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High-Resolution Neutron Powder Diffraction Studies* of the Structure of CsDSO₄

BY A. V. BELUSHKIN

Joint Institute for Nuclear Research, 141980 *Dubna, USSR*

W. I. F. DAVID AND R. M. IBBERSON

*Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX*11 0*QX, England*

AND L. A. SHUVALOV

Institute of Crystallography, 117333 *Moscow, USSR*

Abstract

High-resolution neutron powder diffraction data were used to determine the crystal structure of the superionic conductor CsDSO₄ at 300 K (low-conductivity phase) and at 448 K (superionic phase). A full structural analysis was performed, using the Rietveld method, to obtain previously unknown atomic positions, site occupancies and temperature factors for the light atoms. The mechanism of deuterium diffusion is discussed. At 300 K: monoclinic, $P2_1/c$, $a = 7.78013$ (9), $b = 8.13916$ (2), $c = 7.72187$ (9) Å, $\beta = 110.8720$ (4)°, $R_{wp} = 4.19\%$ for 7331 profile points (844 reflections). At 448 K: tetragonal, $I4_1/amd$, $a = 5.74147$ (9), $c = 14.31508$ (26) Å, $R_{wp} = 2.21\%$ for 8289 profile points (194 reflections).

1. Introduction

Deuterated caesium hydrogen sulfate, CsDSO₄, belongs to a class of crystalline compounds which have hydrogen bonds of the type $MXAO_4$ (M = Cs, Rb; X = H, D; A = S, Se). All these materials undergo a phase transition to a superionic state. The phase transition is characterized by a sharp increase in conductivity (by three to four orders of magnitude, up to $10^{-2}\,\Omega^{-1}\,cm^{-1}$) and by a large spontaneous shear strain (10^{-2}) (Baranov, Shuvalov & Schagina, 1982, 1984; Baranov, Shuvalov, Fedosyuk & Schagina, 1984; Yokota, 1982). The transition temperature (T_c) for CsDSO₄ is 412 K (Baranov, Shuvalov & Schagina, 1984). Previous X-ray and neutron diffraction data showed the phase (II) structure, below T_c, to be monoclinic, space group $P2_1/c$, and the phase (I) structure, above T_c, to be tetragonal, space group $I4_1/amd$ (Merinov, Baranov, Maksimov & Shuvalov, 1986; Balagurov, Beskrovnyi & Savenko, 1987; Merinov, Baranov, Shuvalov & Maksimov, 1987). The crystal structures of CsDSO₄ (I) and CsDSO₄ (II) are isomorphic with the corresponding phases of CsHSO₄, CsHSeO₄ and CsDSeO₄ (Balagurov, Belushkin & Beskrovnyi, 1985; Belushkin, Natkaniec, Plakida, Shuvalov & Wasicki, 1987). It is therefore believed that conclusions as to the crystal structure and mechanism of conductivity

for one of the compounds will hold for the whole family.

The structure of CsDSO$_4$ (II) has largely been determined (Merinov, Baranov, Maksimov & Shuvalov, 1986; Balagurov, Beskrovnyi & Savenko, 1987). In the superionic phase two structural models now exist (Merinov, Baranov, Shuvalov & Maksimov, 1987; Jirak, Dlouha & Vratislav, 1987) which differ with respect to the oxygen and hydrogen (deuterium) positions – further investigation thus seemed timely. The present paper reports the results of a high-resolution neutron powder diffraction study of CsDSO$_4$ in both the monoclinic phase (II), at room temperature, and the tetragonal phase (I), at 448 K. Emphasis is placed on the determination of atomic coordinates and temperature factors for O and D atoms in the superionic phase and the relevance of these results to the postulated models both of the crystallographic structure and proton diffusion mechanisms.
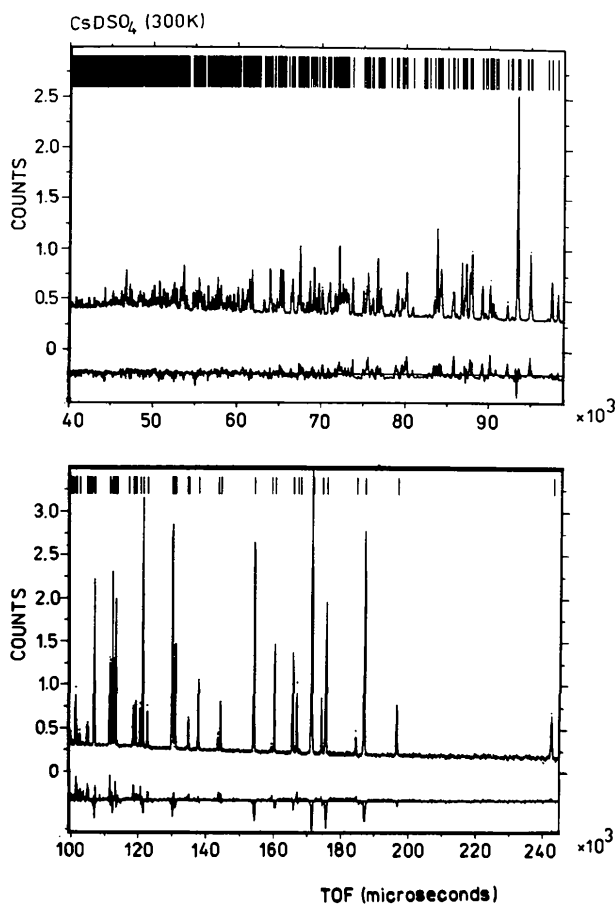

