

ANHYDROUS SULPHATES. I : REFINEMENT OF THE CRYSTAL STRUCTURE OF CELESTITE WITH AN APPENDIX ON THE STRUCTURE OF THENARDITE

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ABSTRACT

Three-dimensional counter-diffractometer data and a full-matrix least-squares method have been used to refine the crystal structure of celestite, SrSO_4 , $a = 8.360(1)$, $b = 5.352(1)$, $c = 6.858(1)\text{\AA}$, space group $Pnma$. The final R -factor for 355 observed reflections was 4.1%.

Bond-strength considerations show that the Sr atom is twelve-coordinate, resulting in formal charge balance of all anions. Structural distortion can be related to the geometry of the large cation site and cation-cation repulsions. Celestite is isostructural with barite and anglesite, and the geometry of the tetrahedral SO_4 group is identical in all three structures. A type I stability diagram for the divalent metal sulphates of the form $M^{2+}\text{SO}_4$ shows that anhydrite (CaSO_4) is intermediate between the barite structures (M^{2+} coordination = 12) and the nickel sulphate structures (M^{2+} coordination = 6), and lies in the stability field of the mercuric sulphate structures (M^{2+} coordination = 4). However, the ionic radius of Ca^{2+} is incompatible with the bond strength requirements of tetrahedral coordination for a third row cation, thus forcing CaSO_4 to crystallize in a structure with a higher M^{2+} (and anion) coordination number.

INTRODUCTION

Celestite is the most common strontium mineral in the earth's crust and is the main commercial source of strontium. Although it does occur as a primary phase in hydrothermal veins, its principal parageneses are sedimentary environments. It is commonly found as fissure and cavity fillings in dolomitic limestones and as concretions and nodules in clays and marls.

Celestite (SrSO_4) is isostructural with barite (BaSO_4) and anglesite (PbSO_4), the structures of which were first determined by James & Wood (1925). Two-dimensional refinements of barite and anglesite by Sahl (1963) confirmed the structures suggested by James & Wood (1925). A refinement of the structure of celestite was reported by Garske & Peacor (1965); however, the S-O distances listed by them are rather large ($\langle \text{S-O} \rangle = 1.52\text{\AA}$) and they suggested that further refinement of all three structures was desirable. An accurate refinement of the struc-

ture of barite was presented by Colville & Staudhammer (1967); this showed that the S-O distances given for barite by Sahl (1963) were too long, and that the refined bond lengths were in fact statistically identical to those of anglesite. Comparison of the S-O bond lengths in barite (Colville & Staudhammer 1967) and anglesite (Sahl 1963) with those of celestite (Garske & Peacor 1965) showed that differences of up to 0.1\AA occur. The structure of celestite was refined in this study to compare the geometry of the sulphate group in this series, and to examine the relationship between these minerals and the structure of anhydrite which has recently been refined (Hawthorne & Ferguson, 1975a).

EXPERIMENTAL

The crystals used in this investigation were from Bristol, England. Single-crystal precession photographs confirmed the space group $Pnma$ and least-squares refinement of 15 reflections automatically aligned on a 4-circle diffractometer gave the following cell dimensions: $a = 8.360(1)$, $b = 5.352(1)$, $c = 6.858(1)\text{\AA}$, $V = 306.81\text{\AA}^3$. These values correspond closely to those for synthetic SrSO_4 (Swanson & Fuyat 1953), indicating no significant solid solution of other components in the structure.

The crystal used in the collection of the intensity data was a regular cleavage fragment which showed sharp extinction under the polarizing microscope and had ~ 0.15 mm average dimension. The experimental procedure was as described by Hawthorne & Ferguson (1975b). A total of 548 reflections were collected out to a value of $65^\circ 2\theta$ ($\text{MoK}\alpha$ radiation). The crystal faces were indexed using a spindle stage with an over-all geometry corresponding to that of the χ and ϕ circles of the diffractometer together with the calculated setting angles for the data collection. Polyhedral absorption corrections were carried out with maximum and minimum transmission factors of 6.91 and 3.54 respectively. This was followed by the standard corrections for Lorentz, polarization and background effects. A reflection was considered as

observed if its magnitude exceeded four standard deviations based on counting statistics; this resulted in 355 observed reflections.

