# 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, SrSO4, a = 8.360(1), b = 5.352(1), c = 6.858(1)Å, 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<sub>4</sub> group is identical in all three structures. A type I stability diagram for the divalent metal sulphates of the form  $M^{2+}SO_4$  shows that anhydrite (CaSO<sub>4</sub>) 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<sup>2+</sup> is incompatible with the bond strength requirements of tetrahedral coordination for a third row cation, thus forcing CaSO, 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<sub>4</sub>) is isostructural with barite (BaSO<sub>4</sub>) and anglesite (PbSO<sub>4</sub>), 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  $(\langle S-O \rangle = 1.52\text{\AA})$  and they suggested that further refinement of all three structures was 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 0.1Å 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)Å, V =306.81Å<sup>3</sup>. These values correspond closely to those for synthetic SrSO<sub>4</sub> (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  $\sim 0.15$  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  $65^{\circ}2\theta$  (MoK $\alpha$  radiation). The crystal faces were indexed using a spindle stage with an over-all geometry corresponding to that of the  $\chi$  and  $\phi$  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 backdesirable. An accurate refinement of the struc- Eground 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 leastsquares program RFINE (Finger 1969). Full matrix refinement of all variables for an isotropic thermal model resulted in convergence at R- and  $R_w$ -factors<sup>1</sup> of 5.3 and 5.6% respectively (observed data only). Temperature factors were converted to anisotropic of the form

$$\exp \begin{bmatrix} 3 & 3 \\ -\sum & \sum \\ i=1 & j=1 \end{bmatrix} h_i h_j \beta_{ij}$$

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

$$\begin{split} {}^{1}R &= \Sigma[|F_{obs}| - |F_{eals}|]/\Sigma |F_{obs}|; \\ R_{w} &= [\Sigma w[|F_{obs}| - |F_{eals}|]^{2}/\Sigma w_{i}F_{obs}^{2}]^{\frac{1}{2}}, \ w = 1 \end{split}$$





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ment. Refinement of all variables resulted in convergence at *R*-factors of 4.1% (observed) and 7.1% (all data) and  $R_{W}$ -factors of 4.7% (observed) and 7.8% (all data). Observed and calculated structure factors are listed in Table 1,

atomic coordinates and equivalent isotropic temperature factors in Table 2 and anisotropic temperature factor coefficients in Table 3. Interatomic distances and angles and the magnitudes and orientations of the principal axes of the

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# TABLE 1. OBSERVED AND CALCULATED STRUCTURE FACTORS FOR CELESTITE.

