Canadian Mineralogist
Vol. 13, pp. 181-187 (1975)

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, $SrSO_4$, $a = 8.360(1)$, $b = 5.352(1)$, $c = 6.858(1)$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_4 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 ($CaSO_4$) 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 ($<\text{S-O}> = 1.52$Å) and they suggested that further refinement of all three structures was desirable. An accurate refinement of the structure 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 folowing cell dimensions: $a = 8.360(1)$, $b = 5.352(1)$, $c = 6.858(1)$Å, $V = 306.81$Å^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°2θ (Mo$K\alpha$ 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-factors[1] 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-

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[1] $R = \Sigma[|F_{obs}| - |F_{calc}|]/\Sigma|F_{obs}|$;
$R_w = [\Sigma w[|F_{obs}| - |F_{calc}|]^2/\Sigma w F_{obs}^2]^{\frac{1}{2}}$, $w = 1$

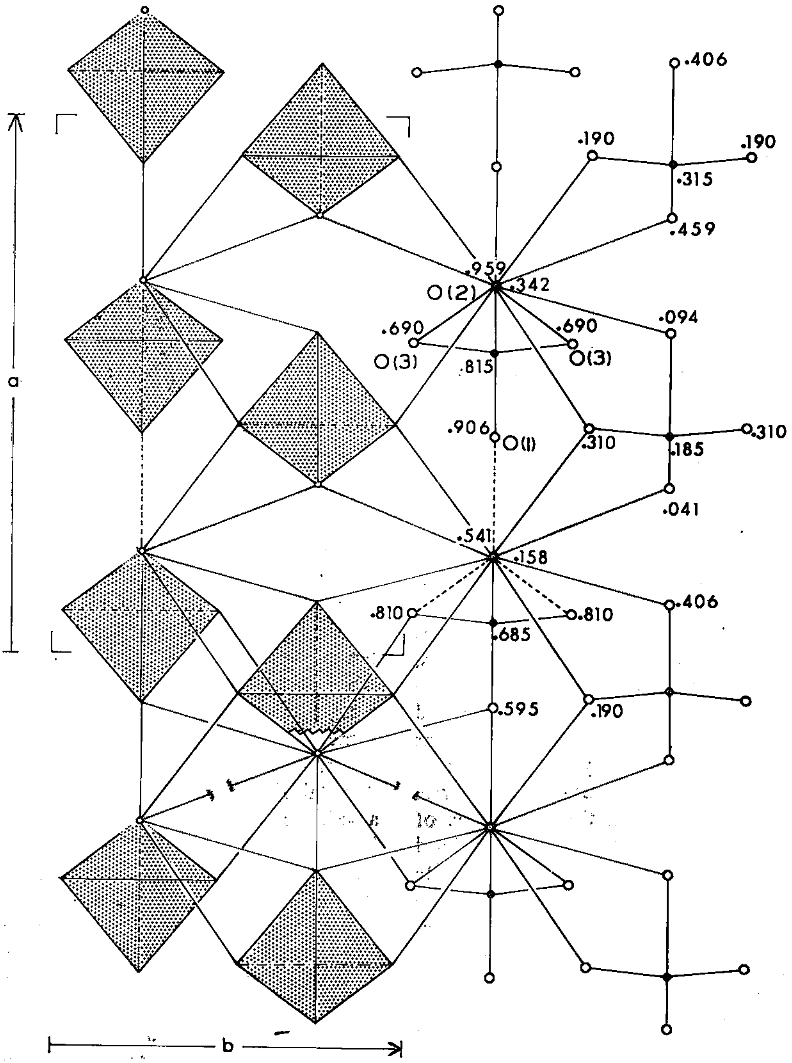

FIG. 1. The crystal structure of celestite viewed down the c-axis.

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

TABLE 1. OBSERVED AND CALCULATED STRUCTURE FACTORS FOR CELESTITE.

