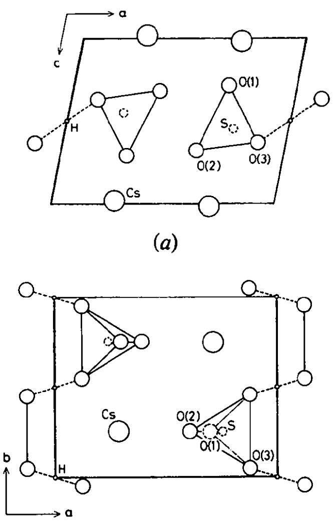

(a)

(b)

Fig. 1. (a) The b axis and (b) c axis views of the $CsHSO_4$ structure. The hydrogen bonds are drawn with broken lines.

Discussion. A map of residual electron density computed after the final refinement showed an irregular maximum of 1·6 e $Å^{-3}$ near Cs, maxima of 0·7–1·3 e $Å^{-3}$ near S, O(1), O(2) and O(3), and no peaks >0·6 e $Å^{-3}$ in the remaining places.

As depicted in Fig. 1, Cs and SO_4 lie on the mirror planes at $y = \frac{1}{4}$ and $\frac{3}{4}$. The separate chains of hydrogen bonds run along the *b* axis one-dimensionally. This structure is not isomorphous with those of ferroelectric $RbHSO_4$ (Ashmore & Petch, 1975) and NH_4HSO_4 (Nelmes, 1972), or with the nonferroelectric $NaHSO_4$ and $KHSO_4$ (Sonneveld & Visser, 1978). It is interesting that the structure of $CsHSO_4$ resembles rather that of CsH_2PO_4 in the paraelectric phase (Matsunaga, Itoh & Nakamura, 1980) apart from the presence of an extra H in CsH_2PO_4, which combines O(1) and $O(2^{ii})$.

As shown in Table 2, the shape of SO_4 is rather regular while the bond length S—O(3) is somewhat longer than S—O(1) and S—O(2). Remembering that O(3) and $O(3^{v})$ are linked by H^{vi}, we can attribute the greater length of the S—O(3) bond to the formation of the hydrogen bond as in the case of other $AHSO_4$-type compounds (Sonneveld & Visser, 1978).

As mentioned above, the peak of H electron density is not located exactly at the 2(*c*) site of (0·0, 0·0, 0·5) but two peaks of height 0·6 e $Å^{-3}$ are observed near the positions of (0·00, 0·05, 0·55) and (0·00, −0·05, 0·45). Although the peak height is the same as that of ripples on the Fourier map, this result implies that the structure has a disordered H atom. From this structure, it is expected that a phase transition which brings H atoms into an ordered state occurs below room temperature.

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An X-ray Diffraction Refinement of the Structure of Natural Natrolite

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Abstract. $Na_2Al_2Si_3O_{10}.2H_2O$, orthorhombic, *Fdd*2, $a = 18{\cdot}325\ (5)$, $b = 18{\cdot}653\ (5)$, $c = 6{\cdot}601\ (5)$ Å, $V = 2256$ $Å^3$, $Z = 8$, $D_c = 2{\cdot}135$, $D_o = 2{\cdot}15$ Mg m^{-3}. The atomic positions have been determined from single-crystal X-ray diffraction data. The final *R* value for 400 independent observed reflections is 0·056. Si,Al is coordinated to four O atoms. The average Al—O and Si—O distances are 1·746 (2) and 1·619 (2) Å respectively. The average O—H distance is 1·044 (2) Å.

Introduction. Natrolite is one of the natural hydrated aluminosilicate zeolites. First reports of its crystal structure were presented by Pauling (1930), Taylor, Meek & Jackson (1933) and Meier (1960). According

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Table 1. *Final atomic coordinates and isotropic temperature factors with e.s.d.'s in parentheses*

	x	*y*	*z*	*B* (Å^2)
Si(1)	0	0	0	1·16 (5)
Si(2)	0·1535 (1)	0·2110 (1)	0·6277 (15)	2·16 (5)
Al	0·0379 (1)	0·0937 (1)	0·6193 (10)	2·38 (5)
O(1)	0·0226 (2)	0·0688 (1)	0·8703 (20)	0·11 (5)
O(2)	0·0692 (2)	0·1821 (1)	0·6168 (20)	0·05 (5)
O(3)	0·0978 (2)	0·0333 (2)	0·5078 (20)	0·90 (5)
O(4)	0·2066 (2)	0·1535 (2)	0·7285 (20)	0·67 (5)
O(5)	0·1809 (2)	0·2279 (2)	0·3968 (20)	0·20 (5)
O(*W*)	0·0571 (2)	0·1889 (2)	0·1145 (20)	0·99 (5)
Na	0·2194 (1)	0·0309 (1)	0·6231 (15)	0·86 (5)
H(1)	0·0481 (5)	0·1344 (5)	0·0698 (20)	4·35 (5)
H(2)	0·1012 (5)	0·1795 (5)	0·2042 (20)	4·09 (5)

