Refinement of the Crystal Structure of Thenardite, Na$_2$SO$_4$(V)

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The crystal structure of thenardite, Na$_2$SO$_4$(V), has been analysed and refined by the method of least squares on the basis of three-dimensional X-ray diffractometer data down to a final R value of 3.6 % for about 800 independent reflections. At 25°C the orthorhombic (*Fddd*) unit cell has the dimensions $a = 5.8596$, $b = 12.3044$, $c = 9.8170$ Å. The investigation has confirmed the general features of the atomic arrangement reported in 1932 by Zachariasen and Ziegler. The crystal structure may be described in terms of distorted NaO$_6$ octahedra and nearly regular SO$_4$ tetrahedra. All S$-$O distances in these are 1.476 ± 0.001 Å.

T his investigation was performed in order to elucidate the size and configuration of the sulphate ion as precisely as possible. For this reason the thenardite phase is convenient since all S$-$O distances are equal due to the space group (*Fddd*) where the sulphur atom is fixed in a special point position with 222 point symmetry. Moreover, it is interesting to compare the regularity and dimensions of the sulphate ion in different sulphates.

The phase diagram of sodium sulphate shows some very interesting features. According to Gmelin[1] there are eight different anhydrous phases of sodium sulphate. The crystallographic data of most of these phases are quite unsatisfactory and insufficient. The phase Na$_2$SO$_4$(V) is usually called thenardite after the mineral. It is reported to be stable between 32°C and about 180°C.[1] It seems that the presence of traces of H$_2$O in inclusions changes the conditions for the stability of thenardite.[2]

The present results have confirmed the general features of the atomic arrangement reported in 1932 by Zachariasen and Ziegler.[3]

EXPERIMENTAL

Preparation of the crystals. When a water solution of sodium sulphate is evaporated above 32°C, crystals of thenardite are formed (but below 32°C Na$_2$SO$_4$.10H$_2$O crystals are obtained). There are several contradictory recommendations in the literature as to

proper conditions for the evaporation process.[1,2] A fairly quick evaporation overnight at 70°C gave the most well-developed crystals. This was the best result from a series of experiments. These crystals also gave the most distinct powder diffraction pattern. The sample contained small amounts of moisture; on ignition the loss of H_2O was 0.14 %.

X-Ray powder diffraction data. The powder pattern of the sample was found to be in good accordance with the data given by Swanson and Fuyat.[4] Values for the cell dimensions were calculated from a photograph taken with strictly monochromatized $CuK\alpha_1$ radiation ($\lambda = 1.54050$ Å) in a Guinier-Hägg type focusing camera. Potassium chloride ($a = 6.29228$ Å)[5] was used as an internal standard. The lattice parameters were

Table 1. X-Ray powder data for Na_2SO_4(V) at 25°C. $CuK\alpha_1$ radiation ($\lambda = 1.54050$ Å).

hkl	$\sin^2\theta$ obs	$\sin^2\theta$ calc	I_{obs}	d (Å) obs	d (Å) calc
111	0.02736	0.02735	60	4.6567	4.6572
022	0.04028	0.04030	16	3.8378	3.8369
131	0.05873	0.05870	47	3.1784	3.1791
040	0.06278	0.06270	41	3.0742	3.0761
113	0.07660	0.07660	100	2.7830	2.7830
220	0.08478	0.08479	45	2.6453	2.6452
202	0.09370	0.09374	1	2.5163	2.5158
004	0.09859	0.09850	1	2.4531	2.4542
133	0.10799	0.10795	5	2.3439	2.3443
222	0.10931	0.10940	22	2.3297	2.3287
151	0.12142	0.12140	4	2.2105	2.2106
044	0.16124	0.16120	4	1.9182	1.9185
311	0.16562	0.16559	2	1.8927	1.8929
153	0.17070	0.17065	47	1.8643	1.8646
115	0.17508	0.17510	6	1.8408	1.8407
224	0.18336	0.18330	6	1.7988	1.7991
260	0.21026	0.21019	21	1.6798	1.6801
313	0.21490	0.21484	12	1.6616	1.6618
244	0.23030	0.23031	6	1.6050	1.6050
262	0.23472	0.23481	3	1.5898	1.5895
026	0.23732	0.23730	3	1.5811	1.5812
333	0.24618	0.24619	20	1.5524	1.5524
351	0.25967	0.25964	3	1.5116	1.5116
173	0.26471	0.26470	10	1.4971	1.4971
400	0.27651	0.27647	1	1.4648	1.4649
206	0.29073	0.29074	11	1.4285	1.4285
371	0.35370	0.35369	4	1.2951	1.2951

refined from 27 reflections (Table 1) by the method of linear regression using the program POWDER.[6] The dimensions of the orthorhombic unit cell (with standard deviations) at 25°C are:

$$a = 5.8596 \pm 5 \text{ Å} \qquad (5.863)$$
$$b = 12.3044 \pm 12 \text{ Å} \qquad (12.304) \quad \text{Ref. 4.}$$
$$c = 9.8170 \pm 10 \text{ Å} \qquad (9.821)$$