		ĸ	1. F(085	1	FICALES		e K	ι,	1085	FICALCI	,		L	F(085)	F (CALC)		ь в	L	F (085)	FICALC1
		8	2 92.22	*	28.884		1	: :	3.414 8.948	22.339				7.434 #	1.693		1. 1	ę	11.574 =	13.357
		ē	6 95.84	6	93.212	-	<del>; ;</del>	4	7.669	18-161			- i -	42.705	43.354		1 1	ź	56-533	57.840
		Ö 1	10 19-66	ā =	20.101		3 1	7 1	4.694 *	890.9 897.53		ž		28.935	28.581		1 3		6.794 +	4.223
	•	į	5 .75.95	i,	74-043		; ;	i	7.018	\$5.193 33.514	-		- ÷	17.847	11-030		7 9	î	14.941 +	12.743
		į	9 39.74	÷	38.528	-	<u>;</u>	<u>i</u>	1.360	20.000			1	28.102	29.463		1 2	5	32.200	31.731
		2	2 19.21	5	14.944			5 3	9.216	41.024		ŏ	4	13.390 *	7.880		1 3	-	13.930	3.214
ě			6 66.24	6	67-304		2 5	7 4	2.510	28.116	-5	- ö		34-504			7 6	2	36-727	-39-114
ē			28.49	ģ	28.090	-	2 4		6.489	21.420	· .	ō	9	26.816	28.468		8 0	2	39.780	40.598
0			3 7.76		2.079		2 0	2	4.906 #	3.239		1	2	49.237	54.923		<u>.</u>		32.340	12.345
ě	1		7 11.98	i.	13.794		2 0		3.364 *	15-114	.5	1	-	34.673	36+345		8 0	ě	64.056	62.332
ē			0 144.67	i	142.682	-	<u>.</u>	<u> </u>	A. 775	10-881		i	6	9.863 *	11.262		8 0	á	27.001	27.064
ġ			4 46.43		42.862		2 1	1 1	2.517 .	27.247	5	i	8	5.742	46.388		<u>å i</u>	i	25-437	26.891
ě			6 32.70		30.663	_	2 1	*	8.680 *	1.761		2	<u>i</u> i	1.909	47.412		8 1	4	11.339 =	9.783
ě			1 11.15	ē.	12.360		3 0	1 1	4.485	38.850 91.233	5	2	å e	4.639	93.200		8 1	õ	2.856 *	3.797
		•	G 71.61		76.523		3 0	3 11 4	8.053 *	108.030 2.658		ź		2.025	23.406		<u> </u>	2	24.669	25.658
ě			4 31.47	5	10.060		10	5 2	-5.771 -8.720 m	25.985				24-015	26.575		8 2	4	32.429	10.329
ě	ž		1 21.68		20.905		3. 0	7 4	1.935 3.783 •	41.868	5	2	9 3	2.847	28.601		8 2	?	4.880 *	2.412
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į	ă		2 97.65		94.116	-	1 1		3.242	57.174	. 4		4	6.547	6C.439 - 23-695-		8 3	3	3.671 • 10.182 •	5.833
Ī			4 51.67		11.631			5 1	3.253	35.015	5	3	6 1	4.555 *	14-105		8 3	3	40.072	38.909
	0		6 3.95		4.141		; ;	7 1	8.491	13.296	. 5	1	á .	4.138	35.847			<u> </u>	4.736.	5.711
i	ē		8 56-535		58.250	_	1		10.929	21.018	4		<u> </u>	2.273 .	27.805		8 4	1	10.162 •	9.890
į	- Į		1 44.12		43.497		; ;	3.9	8.553	3.202	1		1	8-140 *.	5.815		8 4	4	30.330 25.042	24.405
î	i		3 95.846		\$4.721		1 2	4 .2	8.941	40.401 26.789	1	3	7 2	7.200	26.829		8 4		6+185 * +7+886	40-802
ļ.	i		5 9.80	:	2.995	-	3 3	÷ 1	0.865	29.662			1 1	7.165	16.776		8 5 8 5	· °	5.787 * 9.993 *	11.722
, î	į		7 46.441	· ·	45.028		1 1	; ;	9.697 .0	11.682	5	-	5 5	4.700	36.349		8 5	23	4.236 * 13.578 *	1.661
1	Ŧ		9 28.667		28.697		1 1	1 1	5-975 *	14.447 64.787	,	-	5 1	4.591 +	15.407		A 6	2	47.019	46.144
į	ż		1 28.762		26.541		1.1	5 2	7.907	28.144			1 2	2.941	23.296		4 û 7 û	. 2	8. 520 A 37. 944	12-110
÷	÷		L6.802	<u> </u>	14.000		; ;	2	5.991	38.083 14.178	2	ě	5 4	3.455	45.650		9 G 9 G	3	15.620 * 27.826	26.197
Ĩ	3		25.360		26.333		3 3	1	5.443 *	8.226	5			3.971 *	13.433		<u>i </u>	. å.	12.014 *	12.158
Ī	- 1		28.883		31.494	_	; ;	9 2	1.935	19.938			2 1	1.913	15.571		9 O 9 I	1	20.739 19.942	16.160
÷	-;	_	18.912	•	5.888		1 :	2 1	8-115	14.157	6	ő	á 1	9.169	18.832		9 1 9 1	2	34.371 39.72J	37.022
į	- 1		33-425		36.710		1 1	4 1	2.577 +	4.592	ė	å	2	9.337 *	e.223	-	å 1	- :	38.680	37.835
Î	į	j	64.364		63.711		1 1	, i	0.719 *	\$.794		<u>-</u>		2.894	27.272		9. 1	\$	7.123 •	6.004
÷	÷	-	11.004		12-209		1	8	2.399 *	7.589	ė	ő	8 2	0.756	21.908		9 2 9 2	2	45.337 43.172	50.09Z 41.437