to Breck (1978), natrolite falls into the fifth structural group of zeolites. The crystals of the minerals of this group show a characteristic fibrous habit.

A 0·3 × 0·2 × 0·8 mm single crystal of natural natrolite $Na_{14.40}K_{0.5}Ca_{0.8}Al_{16.34}Fe_{0.004}Si_{23.96}O_{80}\cdot 16H_2O$, or schematic $Na_{14}CaAl_{16}Si_{24}O_{80}\cdot 16H_2O$ (locality: Těchlovice, Bohemia), was measured by the Weissenberg equi-inclination method [λ(Cu $K\bar{\alpha}$) = 1·5418 Å] on the VEB Precision Mechanik goniometer with the reflections recorded on film. The intensities were determined on the Joyce–Loebl MK IIICS densitometer. The set of 400 independent measured reflections was corrected for the Lp factor and for absorption (μ = 2·7 mm^{-1}) by a standard version of the *DATAP* 2 program (Lingren, 1975). Approximate values of scale factors for particular layer lines were calculated by the *LALS* program (Lingren, 1975).

The orthorhombic cell parameters, confirmed approximately from single-crystal photographs, were refined using powder data obtained on a Guinier camera with Cu $K\bar{\alpha}$ radiation and $Pb(NO_3)_2$ as internal standard (a_0 = 7·8566 Å). Systematic absences ($h + l \neq 4n$, $k + l \neq 4n$) confirmed the space group *Fdd*2. These results agree with earlier data (Taylor *et al.*, 1933; Meier, 1960).

Approximate positions of the three independent *T* atoms (*T* = Si,Al) could easily be determined from the Patterson syntheses of the three projections using the NHPP procedure (van der Meer, 1978). The positions of the fifth O atom and one Na atom were obtained by trial and error, with the use of F_o and $F_o - F_c$ syntheses of the three projections ($\sin\theta/\lambda_{\max}$ = 0·6 Å^{-1}). The structure parameters were refined in 10 cycles with the *LALS* least-squares program (Lingren, 1975) by using isotropic thermal factors and the Cruickshank weighting scheme, yielding an *R* factor of 0·08. Subsequently, coordinates of H atoms, calculated from the angular dependence of the splitting of *p–p* doublets in the NMR spectra (Pechar, 1981), were included in the refinement. After another 10 cycles, the *R* factor decreased to 0·056.

Table 2. *Interatomic distances* (Å) *and bond angles* (°) *calculated from the final atomic coordinates*