REFINEMENT

Neutral scattering factors were taken from Cromer & Mann (1968) with anomalous dispersion corrections from Cromer & Liberman (1970). The final atomic parameters of Garske & Peacor (1965) were used as input to the least-squares program RFINE (Finger 1969). Full matrix refinement of all variables for an isotropic thermal model resulted in convergence at R -

and R_w -factors¹ of 5.3 and 5.6% respectively (observed data only). Temperature factors were converted to anisotropic of the form

$$\exp \left[- \sum_{i=1}^3 \sum_{j=1}^3 h_i h_j \beta_{ij} \right]$$

and a correction was made for (isotropic) extinction (Zachariasen 1968) with the extinction coefficient included as a variable in the refine-

$$^1R = \frac{\sum [|F_{\text{obs}}| - |F_{\text{calc}}|]}{\sum |F_{\text{obs}}|};$$

$$R_w = \left[\frac{\sum w [|F_{\text{obs}}| - |F_{\text{calc}}|]^2}{\sum w |F_{\text{obs}}|^2} \right]^{1/2}, w = 1$$

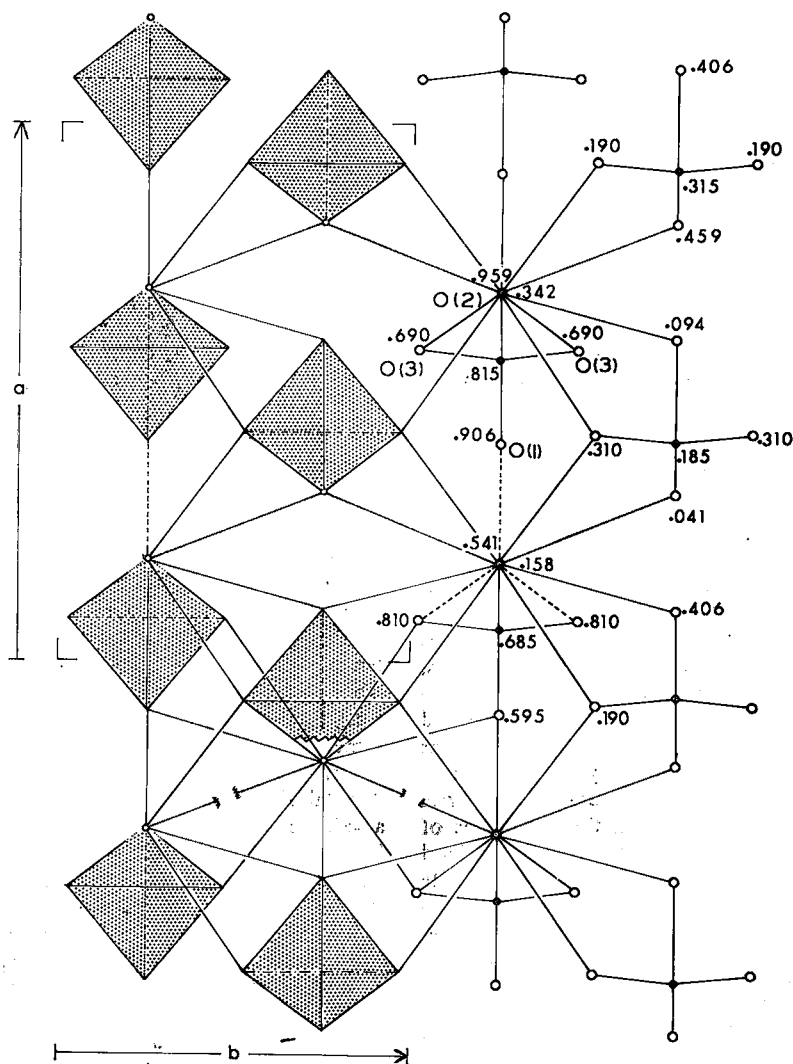


FIG. 1. The crystal structure of celestite viewed down the c -axis.

thermal ellipsoids were calculated with the program ERRORS (L. W. Finger, personal communication) and are presented in Tables 4 and 5 respectively.