From X-ray photographic methods (oscillations and Weissenberg photographs around the a and c axes) the space group was, from the reflections systematically absent, uniquely determined as No. 70, $Fddd$[7] in agreement with Zachariasen and Ziegler. The crystal selected for collection of X-ray data had the dimensions 0.15 mm (in the direction of the c axis) × 0.06 mm × 0.03 mm and was mounted along the c axis. The X-ray intensity data were collected with $\theta - 2\theta$ scan technique on an automatic single-

crystal diffractometer Siemens AED (Automatischer Einkristall-Diffraktometer) equipped with a graphite monochromator and a scintillation detector. MoKα radiation was used. All independent reflections with $\theta \lesssim 50°$ were measured at a temperature of 22°C. Punched paper tape was used as input/output medium for the diffractometer. The computer programs used for the calculations involved in the present work are summarized in Table 9. A survey of the IBM 360/75 programs used at this institute is also given in a paper by Brandt and Nord.[8]

All reflections with $\sigma(I_{net})/I_{net} < 0.50$ were accepted leaving 812 reflections from about 900 measured ones. The net intensities were corrected for Lorentz, polarization and absorption ($\mu = 10.3$ cm^{-1}) effects.

REFINEMENT OF THE CRYSTAL STRUCTURE

All atom position parameters were readily determined from peaks in a three-dimensional Patterson function $P(uvw)$. These parameters agreed within a few per cent with those given by Zachariasen and Ziegler. The crystal structure was then refined by the full-matrix least-squares program LALS minimizing $\sum w(|F_{obs}| - |F_{calc}|)^2$. Hughes' weighting function[9] with $h = 4$ was used in the final refinements. The atomic scattering curves applied were those for S^0, Na^+, and O^-. Correction was made for the real part of the anomalous dispersion. After a few cycles with isotropic temperature factors the reliability index $R = \sum||F_{obs}| - |F_{calc}||/\sum|F_{obs}|$ dropped to 5.0 %. When all atoms in the model were allowed to vibrate anisotropically (within the restrictions fixed by the space group symmetry) the final R was reduced to 3.6 % for all 812 reflections. This large drop in weighted and unweighted R values from the isotropically to the anisotropically refined model enables the Hamilton test[10] to show, that the model with anisotropically vibrating atoms is the more realistic one. The weighting scheme obtained in the final cycle of the anistropic refinement is shown in Table 2. Reflections with $1.20 < |F_{obs}/F_{calc}| < 0.70$ were given zero weight in the refinement.

A list of the observed and calculated structure factors is presented in Table 3. The atomic parameters arrived at in the last cycle of anisotropic refinement are listed in Table 4. The temperature factors obtained in the

Table 2. Weight analysis obtained in the final cycle of the anisotropic least-squares refinement of thenardite. w = weighting factor, $\Delta = ||F_{obs}| - |F_{calc}||$.

Interval F_{obs}	$\overline{w\Delta^2}$	Number of independent reflections	Interval $\sin\theta$	$\overline{w\Delta^2}$	Number of independent reflections
0.0 — 7.4	1.08	75	0.000 — 0.362	1.35	84
7.4 — 9.3	1.15	76	0.362 — 0.456	1.31	93
9.3 — 11.5	1.08	76	0.456 — 0.522	1.11	81
11.5 — 13.6	0.91	75	0.522 — 0.575	0.96	85
13.6 — 16.5	0.88	77	0.575 — 0.619	0.88	81
16.5 — 20.3	0.90	75	0.619 — 0.658	0.77	82
20.3 — 26.4	0.86	75	0.658 — 0.693	0.85	70
26.4 — 35.9	1.31	74	0.693 — 0.724	0.97	66
35.9 — 51.8	0.97	75	0.724 — 0.753	0.81	68
51.8 — 206.1	0.87	76	0.753 — 0.780	0.72	44

Table 3. Observed and calculated structure factors of thenardite, $Na_2SO_4(V)$.

h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c

Table 4. The crystal structure of $Na_2SO_4(V)$, thenardite.