Fig. 1. Observed (points), calculated (line) and difference plot for the diffraction profile of CsDSO$_4$ at room temperature. (Tick marks indicate the calculated peak positions.)

2. Experimental

The large spontaneous strain mentioned above makes neutron single-crystal measurements practically impossible (Merinov, Baranov, Maksimov & Shuvalov, 1986). The powder sample was prepared as described elsewhere (Belushkin, Natkaniec, Plakida, Shuvalov & Wasicki, 1987), and was dried in air before being reground and hermetically contained in a standard 4 mm diameter vanadium can under a nitrogen atmosphere. The latter procedure was adopted to minimize the possiblity of deuterium–hydrogen exchange which has been reported to occur in the superionic phase (Jirak, Dlouha & Vratislav, 1987).

High-resolution neutron powder diffraction data were collected at temperatures of 300 K ($T < T_c$) and 448 K ($T > T_c$) on the High Resolution Neutron Powder Diffractometer (HRPD) at the pulsed spallation neutron source ISIS, England (David, Akporiaye, Ibberson & Wilson, 1988). For each phase, data were recorded within the neutron time-of-flight region 30–270 ms, corresponding to a d-spacing range of 0·6–5·4 Å, for a period of approximately 12 h. Data were collected in backscattering, $2\theta_{av} = 168\cdot329°$, with a resolution of $\Delta d/d = 8 \times 10^{-4}$ and normalized for the spectral distribution of the incident flux using previously recorded vanadium data. Analysis was performed using the time-of-flight profile-refinement program suite developed at ISIS (David, Akporiaye, Ibberson & Wilson, 1988) which utilizes the Cambridge Crystallography Subroutine Library ($CCSL$) (Brown & Matthewman 1987).

3. Results and discussion

3.1. Structure of CsDSO$_4$ at 300 K

The high quality of data collected at 300 K permitted a full structural refinement to be performed for the monoclinic phase. The observed and calculated profiles are shown in Fig. 1 with the final crystallographic and profile parameters given in Table 1. It should be noted that the difference plot shown in Fig. 1 includes a minor impurity phase from CsHSO$_4$. The room-temperature structure of CsHSO$_4$ is known to differ from that of CsDSO$_4$ (Balagurov, Belushkin & Beskrovnyi, 1985; Belushkin, Natkaniec, Plakida, Shuvalov & Wasicki, 1987), namely CsHSO$_4$ has an additional metastable phase (III). This phase transition, (III)→(II), may be regarded as irreversible and occurs at a temperature of 330–370 K. The existence of phase (III) is prohibited beyond a level of 50% deuteration.