DISCUSSION

The structure of celestite consists of isolated (SO₄) tetrahedra linked by Sr atoms, as shown in Figure 1. The six shortest Sr-O bonds link together a layer of tetrahedra in the X-Y plane, and these layers are bonded together by the longer (weaker) Sr-O bonds; this accounts for the perfect (001) cleavage exhibited by the minerals of this group. The tetrahedral bond lengths and angles obtained here are statistically identical with those of barite and anglesite (see Table 6) and differ significantly from those reported by Garske & Peacor (1965). This indicates that the tetrahedral distortions that do occur in this series

TABLE 2. ATOMIC POSITIONS AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS FOR CELESTITE

	x	y	z	B _{equiv.}
Sr	0.1841 (1)	1/4	0.1582 (2)	0.85 (2)
S	0.4379 (3)	3/4	0.1849 (3)	0.53 (4)
O(1)	0.5970 (9)	3/4	0.0937 (10)	1.56 (14)
O(2)	0.3101 (9)	3/4	0.0406 (11)	1.34 (13)
O(3)	0.4219 (6)	0.9745 (9)	0.3101 (7)	1.00 (9)

TABLE 3. ANISOTROPIC TEMPERATURE FACTORS FOR CELESTITE

	β ₁₁	β ₂₂	β ₃₃	β ₁₂	β ₁₃	β ₂₃
Sr	0.00289 (11)	0.01022 (32)	0.00334 (16)	0	0.00010 (18)	0
S	0.00284 (27)	0.0044 (64)	0.00182 (44)	0	0.00009 (30)	0
O(1)	0.00325 (95)	0.01042 (348)	0.00814 (154)	0	0.00325 (94)	0
O(2)	0.00495 (84)	0.01082 (301)	0.00612 (134)	0	-0.00191 (98)	0
O(3)	0.00397 (69)	0.00548 (140)	0.00668 (91)	-0.00107 (94)	0.00077 (76)	-0.00082 (91)

TABLE 4. SELECTED INTERATOMIC DISTANCES AND ANGLES FOR CELESTITE

		Sr-O(1)	2.516 (8)
		Sr-O(1) x2	3.254 (6)
		Sr-O(2) x2	2.987 (4)
		Sr-O(2) x2	2.622 (8)
		Sr-O(3) x2	2.688 (6)
		Sr-O(3) x2	2.651 (8)
		Sr-O(3) x2	2.816 (6)
		<Sr-O>	2.827
		O(1)-S-O(2)	112.0 (5)°
		O(1)-S-O(3) x2	109.1 (3)
		O(2)-S-O(3) x2	109.1 (3)
		O(3)-S-O(3)	108.2 (4)
		<O-S-O>	109.5
		O(1)-O(2)	2.426 (14)
		O(1)-O(3) x2	2.406 (9)
		O(2)-O(3) x2	2.495 (9)
		O(3)-O(3)	2.403 (11)
		<O-O>	2.405
		S-O(1)	1.470 (8) Å
		S-O(2)	1.466 (9)
		S-O(3) x2	1.483 (6)
		<S-O>	1.473