Space group: (No. 70)   *Fddd*.

Unit cell dimensions: $a = 5.8596 \pm 5$ Å
$b = 12.3044 \pm 12$ Å
$c = 9.8170 \pm 10$ Å
$V = 707.8$ Å^3. $D_{calc} = 2.666$ g/cm^3, $D_{obs} = 2.65$ g/cm^3.

Cell content: $8Na_2SO_4$.

Arrangement of atoms (f denotes translations characteristic of a face centered lattice):
8 S in   8(a): $\pm (\frac{1}{8}, \frac{1}{8}, \frac{1}{8})_f$
16 Na in 16(g): $\pm (\frac{1}{8}, \frac{1}{8}, z)_f, \pm (\frac{1}{8}, \frac{1}{8}, \frac{1}{4} - z)_f$
32 O in 32(h): $\pm (x, y, z)_f, \pm (x, \frac{1}{4} - y, \frac{1}{4} - z)_f, \pm (\frac{1}{4} - x, y, \frac{1}{4} - z)_f \pm (\frac{1}{4} - x, \frac{1}{4} - y, z)_f$

Fractional atomic coordinates

Atom	$x \pm \sigma(x)$	$y \pm \sigma(y)$	$z \pm \sigma(z)$
S	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$
Na	$\frac{1}{8}$	$\frac{1}{8}$	0.4414 ± 1
O	-0.0203 ± 2	0.0572 ± 1	0.2137 ± 1

Anisotropic thermal parameters ($\times 10^5$).
$$T = \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)].$$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	518 ± 6	113 ± 2	206 ± 3	0	0	0
Na	926 ± 11	192 ± 3	432 ± 5	35 ± 8	0	0
O	1041 ± 12	207 ± 3	345 ± 5	-297 ± 10	319 ± 12	65 ± 5

isotropic refinement were $B_S = 0.74 \pm 0.01, B_{Na} = 1.30 \pm 0.02, B_O = 1.29 \pm 0.02$ Å^2. A three-dimensional ΔF Fourier synthesis was then computed with the anisotropic model. This showed no peak or hole greater than 0.6 eÅ^{-3}. A close inspection of Table 3 shows that the extinction effects are so small that they are negligible.

DESCRIPTION AND DISCUSSION OF THE CRYSTAL STRUCTURE

The crystal structure may be described in terms of nearly regular SO_4 tetrahedra and distorted NaO_6 octahedra. In fact, the NaO_6 octahedra are more distorted than Zachariasen and Ziegler reported. The interatomic distances and standard deviations (σ) and some angles of interest are listed in Table 5. No corrections have been made for the thermal vibration.

The sodium atoms are each surrounded by 6 oxygen atoms, two at 2.334 Å, two at 2.426 Å, and two at 2.534 Å, forming distorted NaO_6 octahedra with a 2-fold axis parallel to the c axis. These $Na-O$ distances are quite in accordance with those reported in other compounds, *e.g.* Na_2SO_4 $10H_2O$.[11] All the sulphate ions are separated from each other by distances > 3 Å for two oxygen

Table 5. Interatomic distances (Å) with standard deviations and some angles in $Na_2SO_4(V)$. All angles have standard deviations of $\pm 0.05°$ or less. No corrections have been made for thermal vibration. Atom denotations used in Table 5, Table 7, and Fig. 2: S, Na, and O(1) in (x, y, z), O(2): $(x, \frac{1}{4}-y, \frac{1}{4}-z)$, O(3): $(\frac{1}{4}-x, y, \frac{1}{4}-z)$, O(4): $(\frac{1}{4}-x, \frac{1}{4}-y, z)$, O(5): $(\frac{1}{2}+x, \frac{1}{4}-y, \frac{3}{4}-z)$, O(6): $(\frac{1}{4}+x, -y, \frac{1}{4}+z)$, O(7): $(-\frac{1}{4}-x, y, \frac{3}{4}-z)$, O(8): $(-x, \frac{1}{4}+y, \frac{1}{4}+z)$. Oxygen-oxygen edges shared by SO_4 and NaO_6 are marked (*).