The atomic coordinates (Table 1) and anisotropic temperature factors (Table 2) now accurately obtained confirm the previously proposed structure (Merinov, Baranov, Maksimov & Shuvalov, 1986)

Table 1. *Final crystallographic data for* $CsDSO_4$ (300 K)

Monoclinic, space group $P2_1/c$ (No. 14), $a = 7.78013$ (9), $b = 8.13916$ (2), $c = 7.72187$ (9) Å, $\beta = 110.8720$ (4)°. Refined D/H ratio $= 0.769$ (6), $R_E = 1.52$, $R_p = 4.48$, $R_{wp} = 4.19\%$, $\chi^2 = 7.6$ for 7331 profile points (844 reflections) and 94 basic variables. The positional parameters are given as fractional coordinates $\times 10^5$.

$$U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	$U_{eq}(Å^2)$
Cs	21493 (27)	12919 (23)	20619 (24)	0.76 (9)
S	75359 (53)	12825 (44)	27893 (50)	0.94 (16)
O1	58804 (34)	22135 (33)	12787 (38)	2.29 (11)
O2	89595 (29)	24617 (26)	36013 (27)	1.99 (9)
O3	66652 (28)	6829 (23)	40774 (27)	1.71 (9)
O4	80616 (31)	−407 (23)	18550 (28)	2.25 (10)
D	63331 (45)	21029 (35)	548120 (46)	1.77 (17)

Table 2. *Final values of anisotropic thermal parameters* $(Å^2)$ *for* $CsDSO_4$ (300 K)

The anisotropic thermal parameters are defined as $\exp[-\frac{1}{4}(B_{11}ha^*ha + ... + 2B_{23}kb^*lc^* + ...)]$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cs	1.67 (11)	0.39 (8)	0.24 (9)	0.20 (8)	0.35 (7)	0.24 (9)
S	1.23 (18)	0.78 (15)	1.01 (17)	0.45 (17)	0.64 (16)	0.69 (16)
O1	1.89 (12)	3.03 (13)	2.05 (11)	0.53 (10)	0.82 (10)	1.01 (10)
O2	2.26 (11)	1.82 (10)	2.02 (11)	−1.46 (9)	0.93 (9)	−1.15 (9)
O3	2.53 (11)	1.72 (11)	1.66 (11)	−0.39 (7)	1.71 (9)	0.26 (7)
O4	5.21 (14)	0.57 (9)	2.35 (11)	0.04 (9)	3.04 (10)	0.02 (8)
D	3.60 (22)	0.61 (17)	1.61 (20)	−0.03 (11)	1.57 (15)	−0.48 (11)

for $CsDSO_4$. Table 3 compares some atomic distances with the previous estimates (Merinov, Baranov, Maksimov & Shuvalov, 1986). The O1 and O3 atoms which participate in the hydrogen bonds are seen to lie further from the S atom than O2 and O4, leading to a distortion of the SO_4 tetrahedron. The deuterium bonds configure so as to form zigzag chains along the [001] direction. The D atoms are fully ordered with a D atom positioned 0.68 Å nearer to O1 than to O3, and with an O1—D—O3 angle of 166.5°. These room-temperature data are in very good agreement with previous results (Merinov, Baranov, Maksimov & Shuvalov, 1986; Balagurov, Beskrovnyi & Savenko, 1987), the X-ray and neutron results showing no significant disagreement. Fig. 2 illustrates the room-temperature structure.

Analysis of the room-temperature data also provided information which was important for the high-temperature structure determination: the degree of deuteration was refined and found to be 76.9 (6)%; extinction and absorption parameters were estimated.

3.2. *Structure of the superionic phase of* $CsDSO_4$ *at* 448 K

As stated above the crystal structure of superionic phase (I) $CsDSO_4$ is tetragonal, with space group $I4_1/amd$. The atomic coordinates for the heavy atoms as determined by X-ray diffraction (Merinov, Baranov, Shuvalov & Maksimov, 1987) are in good agreement with earlier neutron diffraction results

Table 3. *Some interatomic distances* (Å) *for* $CsDSO_4$ (300 K) *compared with the results of Merinov et al.* (1986)

The atomic notations refer to Table 1. Hydrogen-bond angle O1—D—O3' is 166.6 (6)°.

