWO<sub>6</sub>), the H–H<sub>2</sub>O (D–D<sub>2</sub>O) interactions would be removed, and the protons (deuterons)

could then most probably 'relax' into the nearby ( $\sim 0.3$  Å), available 48(*f*) sites.

The D–O distance of 1.024 (9) Å at 300 K [1.021 (10) Å at 12 K] in DTaWO<sub>6</sub> is comparable to a bonding distance of 1.01 (1) Å in solid D<sub>2</sub>O (*International Tables for X-ray Crystallography*, 1968; see Table 4.1.8, p. 272). This indicates that the D–O interaction in DTaWO<sub>6</sub> is a bonding interaction and, therefore, this compound would be more correctly thought of as a deuterated hydroxide.

One parameter critical to the understanding of ionic conduction in solids is the distance between the available nearest-neighbor sites for the conducting ion. The nearest neighbor deuteron–deuteron distances in DTaWO<sub>6</sub> of 2.653 (2) Å at 300 K and 2.652 (2) Å at 12 K are not inconsistent with the proposed phonon-assisted tunneling mechanism of deuteron conduction (Butler & Biefeld, 1979; Biefeld, Butler & Azevedo, 1981). In the absence of good deuteron conductivity data on DTaWO<sub>6</sub>, it is difficult to assess the likelihood of this mechanism in explaining deuteron conduction in DTaWO<sub>6</sub> from the structural information cited herein.

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ZING-P' is the prototype of a new pulsed neutron source, IPNS-I, which commenced operation in May, 1981. IPNS-I is a national user facility for condensed-matter research, available to all qualified scientists according to policies established by the US Department of Energy. Inquiries should be addressed to Dr T. G. Worlton, Scientific Secretary, IPNS Program, Argonne National Laboratory, Argonne, Illinois 60439.

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## Application of Modulated Structure Analysis to Polytypes. II. Determination of a 66R SiC Polytype

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### Abstract

A new polytype structure of 66R SiC ( $R3m$ ,  $a = 3.078$ ,  $c = 166.188$  Å) was determined by the use of the method of modulated structure analysis described in part I [Yamamoto (1981). *Acta Cryst.* **A37**, 838–842]. The  $R$  factor smoothly converged from 0.68 for an initial state to 0.031 for a final result after 26 cycles and the stacking sequence described by the Zhdanov symbol  $[23233333]_3$  was obtained. To confirm that the final result is independent of initial parameter selection, the least-squares program was initiated from another starting point and different final parameters describing the same stacking sequence were obtained. Therefore, this method can be used for SiC polytype analysis without special consideration for initial parameters.

### Introduction

In the first part of this series [Yamamoto, 1981; referred to as (I) in the following], the theoretical basis of the method used here was given and analyses based on this theory were applied to the known structures of 21H SiC and 66R ZnS polytypes. In this paper, we describe the application of this method to the determination of the stacking sequence of a 66R SiC crystal which has the rhombohedral space group  $R3m$ .

### Theory

The determination of SiC polytypes is similar to that of ZnS polytypes because these two materials have similar

structures: the stacking sequence to be determined in both cases is that of tetrahedra which consist of  $\text{SiC}_4$  or  $\text{ZnS}_4$  and share their corners. In this respect, the determination of a 66R SiC polytype is completely analogous to that of 66R ZnS which was mentioned in (I). In this section, the theory is briefly reviewed.

In the refinement of polytype structures of SiC, we can conveniently use the periodic intensity distribution function  $S(h_1, h_2, h_3, h_4)$  instead of the usual structure factor  $F(h_1, h_2, h_3, h_4)$  (Tokonami, 1966; Takeda, 1967). This is defined in the present notation by

$$S(h_1, h_2, h_3, h_4) = \frac{F(h_1, h_2, h_3, h_4)}{F_0(h_1, h_2, h_3, h_4)} M, \quad (1)$$

where  $M$  is the number of SiC layers in the unit cell ( $M = 66$  in the present case),  $h_1, h_2, h_3, h_4$  are integers which designate reflections by the relation  $\mathbf{h} = h_1 \mathbf{a}^* + h_2 \mathbf{b}^* + (h_3 + h_4/M) \mathbf{c}^*$  and  $F_0(h_1, h_2, h_3, h_4)$  is the structure factor of the structure consisting of one SiC layer with the period  $M$ .  $S(h_1, h_2, h_3, h_4)$  corresponds to the structure factor for the point atom with one electron located at the center of each  $\text{SiC}_4$  tetrahedron. This is calculated from

$$S(h_1, h_2, h_3, h_4) = \sum_{\mu} \sum_{\nu=1}^M P^{\mu}(x_j^{\mu}) \times \exp \left\{ 2\pi i \sum_{j=1}^4 h_j x_j^{\mu} \right\}, \quad (2)$$

where the summation with respect to  $\mu$  runs over the  $A$ ,  $B$ ,  $C$  sites;  $x_1^A, x_2^A, x_3^A$  ( $\mu = A$ ) are the usual three-dimensional coordinates of the  $A$  site in the