|				
SO₄ group	S — O(1,2,3,4)	1.476 ± 1	O(1) — S — O(2)	109.55°
	O(1) — O(2)	2.412 ± 2	O(1) — S — O(3)	111.15°
	O(1) — O(3)	2.435 ± 2	O(1) — S — O(4)	107.74°
	O(1) — O(4)*	2.384 ± 2	Average:	109.48°
NaO₆ group	Na — O(1,4)	2.534 ± 1	O(1) — Na — O(4)	56.13°
	Na — O(5,7)	2.426 ± 1	O(1) — Na — O(6)	81.64°
	Na — O(6,8)	2.334 ± 1	O(6) — Na — O(7)	81.89°
			O(1) — Na — O(7)	86.43°
	O(1) — O(4)*	2.384 ± 2	O(7) — Na — O(8)	93.97°
	O(6) — O(7)	3.120 ± 2	O(1) — Na — O(8)	108.09°
	O(1) — O(6)	3.186 ± 2	O(5) — Na — O(7)	134.82°
	O(1) — O(7)	3.397 ± 2	O(1) — Na — O(5)	137.74°
	O(7) — O(8)	3.481 ± 2	O(6) — Na — O(8)	169.27°
	O(1) — O(8)	3.942 ± 2		
	O(5) — O(7)	4.479 ± 2		
	O(1) — O(5)	4.626 ± 2		
	O(6) — O(8)	4.648 ± 2		
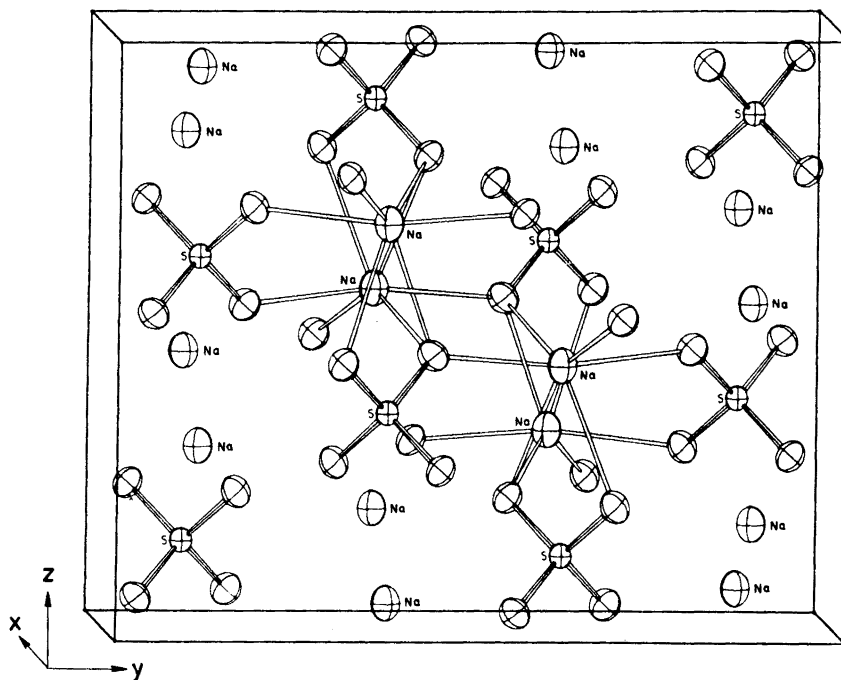
Fig. 1. The crystal structure of thenardite. One unit cell with eight sulphate ions and four NaO_6 octahedra is shown.

atoms belonging to different sulphate groups (Table 5). The SO_4 tetrahedra
are nearly regular. All $S-O$ distances are equal, 1.476 ± 0.001 Å, due to the
space group since the sulphur atom is fixed in a special point position with
222 point symmetry. Each SO_4 tetrahedron shares two of its edges with
two different NaO_6 octahedra. The longest $Na-O$ distance of 2.534 Å re-
presents the distances to oxygens forming the shared tetrahedral edge. The
remaining corners of the NaO_6 octahedron are shared with another four SO_4
tetrahedra thus giving a three-dimensional framework. Fig. 1 shows a three-
dimensional model of the crystal structure. It has been produced by the plot
program ORTEP.[12] Fig. 2 is an ORTEP plot picture showing one NaO_6
octahedron.
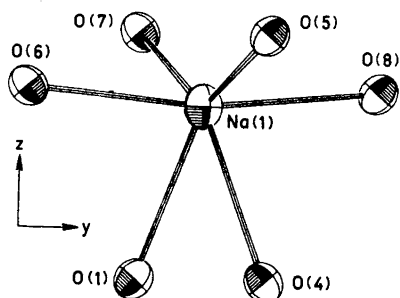
Fig. 2. One NaO_6 octahedron showing
the coordination of oxygen atoms around
a sodium atom in thenardite. The atoms
have been numbered as in Tables 5 and 7.

Table 6. Analysis of anisotropic thermal parameters.