Cs environment			SO_4 tetrahedra		
		Merinov *et al.*			Merinov *et al.*
Cs—O2'	3.099 (6)	3.112 (4)	S—O1	1.589 (8)	1.567 (5)
Cs—O4'	3.120 (8)	3.116 (5)	S—O2	1.430 (7)	1.438 (4)
Cs—O4'	3.140 (6)	3.148 (5)	S—O3	1.472 (5)	1.454 (6)
Cs—O3'	3.219 (6)	3.213 (5)	S—O4	1.435 (9)	1.439 (6)
Cs—O2'	3.227 (5)	3.236 (4)	O1—O2	2.436 (6)	2.416 (6)
Cs—O2'	3.253 (6)	3.252 (5)	O1—O3	2.378 (6)	2.343 (7)
Cs—O1	3.257 (7)	3.253 (6)	O2—O3	2.426 (6)	2.418 (7)
Cs—O4'	3.310 (8)	3.315 (5)	O2—O4	2.405 (8)	2.297 (6)
Cs—O3	3.334 (7)	3.325 (4)	O3—O4	2.409 (6)	2.416 (8)
Cs—O1'	3.689 (5)	3.685 (5)			
Cs—O1'	3.711 (5)	3.736 (4)			
Cs—O3'	3.870 (6)				

Hydrogen bonds		
		Merinov *et al.*
O1—O3'	2.633 (5)	2.626 (8)
O1—D'	0.983 (5)	–
O3'—D'	1.667 (8)	~1.7

(Jirak, Dlouha & Vratislav, 1987). From previous work, however, two models for the O and D atomic positions have been proposed – 16(h) and 8(e) sites (Merinov, Baranov, Shuvalov & Maksimov, 1987) and 32(i) and 16(f) sites (Jirak, Dlouha & Vratislav, 1987) for the respective atoms. Distinction between the two models is necessary as is consideration of the optical spectroscopy data (Pham-Thi, Colomban, Novak & Blinc, 1985, 1987; Dmitriev, Loshkarev, Rabkin, Shuvalov & Yuzyuk, 1986) which indicates rotation of SO_4—H groups in the superionic phase, incompatible with either of the previously proposed structural models.

In order to reduce the number of variables in the high-temperature refinement, sample characteristics were fixed to those obtained from the room-temperature data wherever possible. The analysis was further simplified to that of a single-phase profile since $CsDSO_4$ and $CsHSO_4$ are isostructural at 448 K in the superionic phase. The profile analysis
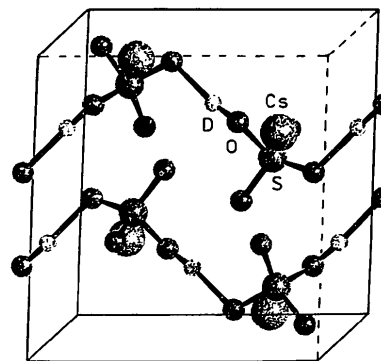

Fig. 2. Schematic view of the room-temperature structure of $CsDSO_4$. The zigzag chains of hydrogen bonds are clearly seen.

was carried out in two stages, determining initially the location of the O atoms whilst imposing strict constraints to effectively fix the heavy atoms.

Assuming the 32(i) site model for oxygen (Jirak, Dlouha & Vratislav, 1987) it proved impossible to attain a good profile fit or any measure of convergence with the refinement. Difference Fourier maps were constructed for planes perpendicular to the [001] and [010] directions and revealed a considerable excess of atomic density near the chosen oxygen positions as shown in Fig. 3(a). On the basis of the difference Fourier maps new atomic coordinates for oxygen were calculated and found to be in close agreement with those already proposed (Merinov, Baranov, Shuvalov & Maksimov, 1987). Adoption of the 16(h) positions for oxygen improved the profile fit whilst essentially removing the previous excess scattering density observed in the difference Fourier map (see Fig. 3b). Despite improvements to the profile fit, on examination the model seemed unrealistic, forcing a very large distortion on the SO$_4$ tetrahedra. Subsequently a model having two 32(i) sites for oxygen was tried. Whilst only slightly improving the profile fit the dubious distortion of the SO$_4$ tetrahedron was no longer imposed and consideration of the interatomic distances revealed the possibility of hydrogen bonding from the 16(f) (bond distance ca 2·6 Å) and 8(e) (bond distance is ca 2·8 Å) positions. The refinement (which included variation of lattice parameters, all atomic parameters, isotropic thermal parameters and site occupancies) did not converge ideally, i.e. there was a strong correlation between the deuterium coordinates and the oxygen-site occupancies. Consequently, during the final stages of refinement the deuterium coordinates were constrained to lie between oxygens participating in hydrogen bonds and the oxygen-site occupancy was fixed at the ideal value of 0·25. Such restraints were not found to affect the quality of the

Table 4. *Final crystallographic data for superionic phase* CsDSO$_4$ (448 K)

Tetragonal, space group $I4_1/amd$ (No. 141), $a = 5·74147$ (9), $c = 14·31508$ (26) Å. $R_E = 1·53$, $R_p = 2·54$, $R_{wp} = 2·21\%$, $\chi^2 = 2·1$ for 8289 profile points (194 reflections) and 21 basic variables.