SiO_4 tetrahedra			
Si(1)–O(1$^{\mathrm{i}}$)	1·597 (5)	Si(2)–O(3$^{\mathrm{i}}$)	1·599 (5)
Si(1)–O(5$^{\mathrm{i}}$)	1·647 (7)	Si(2)–O(4)	1·594 (5)
Si(2)–O(2)	1·638 (5)	Si(2)–O(5)	1·635 (5)
O(1)–Si(1)–O(1$^{\mathrm{i}}$)	108·56 (10)	O(2)–Si(2)–O(5)	108·18 (10)
O(1)–Si(1)–O(5)	108·81 (10)	O(3$^{\mathrm{i}}$)–Si(2)–O(4)	110·59 (10)
O(5)–Si(1)–O(5$^{\mathrm{i}}$)	110·35 (10)	O(3$^{\mathrm{i}}$)–Si(2)–O(5)	110·05 (10)
O(2)–Si(2)–O(3$^{\mathrm{i}}$)	106·69 (10)	O(4)–Si(2)–O(5)	109·56 (10)
O(2)–Si(2)–O(4)	111·84 (10)		
AlO_4 tetrahedra			
Al–O(1)	1·743 (5)	Al–O(3)	1·737 (5)
Al–O(2)	1·746 (5)	Al–O(4)	1·756 (5)
O(1)–Al–O(2)	108·29 (10)	O(2)–Al–O(3)	113·63 (10)
O(1)–Al–O(3)	109·33 (10)	O(2)–Al–O(4)	99·71 (10)
O(1)–Al–O(4)	99·05 (10)	O(3)–Al–O(4)	97·44 (10)
Cation and water			
O(*W*)–H(1)	1·071 (10)	Na–O(*W*$^{\mathrm{ii}}$)	1·758 (8)
O(*W*)–H(2)	1·017 (10)	O(*W*$^{\mathrm{i}}$)–O(*W*$^{\mathrm{ii}}$)	3·908 (8)
Na$^{\mathrm{i}}$–O(*W*)	2·392 (5)	O(2$^{\mathrm{i}}$)–O(2$^{\mathrm{ii}}$)	4·162 (10)
Na$^{\mathrm{ii}}$–O(*W*)	2·411 (5)	Na$^{\mathrm{ii}}$–H(2)	3·527 (10)
Na–O(2$^{\mathrm{i}}$)	2·532 (7)	Na$^{\mathrm{ii}}$–Na$^{\mathrm{i}}$	3·671 (5)
Na–O(3)	2·355 (7)	H(1)–H(2)	1·562 (4)
Na–O(4)	2·402 (5)	H(1)–O(1$^{\mathrm{i}}$)	1·857 (10)
Na–O(2$^{\mathrm{ii}}$)	2·599 (8)	H(2)–O(5)	2·136 (10)
Na–O(*W*$^{\mathrm{i}}$)	2·411 (8)	H(2)–O(5$^{\mathrm{i}}$)	1·878 (10)
Na$^{\mathrm{i}}$–O(*W*)–Na$^{\mathrm{ii}}$	99·58 (10)	O(*W*)–H(2)–O(5)	144·8 (10)
O(*W*$^{\mathrm{i}}$)–Na–O(*W*$^{\mathrm{ii}}$)	138·70 (10)	O(2$^{\mathrm{i}}$)–Na–O(2$^{\mathrm{ii}}$)	108·41 (10)
H(1)–O(*W*)–H(2)	96·81 (10)	O(3)–Na–O(4)	86·78 (10)
O(*W*)–H(1)–O(1$^{\mathrm{i}}$)	149·26 (10)		
Oxygens			
O(1)–O(2)	2·828 (7)	O(3)–O(4)	3·268 (6)
O(1)–O(3)	2·839 (7)	O(3$^{\mathrm{i}}$)–O(4)	2·625 (6)
O(1)–O(4$^{\mathrm{i}}$)	2·662 (7)	O(3)–O(5)	2·650 (8)
O(1)–O(5)	2·638 (10)	O(4)–O(5)	2·635 (8)
O(1)–O(1$^{\mathrm{i}}$)	3·064 (10)	O(*W*)–O(1)	2·831 (9)
O(2)–O(3)	2·915 (7)	O(*W*)–O(2)	3·325 (9)
O(2)–O(4)	2·677 (7)	O(*W*)–O(3)	3·811 (9)
O(5)–O(5$^{\mathrm{i}}$)	2·402 (6)	O(*W*)–O(4$^{\mathrm{i}}$)	2·968 (9)
O(2)–O(3$^{\mathrm{i}}$)	2·597 (6)	O(*W*)–O(5)	3·025 (9)
O(2)–O(5)	2·651 (6)		

Symmetry code: Na$^{\mathrm{i}}$ $\frac{1}{4} - x, \frac{1}{4} + y, z - \frac{3}{4}$; Na$^{\mathrm{ii}}$ $x - \frac{1}{4}, \frac{1}{4} - y, z - \frac{1}{4}$; O(1$^{\mathrm{i}}$) $x, y, z - 1$; O(2$^{\mathrm{i}}$) $\frac{1}{4} + x, \frac{1}{4} - y, \frac{1}{4} + z$; O(2$^{\mathrm{ii}}$) $\frac{1}{4} - x, y - \frac{1}{4}, z - \frac{1}{4}$; O(3$^{\mathrm{i}}$) $\frac{1}{4} - x, \frac{1}{4} + y, \frac{1}{4} + z$; O(4$^{\mathrm{i}}$) $\frac{1}{4} - x, \frac{1}{4} - y, \frac{3}{4} + z$; O(5$^{\mathrm{i}}$) $\frac{1}{4} - x, \frac{1}{4} - y, z - \frac{1}{4}$; O(*W*$^{\mathrm{i}}$) $\frac{1}{4} + x, \frac{1}{4} - y, \frac{1}{4} + z$; O(*W*$^{\mathrm{ii}}$) $\frac{1}{4} - x, \frac{1}{4} - y, \frac{3}{4} + z$.