Atom	Axis	Root of mean square amplitude (Å)	R.m.s. radial thermal displacement (Å)
S	1	0.093	
	2	0.095	0.167
	3	0.100	
Na	1	0.120	
	2	0.128	0.228
	3	0.145	
O	1	0.094	
	2	0.136	0.226
	3	0.154	

Table 7. Some interatomic distances (Å) in thenardite.

	Uncorrected	"Independent"
$S-O(1,2,3,4)$	1.476	1.497
$O(1)-O(2), O(3)-O(4)$	2.412	2.427
$O(1)-O(3), O(2)-O(4)$	2.435	2.451
$O(1)-O(4), O(2)-O(3)$	2.384	2.401
$Na-O(1)$	2.534	2.546
$Na-O(5)$	2.426	2.440
$Na-O(6)$	2.334	2.350

Table 8. Data for sulphate groups. Uncorrected and corrected S—O bond distances (in Å) are given for six carefully determined sulphate structures. The corrected distances have all been calculated in the same manner, *i.e.* assuming the riding motion model.

Compound: Ref.:	$Na_2SO_4(V)$ This work	$Li_2SO_4.H_2O$ Larson [14]	$MgSO_4.4H_2O$ Baur [15]	$MgSO_4.7H_2O$ Baur [16]	$FeSO_4.7H_2O$ Baur [17]	β-K_2SO_4 McGinnety [18]
Uncorr. bond dist.						
Shortest	1.476 ± 1	1.462 ± 2	1.466 ± 5	1.460 ± 4	1.462 ± 4	1.459 ± 4
Longest	1.476 ± 1	1.482 ± 2	1.480 ± 4	1.482 ± 4	1.488 ± 4	1.473 ± 4
Average	1.476	1.472	1.473	1.471	1.474	1.469
Corrected bond dist.						
Average	1.484	1.480	1.479	1.486	1.486	1.486

Table 9. Computer programs used for the crystallographic calculations. All programs are written in FORTRAN IV for an IBM 360/75 computer except program SIMSA.

Program name and function	Authors
1. LAZY. Calculation of $\sin^2\theta$- and d-values from a Guinier powder photograph after internal standard correction.	A. G. Nord, Stockholm, Sweden.
2. POWDER. Refinement of cell constants. Ref. 6.	O. Lindqvist and F. Wengelin, Göteborg. Modified by A. G. Nord and B. G. Brandt, Stockholm, Sweden.
3. SIP. Generation of steering paper tape for Siemens AED.	R. Norrestam, Stockholm, Sweden.
4. SIMSA. Interpretation and evaluation of paper tape output from Siemens AED. IBM 1800.	R. Norrestam, Stockholm, Sweden.
5. DATAP2. Lp- and absorption correction.	P. Coppens, L. Leiserowitz and D. Rabinovich, Rehovath, Israel. Modified by O. Olofsson and M. Elfström, Uppsala. Further modifications by S. Åsbrink, B. G. Brandt and A. G. Nord, Stockholm, Sweden.
6. DRF. Fourier summations and structure factor calculations.	A. Zalkin, Berkeley, USA. Local modification.
7. LALS. Full matrix least squares refinement of positional and thermal parameters.	P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, Los Angeles, USA. Modified by A. Zalkin, J. O. Lundgren, R. Liminga, C. I. Brändén, A. G. Nord and B. G. Brandt.
8. DISTAN. Calculation of interatomic distances and bond angles with e.s.d.	A. Zalkin, Berkeley, USA. Local modification.
9. ORFFE. Crystallographic function and error program. Ref. 13.	W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge, USA. Modified by L. Kihlborg, Stockholm, Sweden.
10. ORTEP. Thermal ellipsoid plot program for crystal structure illustrations. Ref. 12.	C. K. Johnsson, Oak Ridge, USA.

The anisotropic thermal parameters were analysed to find the axes of the ellipsoids. Some results from program ORFFE are presented in Table 6. The character of thermal vibration may also be studied in Figs. 1 – 2. Table 7 contains some bond lengths in thenardite corrected due to thermal motion. The effect of thermal motion on the distances is calculated assuming the "independent motion" model.[13]

Pertinent data relating to the sulphate group in some compounds are given in Table 8. All "corrected" S – O distances have been calculated in the same manner, i.e. assuming the "riding motion" model.[13] Although the ligand atoms of the different sulphate groups vary, all uncorrected S – O distances as well as all corrected ones are nearly identical. The S – O distances within each sulphate group are also very similar, but the differences exceed the reported standard deviations. However, all these facts show that the sulphate ion in the compounds discussed is fairly stable and it also possesses a high degree of regularity.

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