TABLE 5. MAGNITUDE AND ORIENTATION OF THE PRINCIPAL AXES OF THE THERMAL ELLIPSOIDS FOR CELESTITE

	R.M.S. displacement (Å) ²	Angle to a-axis in degrees	Angle to b-axis in degrees	Angle to c-axis in degrees
Sr	0.089 (2)	100 (16)	90	10 (16)
	0.098 (2)	170 (16)	90	100 (16)
	0.122 (2)	90	0	90
S	0.066 (7)	93 (10)	90	3 (10)
	0.080 (6)	90	0	90
	0.097 (5)	3 (10)	90	87 (10)
O(1)	0.073 (25)	34 (9)	90	124 (9)
	0.160 (15)	124 (9)	90	147 (9)
	0.168 (15)	90	0	90
O(2)	0.104 (22)	57 (8)	90	33 (8)
	0.128 (14)	90	0	90
	0.154 (14)	33 (8)	90	123 (8)
O(3)	0.084 (13)	73 (17)	18 (15)	85 (16)
	0.113 (12)	41 (22)	100 (21)	129 (22)
	0.135 (10)	55 (21)	105 (12)	39 (22)

of structures are a function of the geometry of the structure rather than the chemistry of the large cation. The Sr is surrounded by twelve oxygens; six of these lie between 2.5 and 2.7 Å and bond in the plane of the sheet, four lie between 2.8 and 3.0 Å and the remaining two lie further out at 3.25 Å. Examination of the bond strength table for celestite (see Table 7), calculated using the bond-strength curves of Brown & Shannon (1973) and Brown (1975), shows that all twelve Sr-O interactions are significant. Disregarding the two longest Sr-O interactions (3.254 Å) leads to low bond-strength sums around O(1) and Sr; these discrepancies disappear with the inclusion of these two long bonds to O(1). The coordination polyhedron of Sr is shown in Figure 2a; it consists of a distorted tetrahedron with the triangular base above the Sr and the tetrahedral apex below, with an additional eight staggered meridional anions. This coordination somewhat resembles that of the Ca(2) polyhedron in merwinite (Moore & Araki 1972; Moore 1973) with an additional two meridional anions. This is illustrated in Figures 2c and d which show the corresponding 10-coordinate Sr polyhedron as compared with the ideal merwinite Ca(2) polyhedron.

As is apparent from Table 7, all oxygens are four-coordinate and thus formally charge-balanced. However, the Sr-O distances vary greatly, both because of the site geometry and because of distortion due to cation-cation repulsion. Thus

TABLE 6. COMPARISON OF S-O DISTANCES AND ANGLES FOR BARITE, CELESTITE AND ANGLESITE³

	Barite ¹	Celestite ²	Anglesite ³
S-O(1)	1.472 (7) Å	1.470 (8) Å	1.47
S-O(2)	1.448 (7)	1.456 (9)	1.42
S-O(3) x2	1.484 (5)	1.483 (6)	1.48
	1.472	1.473	1.46
O(1)-S-O(2)	111.8 (5)°	112.0 (5)°	112
O(1)-S-O(3) x2	109.8 (3)	109.1 (3)	110
O(2)-S-O(3) x2	108.6 (3)	109.1 (3)	108
O(3)-S-O(3)	108.2 (3)	108.2 (4)	109
	109.5	109.5	109.5

¹Coville & Staudhammer (1967) ²This study ³Sahl (1963)

TABLE 7. BOND STRENGTH TABLE* FOR CELESTITE

	S	Sr	Σ [†]
O(1)	1.512	0.325 0.054 [‡]	1.945 (1.837) [†]
O(2)	1.589	0.244 0.098 [‡]	2.029
O(3)	1.469 [‡]	0.206 [‡] 0.226 [‡] 0.148 [‡]	2.049
Σ [†]	6.039	2.033 (1.925) [†]	

* Calculated from the curves of Brown & Shannon (1973) and Brown (1975).

[†] Values in parentheses are for a Sr coordination of [10].

a distortion is induced in the SO_4 tetrahedra that compensates for this with a shortening of $\text{S-O}(2)$ and lengthening of the $\text{S-O}(3)$ bonds.