	Site	x	y	z	Site occupancy	B_{iso}(Å^2)
Cs	4(b)	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	1	2·35 (8)
S	4(a)	0	$\frac{1}{4}$	$\frac{3}{8}$	1	8·57 (23)
O1	32(i)	0·0559 (9)	0·5860 (6)	0·2038 (2)	0·25	3·28 (9)
O2	32(i)	0·0273 (15)	0·4928 (6)	0·1607 (3)	0·25	3·28 (9)
D1	16(f)	$\frac{1}{4}$	0·5860 (6)	$\frac{1}{4}$	0·246 (7)	26 (1)
D2	8(e)	0	$\frac{1}{4}$	0·1607 (3)	0·094 (7)	26 (1)

refinement or greatly influence the coordinates and temperature factors of the other atoms. The isotropic temperature factors for deuterium are high, indicating them to be the main contributors to the conductivity of the material. On the basis of the data collected in the high-temperature regime it is impossible to exclude the possible existence of some additional intermediate positions for deuterium.

The final structural and profile parameters are given in Table 4 and the observed and calculated profiles displayed in Fig. 4.

Table 5 lists the interatomic bond distances and angles for the SO$_4$ tetrahedra and the hydrogen bonds. Each tetrahedron is seen to adopt one of four orientations as shown in Table 6. One tetrahedron may be transformed to another by a rotation of
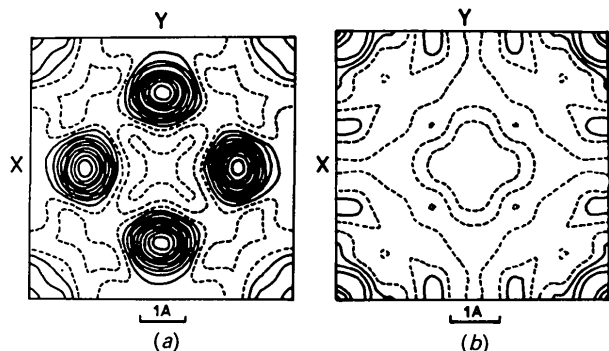

Fig. 3. Difference Fourier maps sectioned at 0·125 on [001] with X parallel to [100] and Y parallel to [010]. (a) The result from the model proposed by Jirak et al. (1987). A pronounced excess of atomic density is seen near the chosen oxygen positions. (b) The result for the model proposed by Merinov et al. (1987).
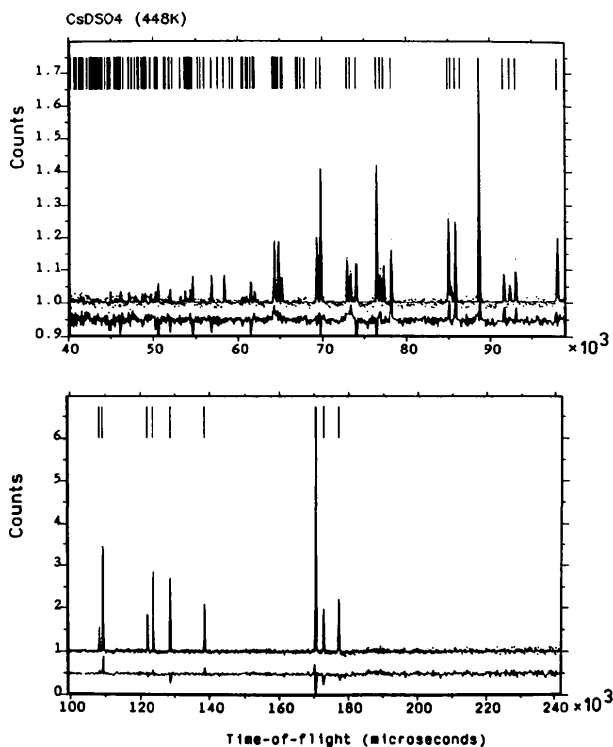

Fig. 4. Observed (points), calculated (line) and difference plot for the diffraction profile of CsDSO$_4$ at 448 K.