-i	į	ġ	21.125		14.642				2.549	44.238	å	8	; ;	9.536	20.083	-	9 2		18.836 6.835 *	4.854
i	÷	i	45.257		46.382			4 2	3.108	22.326			1 6	4.419	16.480		4 3	2	14.229 = 33.417	14.944 34.415
÷			41.498	<u> </u>	42.111	_	1	l z	7.206 *	1:01	÷	1	2 2	2.455 3.661 *	24.952		9 3 9 3	3	29.150 34.693	29.868 35.391
į	- 1	1	19.712	•	17.441		3 6	2 4	4.219 *	3-017	;	1	; ;	7.423	28.292	-	<del>9</del> 4 5 4		29.189	30.178
į		į	23.619		24.789	-	; ;	\$ 1	9.230	14.880	-6	-+	÷ ;	4.919	. 41.404 31.605		9 4 9 4	3	9.583 • 24.218	10.053
+	÷	- i	<u>61-169</u>		48.767		; ;	1 1	8.140 4.782 *	10.419	:	2	0 5	4.252	17.623		\$ \$	ĩ	9.031 + 12.532 +	10.257
i	i	ŝ	9.714	•	4.025		; ;	2 2	3.365	25.276	6 5	2	; ł	5.074 + 6.799	17.116		\$ 3	2	27.498	28.834
Ť	Ť		18.540		14-804	-		0 3	0-085 s 6-530	35.741		2.		4.097 0.323	31.498		14 0	1	27.488 13.506 =	25.421 13.655
÷	- <u>i</u> -	÷	- 48.112		4-174		: :	1 14	1.056	134.001	÷	2	<b>1</b>	0.387 + 4,109 +	5.013		10 0 10 0	3	16.599 * 14.243 *	13.391
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1	ī		2.581		2.169	-	<del>: :</del>	7 6	2.047	41.904	<u>_A</u>			9.3 <i>57</i> 9.452 -	26.747		10 I 10 I	4	53.954 24.976	56.636 30.375
÷	÷		34,343	-	17.514 13.474		4 8	4 L	4.355 *	1.843	:	1	; ;	9.14L 3.763	23.700		LG L LØ L	23	24.990	23.521
i	i	- 5	29.915	2	M-463			2 6	5.719	\$4.619	6 6	;	; ]	6.6e2 5.034	34.968 23.730		10 -1-	\$	25.411	30.639
i	í	I	12.657	:	1.728		<del>: i</del>		4.814	47.698	÷		<del>3 1</del>	4.999	10.200	1	10 1 10 2	â	40.313	35.752
4	-ě	-ĭ		•	1.414		: :	5 10	0.347 = 3.4 <i>8</i> 9	1.201	:	:	; ;	1.356	20.782	1	0 2	ż	29.709	28.590
į,		Ĩ	30.048		1.991		1 İ	7 1	8.900 • 8.121 •	6.093	÷	<b>;</b>	\$ 1	2.042	19.458	1	10 2	\$	22.235	20-850
1	ě	- 7	44.320		4.335	-		0	2.484 B	3.500	:	ŝ	2 2	0.904	\$2.607 19.178			a 1	47.019	45.134
1	÷	-	10.70	• •	4.435			1 7	1.422 .097 *	71.702	6	;	5 3	1.787 4 4.812	17.684		10 3	ž	17.677	16-894
1	ě	1	1:13	•	1:37	:			1.195 .	4.778	÷			7.703	28.754				29. 706	19-991
	Ĭ.	ĩ	125-504	ų	3.414		<u> </u>	<u></u>	. 3.73	15-140			4 1	4.901 €	4.733 13.064			è	14.084	17.142
1	Ĩ	ż	45.827		1.210			9 7	.230	13.805		;	1 1	J.620 5.696 •	3C.224 22.982	1	4	ž	10.533 +	3.060
1	÷		42.387		4.499			; ;	- 500 -	1.754	;		1 7	5.478 . 7.149	2.747		ų į	i	22.604	15.801
į	į	į	37.968	1	4.441	-	<u> </u>	<u>.</u>	- 373 #	12,000	;	ŝ	3 4	9.992 #	47.241		1	3	54.829	53.113
2	į	•	71.252	- 1	0.004			7 1	.677 .	6-670	ļ	ĉ	8 4	7.323 * 1.121	12.793		i ș		19.044	15.863
4	÷.	ż	14.717	: 1	3.437			i ii	.411 +	1.091			1 1	8.185	17.832		<u>i</u>	÷	17.111	37.781
2	i	-	24.597	- 1	7.744	4		1 80	804		ļ	1	3 3	1.857	15.077 24.193	-	i i	÷	14.270 *	14.977
1	ż	•	31.239		3.341		1	1	- 500 +	12.751	i	1	÷ .	9.177 * 7.528	10.698	į	i ŝ	ż	8.057 *	9.468
ĩ	1	-	14.238	i <u>i</u>	4.747		1	5 6	.978	47.335		i	1 .	7.944 .	11.529	1	1 2	•	18-031	14.384
1	i	ĩ	43.295		1.503	-	<u> </u>	<u>i</u>	-475 -	44.438	;	2	2 6	4.913	65.885		įį	į	30.280	33.146
ŧ	1	-	20.242	-	7.337			õ 2	.296	27.444	į	ŝ	; ;	9.130	37.355	1	2 0	ş	18.084	17.237
1	2	i	51-212		4.445			į i	.134 .	6.642	į	3	<u>;</u> ;	3.901 *	8.908	-	2 9		9.768 *	7,376
1	3	ł	14.730	. 1	5-055			4 2	.329	24.718	1	2	8 1	0.386	37.862		1	é	21.701	22.524
Ŧ	:		22.424		1.443	3		ų 1	-589 +	17.176	į	1	1 1	1.873	36.470			ş	3.617 -	2.574
2	4	ż	12.019	• '	6.347		۱. <u>۴</u>	i 41	.134	44.274	İ	į.	2	5.541	29.013		2 2	· · · · ·	10.953 *	2.511