Four major structure types occur in the divalent metal sulphates of the form M^{2+}SO_4 . Figure 3 shows a type I stability diagram (Shannon & Prewitt 1970a) for three of these types, the nickel sulphate group ($\text{M}^{2+} = \text{Ni, Mg, Co, Fe}$ and Mn), the mercuric sulphate group ($\text{M}^{2+} = \text{Hg}$ and Cd) and the barite group ($\text{M}^{2+} = \text{Sr, Pb}$ and Ba). The copper sulphate group ($\text{M}^{2+} = \text{Cu, Zn, Co}^1$ and Mg^1) was omitted for clarity. Despite the fact that only octahedral cation radii were used in the diagram, these structure types are easily distinguished with boundaries between the stability fields at about 0.90 and 1.07 Å. The transition from the barite stability field to the mercuric sulphate stability field, which occurs at ~ 1.07 Å, involves a change in the large cation coordination number from [12] to [4]. The octahedral radius of Ca^{2+} places anhydrite in the mercuric sulphate stability field; however, Ca is not compatible with tetrahedral coordination. It should be noted that this is not entirely a function of ionic radius, as the occurrence of Cd and Hg in tetrahedral coordination implies that an ion the size of Ca^{2+} could occur in this coordination, since for other coordinations Ca^{2+} is intermediate in size between Cd^{2+} and Hg^{2+} (Shannon & Prewitt 1969, 1970b). While this may be rationalized as the inability of Ca to form the significantly covalent bonds necessary for this coordination, this is not implicit in the use of cation radii in this context as "these radii

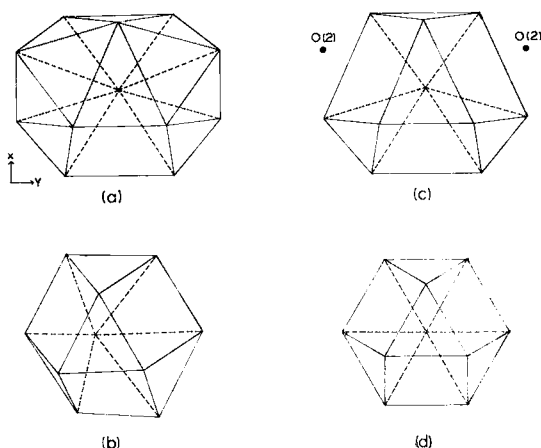


FIG. 2. (a) the [12]-coordinated Sr site in celestite; (b) the [10]-coordinated Ca(2) site in merwinite; (c) the coordination of Sr in celestite, treated as [10] + [2] (note that the O(2) atoms in the figure are not the furthest anions from Sr); (d) the ideal Ca(2) coordination polyhedron in merwinite.

are empirical and include effects of covalence in specific metal oxygen . . . bonds" (Shannon & Prewitt 1969). Another way of approaching this question is to consider the bond strength requirements of the anions in the mercuric sulphate structures. For Ca in tetrahedral coordination, a mean bond strength of 0.5 v.u. is required; using the bond strength curves of Brown & Shannon (1973), the necessary Ca-O^{IV} distance may be calculated, giving a value of 2.10 Å. An ionic radius for tetrahedrally coordinated Ca

¹high-temperature modification.