The final positional and temperature parameters are listed in Table 1.*

Discussion. Interatomic distances and angles are given in Table 2.

Chemical analysis of the studied natrolite yielded a value of 0·60 for the Si/(Si + Al + Fe) ratio. This indicates that natrolite, according to Gottardi (1978), belongs to the ordered zeolites. The Fe atoms replace Al atoms in the tetrahedral sites. The average lengths of

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* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36136 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the Al—O and Si—O bonds are 1·746 (2) and 1·619 (2) Å respectively. In comparison with an ideal natrolite structure, 5% of the M^{1+} (M = Na,K) sites are occupied by M^{2+} (M = Ca,Mg) ions, therefore leaving another 5% vacant. Each Na(K) site is coordinated to six O atoms with an average distance of 2·45 Å forming a strongly distorted octahedron.

The application of the results of NMR measurements made it possible to determine, at least approximately, the positions of the H atoms, and from these data it follows that each water molecule participates in the formation of two hydrogen bonds [H(1)—O(1) 1·859 and H(2)—O(5) 1·878 Å] and two coordination bonds [Na—O(W) 2·412 and Na$^{\rm i}$—O(W) 2·395 Å].

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Structure of Silver(I) Nitrite, a Redetermination

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Abstract. AgNO$_2$, $M_r = 153\cdot9$, orthorhombic, $Imm2$, $a = 3\cdot528\,(1)$, $b = 6\cdot172\,(1)$, $c = 5\cdot181\,(1)$ Å, $V = 112\cdot8\,(1)$ Å^3, $Z = 2$, $D_x = 4\cdot53$ Mg m^{-3}, μ(Ag $K\alpha$) = 4·26 mm^{-1}. The structure of AgNO$_2$ has been redetermined using a four-circle diffractometer with Ag $K\alpha$ radiation. The final R value is 0·024 for 1128 observed reflections. The Ag—N distance is 2·304 (2) Å, suggesting some covalency in the Ag—N bond. A large anisotropy in the atomic thermal vibrations was found.

Introduction. The crystal structure of AgNO$_2$ was first determined by Ketelaar (1936) from rotation and powder photographs and it was reinvestigated by Long & Marsh (1962) on the basis of Weissenberg photographs. Covalent radii of Ag and N atoms are 1·34 and 0·74 Å, respectively, the sum being 2·08 Å. The Ag—N distance derived by Ketelaar was 2·07 (30) Å, indicating complete covalency, whereas Long & Marsh reported it to be 2·47 (8) Å, which suggests a primarily ionic bond. It is probable that the Ag—N bond has appreciable covalency because AgNO$_2$ possesses the character of nitro compounds (for example, Makishima & Tomotsu, 1954). The crystal structure has been reinvestigated in order to determine the Ag—N bond length more accurately.

Crystals of AgNO$_2$ were obtained by recrystallization from an acetonitrile solution of the commercial product in a dark room. Pale-yellow crystals grew as octahedra, exhibiting well developed forms of {110} and {011}. Weissenberg photographs confirmed the crystal geometry reported by Ketelaar (1936). Cell dimensions and intensity data were obtained with a spherical crystal 0·356 (16) mm in diameter on a Rigaku automated four-circle diffractometer at 300 K using Ag $K\alpha$ radiation (λ = 0·5608 Å) monochromated by a graphite plate. Cell dimensions were determined from 20 reflections ($40 < 2\theta < 46°$), and agreed well with those reported by Long & Marsh (1962) (see Table 1). Intensities were collected for 2505 reflections in a hemisphere (the $h\bar{k}l$, $\bar{h}\bar{k}l$, $h\bar{k}\bar{l}$ and $\bar{h}\bar{k}\bar{l}$ sets; $2\theta \leq 100°$), using a θ–2θ continuous-scan technique at a speed of 2° min^{-1} in θ and with a scan width of $(1\cdot3 + 0\cdot5 \tan\theta)°$. The room had been carefully kept dark in order to avoid exposing the specimen to light. During the period of data collection (8 days), intensities of the standard reflections did not decrease although the surface of the specimen turned black owing to the accumulation of metallic silver. A total of 1128 reflections with $|F_o| > 5\sigma(|F_o|)$ were

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