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  $(SO_4)$  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	у		<sup>B</sup> 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)
0(1)	0.5970(9)	3/4	0.0937(10)	1.56(14)
0(2)	0.3101(9)	3/4	0.0406(11)	1.34(13)
0(3)	0.4219(6)	0 9745(9)	0.3101(7)	1.00(9)

	TABLE 3. ANISOTROPIC TEMPERATURE FACTORS FOR CELESTITE							
-	<sup>β</sup> 11	<sup>8</sup> 22	<sup>β</sup> 33	<sup>8</sup> 12	<sup>8</sup> 13	<sup>β</sup> 23		
Sr S 0(1) 0(2)	0.00269(11) 0.00264(27) 0.00325(95) 0.00495(84)	0.01022(32) 0.00444(64) 0.01042(348) 0.01082(301)	0.00334(16) 0.00182(44) 0.00814(164) 0.00612(134)	0 0 0	0.00010(18) 0.00009(30) 0.00320(94) -0.00191(98)	0 0 0		
0(3)	0.00397(69)	0.00548(140)	0.00668(91)	-0.00107(94)	0.00077(76)	-0.00082(91)		

TABLE 4. SELECTED INTERATORIC DISTANCES AND ANGLES FOR CELESTITE									
S-0(1) S-0(2) S-0(3) <s-0></s-0>	x2	1.470(8)Å 1.456(9) 1.483(6) 1.473	Sr-0(1) Sr-0(1) x Sr-0(2) x Sr-0(2) Sr-0(3) x Sr-0(3) x Sr-0(3) x Sr-0(3) x	2.516(8) 2.3.254(6) 2.2.987(4) 2.622(8) 2.685(6) 2.651(6) 2.827					
0(1)-0(2) 0(1)-0(3) 0(2)-0(3) 0(3)-0(3) <0-0>	x2 x2	2.426(14) 2.406(9) 2.495(9) 2.403(11) 2.405	0(1)-S-0(2) 0(1)-S-0(3) x 0(2)-S-0(3) x 0(3)-S-0(3) <0-S-0>	112.0(5)° 109.1(3) 109.1(3) 108.2(4) 109.5					