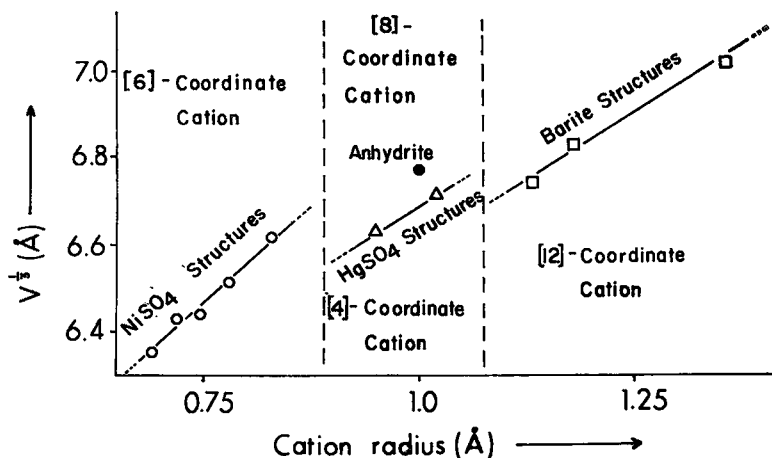


FIG. 3. Type I stability diagram for the divalent metal sulphates M^{2+}SO_4 . The copper sulphate structures have been omitted for clarity.

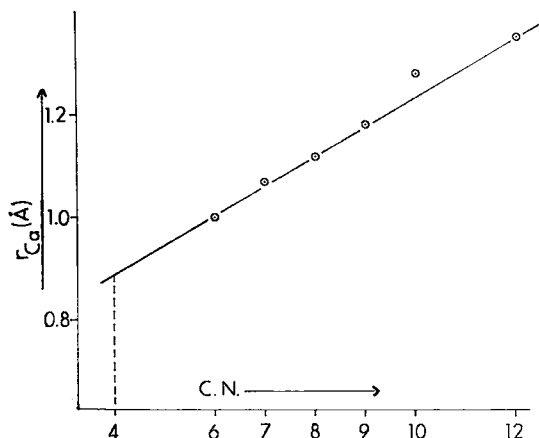


FIG. 4. Ionic radius of Ca^{2+} versus cation coordination number.

may be obtained by extrapolation in Figure 4, giving a value of 0.88\AA , and an expected Ca-O^{IV} distance (based solely on an ionic radius criterion) may be obtained by interpolation between the mean bond lengths for HgSO_4 and CdSO_4 (based on the listed octahedral radii). The expected mean bond lengths based on ionic radii sums are compared with the observed (and interpolated) mean bond lengths below:

$$\begin{aligned} \text{CdSO}_4 & 0.80\text{\AA} + 1.35\text{\AA} = 2.15\text{\AA} \\ \text{Observed Cd-O}^{\text{IV}} & = 2.17\text{\AA} \end{aligned}$$

$$\begin{aligned} \text{HgSO}_4 & 0.96\text{\AA} + 1.35\text{\AA} = 2.31\text{\AA} \\ \text{Observed Hg-O}^{\text{IV}} & = 2.28\text{\AA} \end{aligned}$$

$$\begin{aligned} \text{CaSO}_4 & 0.88\text{\AA} + 1.35\text{\AA} = 2.23\text{\AA} \\ \text{Interpolated Ca-O}^{\text{IV}} & = 2.25\text{\AA} \end{aligned}$$

Based solely on an ionic radius criterion, the agreement here is quite good. However, it was shown above that the anions require a Ca-O^{IV} distance of 2.10\AA to balance the bond strengths, a very large deviation from the above values for Ca. It has been shown (Brown & Shannon 1973) that covalence is related to bond strength, shorter bonds being associated with higher covalence. Thus the previous qualitative conclusion that Ca will not occur in tetrahedral coordination because of its inability to form covalent bonds may be put on a more quantitative basis. The bond strength requirements of the anions require a bond covalence (0.17 v.u.) that is incompatible with the empirical ionic radius of Ca^{IV} which indicates a maximum possible covalence of 0.10 v.u. Consequently, CaSO_4 must crystallize in a structure with a higher cation coordination number.

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APPENDIX

THE CRYSTAL STRUCTURE OF THENARDITE

As part of a continuing study of anhydrous sulphates, the crystal structure of thenardite (Na_2SO_4) was refined. While this work was in progress, an account of the crystal structure of a synthetic thenardite, $\text{Na}_2\text{SO}_4(\text{V})$ was published (Nord 1973). As our results on the natural mineral confirm those of the synthetic phase, this account will be confined to a brief presentation of results.