Table 5. *Interatomic distances* (Å) *and bond angles* (°) *for the* SO₄ *tetrahedra and hydrogen bonds in the superionic phase of* CsDSO₄

SO₄ tetrahedra		Hydrogen bonds [16(*f*)]		Hydrogen bonds [8(*e*)]	
S—O1	1·504 (10)	O1—O1'	2·59 (1)	O2—O2'	2·806 (18)
S—O2	1·570 (5)				
O1—S—O1' = 107·2 (2)		O1—S—O2 = 108·9 (3)		O1—S—O2' = 112·5 (3)	
O1'—S—O2 = 112·5 (3)		O1'—S—O2' = 108·9 (2)		O2—S—O2' = 107·1 (4)	

Table 6. *Four orientations of one* SO₄ *tetrahedron*

	x	y	z	x	y	z
	Orientation No. 1			Orientation No. 2		
O1	0·1640	0·6941	0·0462	−0·1640	0·8059	0·0462
O1'	0·0559	0·5860	0·2038	−0·0559	0·9140	0·2038
O2	−0·2572	0·7227	0·0893	0·2572	0·7773	0·0893
O2'	0·0273	1·0072	0·1607	−0·0273	0·4928	0·1607
	Orientation No. 3			Orientation No. 4		
O1	0·1640	0·8059	0·0462	−0·1640	0·6941	0·0462
O1'	0·0559	0·9140	0·2038	−0·0559	0·5860	0·2038
O2	−0·2572	0·7773	0·0893	0·2572	0·7227	0·0893
O2'	0·0273	0·4928	0·1607	−0·0273	1·0072	0·1607

approximately 30° with respect to the central sulfur atom, an observation consistent with the results of optical spectroscopy (Pham-Thi, Colomban, Novak & Blinc, 1985, 1987). One of the possible orientations of the SO₄ tetrahedra, along with the associated hydrogen-bonding scheme, is shown projected on the *ab* crystal plane in Fig. 5(*a*), with the *ac* plane projection shown in Fig. 5(*b*).

4. Concluding remarks

The structural results obtained can help the interpretation of some experiments performed earlier. As previously known (Baranov, Shuvalov & Schagina, 1984) the temperature of the phase transition to superionic CsHSO₄ is very close to that for CsDSO₄, that is, the isotopic effect is virtually absent. From the experimental data presented above this could be explained by the fact that the mechanism of the superionic phase transition is not governed by deuterons but by disordering of SO₄ tetrahedra, thus isotopic deuterium–hydrogen exchange does not affect T_c. This SO₄ disordering leads to a reconstruction of hydrogen bonds and causes the appearance of unfilled sites for protons (deuterons).

According to specific heat measurements (Komukae, Osaka, Makita, Ozaki, Itoh & Nakamura, 1981) the entropy for the superionic phase transition is 1·32R. The structural data permit calculation of the configurational entropy for the transition. In the low-temperature phase there is only one possible orientation of the SO₄ tetrahedron whilst in the superionic phase there are four. The entropy, ΔS, gives $R\ln 4 = 1·39R$ and so is in good agreement with the experimental value.

On the basis of the structural data some predictions about the diffusion mechanism can be made.

The main contribution to conductivity comes from deuterium, an assumption confirmed by the anomalously large temperature factor for these atoms and also supported by optical spectroscopy (Dmitriev, Loshkarev, Rabkin, Shuvalov & Yuzyuk, 1986) and NMR (Blinc, 1984) data.