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

	ment (A)2	in degrees	in degrees	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)
0(1)	0.073(25)	34(9)	90	124(9)
	0.160(15)	124(9)	- 90	147(9)
	0.168(15)	90	0	90
0(2)	0.104(22)	57(8)	90	33(8)
	0.128(14)	90	0	90
	0.154(14)	33(8)	90	123(8)
0(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 2.7Å and bond in the plane of the sheet, four lie between 2.8 and 3.0Å and the remaining two lie further out at 3.25Å. 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 (3.254Å) 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

		ANGLESITE		
		Baritel	Celestite <sup>2</sup>	Anglesite <sup>3</sup>
S-0(1) S-0(2) S-0(3)	x2	1.472(7)Å 1.448(7) 1.484(5)	1.470(8)Å 1.456(9) 1.483(6)	1.47 1.42 1.48
		1.472	1.473	1.46
0(1)-S-0(2) 0(1)-S-0(3) 0(2)-S-0(3) 0(3)-S-0(3)	x2 x2	111.8(5)° 109.8(3) 108.6(3) 108.2(3)	112.0(5)° 109.1(3) 109.1(3) 108.2(4)	112 110 108 109
		109.5	109.5	109.5

<sup>1</sup>Coville & Staudhammer (1967) <sup>2</sup>This study

study <sup>3</sup>Sahl (1963)

	TABLE 7.	BOND STRENGTH	TABLE*	FOR CELE	STITE
	S	Sr	ΣŤ		
0(1)	1.512	0.325 0.054 <del>1</del> 4	1.945	(1.837)†	
0(2)	1.589	0.244 0.098 <del>*</del> 2	2.029		
0(3)	1.469¥	0.206 <sup>×2</sup> 2 0.226 <sup>×2</sup> 0.148 <sup>×2</sup>	2.049		
Σ†	6.039	2.033(1.9	25)†		
*					

Calculated from the curves of Brown & Shannon (1973) and Brown (1975). YValues 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 S-O(2) and lengthening of the 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  $(M^{2+} = Ni, Mg, Co, Fe$ and Mn), the mercuric sulphate group  $(M^{2+} =$ Hg and Cd) and the barite group  $(M^{2+} = \text{Sr}, \text{Pb})$ and Ba). The copper sulphate group  $(M^{2+} = Cu)$ , Zn, Co<sup>1</sup> and Mg<sup>1</sup>) 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 1.07Å. The transition from the barite stability field to the mercuric sulphate stability field, which occurs at ~ 1.07Å, involves a change in the large cation coordination number from [12] to [4]. The octahedral radius of Ca<sup>2+</sup> 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<sup>2+</sup> is intermediate in size between Cd<sup>2+</sup> and Hg<sup>2+</sup> (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

<sup>1</sup>high-temperature modification.



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<sup>IV</sup> distance may be calculated, giving a value of 2.10Å. An ionic radius for tetrahedrally coordinated Ca



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 0.88Å, and an expected Ca-O<sup>IV</sup> distance (based solely on an ionic radius criterion) may be obtained by interpolation between the mean bond lengths for HgSO<sub>4</sub> and CdSO<sub>4</sub> (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:

- $CdSO_4 \quad 0.80\text{\AA} + 1.35\text{\AA} = 2.15\text{\AA}$ Observed  $Cd-O^{IV} = 2.17\text{\AA}$
- HgSO<sub>4</sub>  $0.96\text{\AA} + 1.35\text{\AA} = 2.31\text{\AA}$ Observed Hg-O<sup>vv</sup> = 2.28Å

CaSO<sub>4</sub> 
$$0.88\text{\AA} + 1.35\text{\AA} = 2.23\text{\AA}$$
  
Interpolated Ca-O<sup>rv</sup> =  $2.25\text{\AA}$ 

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<sup>IV</sup> distance of 2.10Å 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<sup>iv</sup> which indicates a maximum possible covalence of 0.10 v.u. Consequently, CaSO<sub>4</sub> 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,  $Na_2SO_4(V)$  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)Å. These are close to those of synthetic  $Na_2SO_4(V)$  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 A1<sup>1</sup> 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