The material used in this investigation was from Borax Lake, California. Single-crystal precession photographs exhibited orthorhombic symmetry with systematic absences compatible with the space group $Fddd$. Cell dimensions were determined as for celestite, giving the following values: $a = 9.829(1)$, $b = 12.302(2)$, $c = 5.868(1)\text{\AA}$. These are close to those of synthetic $\text{Na}_2\text{SO}_4(\text{V})$ and this composition was assumed for the purposes of refinement. The experimental method was as described above. A total of 742 reflections were collected over two asymmetric units; standard data reduction procedures (no absorption corrections) resulted in 324 unique reflections of which 283 were considered as observed.

Full-matrix least-squares refinement with anisotropic temperature factors and a variable correction for isotropic extinction resulted in convergence at R -factors of 2.4% (observed) and 2.8% (all data), and R_w -factors of 2.6% (observed) and 2.9% (all data). Observed and calculated structure factors are listed in Table A1¹ and final atomic positions and anisotropic temperature factors are presented in Tables A2 and A3. Interatomic distances and angles are given in Table A4 and the magnitudes and orientations of the principal axes of the thermal ellipsoids are given in Table A5.

The results presented here are virtually identical to those of Nord (1973); the small but statistically significant differences that do occur in some of the anisotropic temperature factor

¹Available from the authors on request.

coefficients could be attributed to differences in the refinement procedures and minor absorption effects in both studies.

TABLE A2. ATOMIC POSITIONS AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS FOR THENARDITE

	x	y	z	B_{equiv}
Na	0.4416(1)	1/8	1/8	1.51(2) \AA^2
S	1/8	1/8	1/8	0.85(2)
O	0.2138(1)	0.0572(1)	0.9793(2)	1.43(2)

TABLE A3. ANISOTROPIC TEMPERATURE FACTORS FOR THENARDITE

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na	0.00449(11)	0.00255(6)	0.00914(26)	0	0	0.00021(11)
S	0.00228(7)	0.00160(4)	0.00503(18)	0	0	0
O	0.00359(11)	0.00259(7)	0.00976(32)	0.00031(8)	0.00144(17)	-0.00149(13)

TABLE A4. SELECTED INTERATOMIC DISTANCES AND ANGLES FOR THENARDITE

Na-O ₂	x2	2.538(1) \AA			
Na-O ₁	x2	2.426(1)	S-O ₂	x4	1.479(1) \AA
Na-O ₂	x2	2.334(1)			
Na-O ₆		2.432			
O-O _b	x2	2.415(2)	O-S-O _b		109.41(9) $^\circ$
O-O _f	x2	2.389(2) e	O-S-O _f		107.67(9)
O-O _e	x2	2.444(2)	O-S-O _e		111.36(8)
O-O		2.416	O-S-O		109.48
O-O _f	x1	2.389(2) e	O-Na-O _f		56.15(6)
O-O _g	x2	3.397(2)	O-Na-O _g		86.35(5)
O-O _j	x2	3.944(1)	O-Na-O _j		108.05(5)
O-O _c	x2	3.189(1)	O-Na-O _c		81.67(4)
O-O _h	x2	3.119(2)	O-Na-O _h		81.88(5)
O-O _i	x2	3.481(1)	O-Na-O _i		93.99(4)
O-O _k	x1	4.481(1)	O-Na-O _k		134.93(8)
		3.428	O-Na-O		91.25

Equivalent positions: $a=x, y, z$; $b=1/4-x, 1/4-y, z$; $c=x-1/4, y, 1/4+z$; $d=1/4+x, 1/4-y, 1-z$; $e=1/4-x, y, 1/4-z+2$; $f=3/4-x, y, 3/4-z+1$; $g=1/2-x, y, 1/2-z+1$; $h=1/2-x, y-1/4, 1/4+z$; $i=1/4+x, 1/4+y, z-z$; $k=x, 1/4-y, 1/4-z+1$; $l=3/4-x, 1/4-y, z-1/2$.