Analysis of the interatomic distances shows that in the *ab* plane there is a possibility of jump diffusion *via* the 16(*f*)–8(*e*)–16(*f*) positions; a length of *ca* 2·7 Å. This possibility is associated with a 30° libration of SO₄—H mentioned previously. A second possibility is associated with a 30° rotation (a proton jump length of *ca* 2·7 Å) and a subsequent 90° rotation (a proton jump length of *ca* 2·9 Å) of SO₄—H. This process will lead to diffusion along the [001] crystal direction.
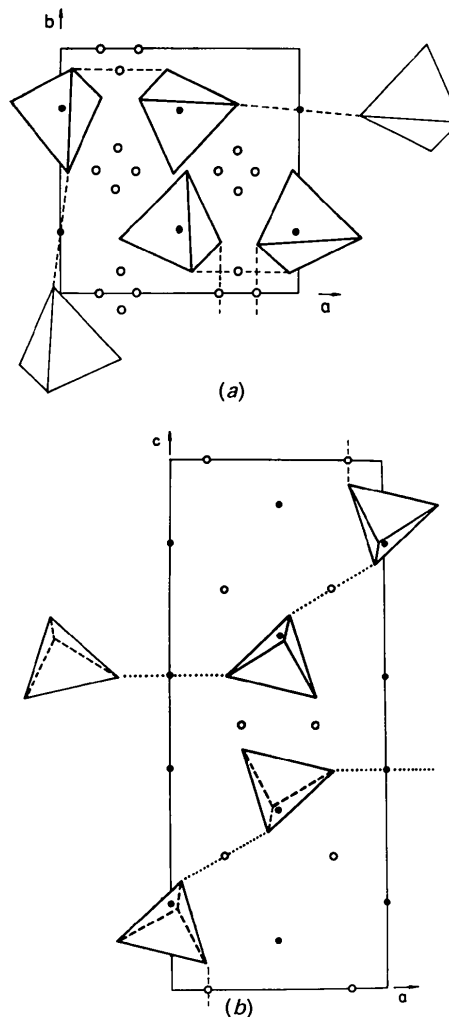

Fig. 5. (*a*) One of the possible orientations of the SO₄ tetrahedra along with the associated hydrogen-bonding scheme as projected on the *ab* crystal plane. (*b*) A second possible scheme as projected on the *ac* crystal plane. Open circles, 16(*f*) deuterium positions; closed circles, 8(*e*) deuterium positions.

The two processes should lead to anisotropic conductivity along and perpendicular to the c direction, an effect which has already received experimental confirmation (Baranov, 1989). The structural results indicate no possiblity of the Cs^+ diffusion as reported elsewhere (Pham-Thi, Colomban, Novak & Blinc, 1987). Haynovskiy, Pavlyuhin & Hayretdinov (1985) reported that in the low-temperature phase the conductivity of $CsHSO_4$ is two orders of magnitude higher than that of $CsDSO_4$, whilst in the superionic phase their conductivities are approximately equal. From this arose the assumption that the diffusion of Cs^+ contributes to the conductivity (Pham-Thi, Colomban, Novak & Blinc, 1987). However as noted above the room-temperature structure of $CsHSO_4$ differs from that of $CsDSO_4$ and so the large difference in conductivity in the low-temperature phases of protonated and deuterated samples cannot be solely assigned to an isotopic effect as previously stated (Haynovskiy, Pavlyuhin & Hayretdinov, 1985).

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A Modulation-Wave Approach to the Structural Description of the Nb2Zrx−2O2x+1 (x = 7·1–10·3) Solid-Solution Field

BY R. L. WITHERS, J. G. THOMPSON AND B. G. HYDE

Research School of Chemistry, Australian National University, GPO Box 4, Canberra, ACT 2601, Australia

Abstract

At the ZrO_2-rich end of the phase diagram, the $Nb_2O_5 + ZrO_2$ system forms a complex $Nb_2Zr_{x-2}O_{2x+1}$ ($x = 7·1–10·3$) solid-solution field which can be structurally characterized as a composite modulated structure. Fourier decomposition of the Galy & Roth [*J. Solid State Chem.* (1973), **7**, 277–285] structure refinement of one composition within this field, *i.e.* $Nb_2Zr_6O_{17}$, in such terms gives the underlying parent metal-atom subcell (*Amma*, $a_M \simeq 5·1$, $b_M \simeq 4·9$, $c_M \simeq 5·2$ Å) and parent O-atom subcell {*Imam*, $a_O = [x/(2x + 1)]a_M$, $b_O = b_M$, $c_O = c_M$} along with specific expressions for the atomic modulation functions describing the structural deviation of the two sublattices from their respective parent subcells. The extinction conditions characteristic of this $Nb_2Zr_{x-2}O_{2x+1}$ ($x = 7·1–10·3$) solid-solution