<sup>&</sup>lt;sup>1</sup>Available 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

					FU	K INCI	MANDITE				
_	-	x				y			В		Begutv.
Na	C	.441	5(1)			1/8			1/8		1.51(2)Å
S		17	В			1/8			1/8		0.85(2)
0	(	1.213	B(1)			0.0572	?(1)	0.	9793(2)		1.43(2)
	тł	ABLE .	A3. ANISO	TROP	IC T	emper/	TURE FAC	TORS	FOR THE	NARD	ITE
	β <sub>11</sub>		<sup>8</sup> 22		ß	33	<sup>B</sup> 12		<sup>β</sup> 13		<sup>β</sup> 23
Na	0.00449	(11)	0.00255(8	) 0	.009	14(26)	0		0		0.00021(11)
5	0.00228	3(7) 3(11)	0.00160(4	1) 0 1) 0	.005	J3(18)		(8) 0	0	171.	0.00140(13)
<u>×</u>	0.00000	/////	0.002351	10	.003	10(32)	0.00031		.00144(	<u>.</u>	-0.00149(13)
	TABL	.E A4	. SELECTE	) IN	TERA	TOMIC	DISTANCE	s and	ANGLES	FOR	THENARDITE
Na-0	)a	x2	2.53	88(1	)Å					_	
Na-(	DZ .	x2	2.42	26 (1	2			S-0a	x4		1.479(1)Ă
na-u	d	XZ	2.3	54(1	1	đ					
Na-(	) 6		2.43	32							
0-02	,	x2	2.4	5(2	)		0	S03-		1	09.41(9)°
0-0;	ŕ	x2	2.30	39 (2	) <sup>8</sup>		0-	S-0f		]	07.67(9)
0+0e	3	x2	2.4	4(2	)		0-	S-0e		]	111.36(8)
0-0			2,41	6			0-	s-0		1	09.48
0-0;	P	xl	2.38	39 (2	}8		0-N	a-Of			56,15(6)
0-02	1	x2	3.39	17(2	)		0-N	a-Dg			86.35(5)
0-0	i	x2	3.94	4(1	)		0-N	a-0 <i>j</i>		1	08.05(5)
0-0	•	x2	3.18	19	}·		0-N	a-0 <i>a</i>			81.67(4)
0-02	1	x2	3.1	9 (2	{		0-N	a-Oh			81.88(5)
0-01	•	x2	3.40	si Li	ł		U N	a-01			93.99(4)
0-04	2	XI	4.40	<u>n (</u> 1	2		0-N	a-uk		2	34.93(8)
			3.4	28			0-N	a-0			91.25
Equi	valent	posi	tions: and	·,y,	8-1	; b=T/	4-2, 1/4	у, я	; o=x -	1/4,	w, 1/4+s;
d=1/	4 12, 1/	'4+y,	1-s; e=1;	4-3	, y,	1/4-1	+2; f=x,	1/4-	y, 1/4-	8+2;	g=3/4-æ,
у, З	3/4-s+1	h=l	/2- <i>x</i> , <i>y</i> , 1	/2-	s+1;	i=1/2	-x, y-1/	4, 1/	4+2; j=	1/4+5	≈, 1/4+y,
Z-8	; <i>k=x</i> , l	14-11	,_1/4-s+l	l=	3/4-4	c, 1/4	-y, s-1/	2.			

<sup>8</sup>denotes edge shared between SO4 and NaO5 polyhedra

TABLE A5.	MAGNITUDE AND	ORIENTATIONS	OF	THE	PRINCIPAL	AXES	OF	THE
	TUCOMA	CIT TREATHE E	ton.	71207	ADDITC			

		RENAR EFFICIATION	FOR INERARDITE	
	R.M.S. Dis-	Angle to a-axis	Angle to b-axis	Angle to <i>o</i> -axis
	placement, Å <sup>2</sup>	in degrees	in degrees	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
\$	0.094(2)	90	90	0
	0.106(2)	0	90	90
	0.111(1)	90	0	90
0	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)
-				

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