^adenotes edge shared between SO₄ and NaO₆ polyhedra

TABLE A5. MAGNITUDE AND ORIENTATIONS OF THE PRINCIPAL AXES OF THE THERMAL ELLIPSOIDS FOR THENARDITE

	R.M.S. Displacement, \AA^2	Angle to a -axis in degrees	Angle to b -axis in degrees	Angle to c -axis in degrees
Na	0.126(2)	90	102(6)	12(6)
	0.140(2)	90	168(6)	102(6)
	0.148(2)	0	90	90
S	0.094(2)	90	90	0
	0.106(2)	90	90	90
	0.111(1)	90	0	90
O	0.100(3)	121(2)	61(2)	46(2)
	0.142(2)	146(4)	120(6)	105(5)
	0.156(2)	78(6)	136(5)	48(3)

REFERENCES

BROWN, I. D. (1975): Bond valence theory — a simple predictive model of chemical bonding in solids. (submitted for publication).
 — & SHANNON, R. D. (1973): Empirical bond-strength-bond length curves for oxides. *Acta Cryst.* A29, 266-282.
 COLVILLE, A. A. & STAUDHAMMER, K. (1967): A re-

finement of the structure of barite. *Amer. Mineral.* 52, 1877-1880.
 CROMER, D. T. & MANN, J. B. (1968): X-ray scattering factors computed from numerical Hartree-Fock wave functions. *Acta Cryst.* A24, 321-324.
 —, & LIBERMAN, D. (1970): Relativistic calculation of anomalous scattering factors for x-rays. *J. Chem. Phys.* 53, 1891-1898.
 FINGER, L. W. (1969): RFINO. A Fortran IV computer program for structure factor calculation and least-squares refinement of crystal structures. Geophys. Lab., Carnegie Inst. Wash. (unpubl.).
 GARSKE, D. & PEACOCK, D. R. (1965): Refinement of the structure of celestite SrSO₄. *Z. Krist.* 121, 204-210.
 HAWTHORNE, F. C. & FERGUSON, R. B. (1975a): Anhydrous sulphates II: Refinement of the crystal structure of anhydrite. *Can. Mineral.* (submitted for publication).
 —, & — (1975b): Refinement of the crystal structure of cryolite. *Can. Mineral.* (submitted for publication).
 JAMES, R. W. & WOOD, W. A. (1925): The crystal structures of barite, celestine and anglesite. *Proc. Roy. Soc. London* 109A, 598-620.
 MOORE, P. B. (1973): Bracelets and pinwheels: A topological-geometrical approach to the calcium orthosilicate and alkali sulphate structures. *Amer. Mineral.* 58, 32-42.
 MOORE, P. B. & ARAKI, T. (1972): Atomic arrangement of merwinite, Ca₃Mg(SiO₄)₂, an unusual dense-packed structure of geophysical interest. *Amer. Mineral.* 57, 1355-1374.
 NORD, A. G. (1973): Refinement of the crystal structure of thenardite, Na₂SO₄(V). *Acta Chem. Scand.* 27, 814-822.
 SAHL, K. (1963): Die Verfeinerung der Kristallstrukturen von PbCl₂ (Cotunnit), BaCl₂, PbSO₄ (Anglesit) und BaSO₄ (Baryt). *Beitr. Mit. Petr.* 9, 111-132.
 SHANNON, R. D. & PREWITT, C. T. (1969): Effective ionic radii in oxides and fluorides. *Acta Cryst.* B25, 925-946.
 — & — (1970a): Effective ionic radii and crystal chemistry. *J. Inorg. Nucl. Chem.* 32, 1427-1441.
 — & — (1970b): Revised values of effective ionic radii. *Acta Cryst.* B26, 1046-1048.
 ZACHARIASEN, W. H. (1968): Extinction and Boormann effects in mosaic crystals. *Acta Cryst.* A28, 421-424.
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