H	K	L	F(OBS)	F(CALC)
0	0	2	92.229	88.884
0	0	4	60.615	65.545
0	0	6	95.846	93.212
0	0	8	40.571	41.350
0	0	10	15.660 *	20.101
0	1	1	27.126	27.302
0	1	5	75.953	74.043
0	1	7	14.347	10.692
0	1	9	39.744	38.528
0	2	0	158.417	156.801
0	2	2	19.215	19.949
0	2	4	65.919	60.737
0	2	6	66.246	67.304
0	2	8	20.860	19.949
0	2	10	28.490	28.090
0	3	1	51.602	45.253
0	3	3	7.769 *	2.079
0	3	5	63.862	62.169
0	3	7	11.981 *	13.796
0	3	9	32.930	29.641
0	4	0	144.673	142.482
0	4	2	51.788	50.261
0	4	4	46.434	42.882
0	4	6	68.998	67.538
0	4	8	32.709	30.868
0	5	1	16.140 *	11.448
0	5	3	11.150 *	12.360
0	5	5	37.006	33.577
0	6	0	71.613	70.523
0	6	2	21.675	23.110
0	6	4	31.473	30.060
0	6	6	38.309	41.433
0	7	1	21.686	20.303
0	7	3	25.129	24.477
0	8	0	50.636	50.105
1	0	1	2.824 *	4.353
1	0	2	97.654	94.116
1	0	3	39.313	34.589
1	0	4	51.677	55.831
1	0	5	7.218 *	7.768
1	0	6	3.952 *	4.143
1	0	7	23.113	23.679
1	0	8	56.539	58.250
1	0	10	18.362	18.708
1	1	1	44.125	43.997
1	1	2	90.421	89.129
1	1	3	95.846	94.727
1	1	4	37.094	42.172
1	1	5	9.808 *	2.595
1	1	6	5.467 *	7.272
1	1	7	46.449	45.028
1	1	8	18.396	22.118
1	1	9	28.687	28.697
1	1	10	19.540	20.181
1	2	1	28.762	26.941
1	2	2	106.697	105.116
1	2	3	16.892	16.088
1	2	4	74.145	73.303
1	2	5	25.360	26.333
1	2	6	7.280 *	3.960
1	2	7	28.883	31.494
1	2	8	53.839	52.368
1	2	9	13.812 *	5.333
1	2	10	20.258	20.848
1	3	1	33.425	30.710
1	3	2	74.145	73.316
1	3	3	64.364	63.711
1	3	4	48.138	48.606
1	3	6	11.006 *	12.208
1	3	7	40.010	39.830
1	3	8	21.125	19.042
1	3	9	21.741	24.196
1	4	2	65.257	60.382
1	4	3	14.148 *	14.804
1	4	4	41.498	42.331
1	4	6	12.475 *	6.837
1	4	7	19.712	17.841
1	4	8	41.374	42.373
1	5	1	23.619	24.789
1	5	2	37.189	36.144
1	5	3	51.182	48.767
1	5	4	25.115	23.999
1	5	5	9.714 *	4.025
1	5	7	26.023	27.630
1	5	8	18.560	14.806
1	6	1	6.597 *	5.134
1	6	2	48.312	46.174
1	6	3	8.709 *	7.024
1	6	4	36.293	34.734
1	6	5	10.988 *	14.737
1	6	6	2.581 *	2.169
1	7	1	9.111 *	12.519
1	7	2	35.383	33.474
1	7	3	20.345	22.059
1	7	4	29.915	30.483
1	7	5	6.056 *	4.093
1	8	1	12.657 *	1.728
2	0	0	28.935	28.149
2	0	1	13.030 *	13.434
2	0	2	20.048	20.177
2	0	3	38.423	41.901
2	0	4	29.728	31.559
2	0	5	44.320	46.339
2	0	6	24.298	25.938
2	0	7	10.706 *	5.854
2	0	8	13.572 *	16.172
2	0	9	26.525	25.267
2	0	10	38.490	34.298
2	1	0	125.506	123.419
2	1	1	101.271	100.923
2	1	2	45.827	51.210
2	1	4	28.660	30.747
2	1	5	62.387	64.499
2	1	6	66.276	70.094
2	1	7	37.968	36.441
2	1	10	22.521	21.500
2	2	0	71.252	70.004
2	2	1	72.337	72.084
2	2	2	14.717 *	13.437
2	2	3	15.952 *	14.568
2	2	4	24.597	27.764
2	2	5	44.750	50.144
2	2	6	31.239	33.341
2	2	7	10.088 *	6.489
2	2	9	16.238 *	14.767
2	3	0	74.868	73.884
2	3	1	63.298	63.503
2	3	2	31.097	29.743
2	3	4	28.242	27.337
2	3	5	51.930	52.023
2	3	6	51.212	54.465
2	3	7	31.177	29.057
2	3	8	16.730	15.089
2	3	9	5.579 *	2.554
2	4	0	22.424	21.663
2	4	1	14.866	14.993
2	4	2	12.019 *	6.387
2	4	3	23.414	22.338
2	4	4	18.940	22.695
2	4	5	30.881	31.423
2	4	6	17.669	18.161
2	4	7	14.694 *	8.696
2	5	0	70.890	68.996
2	5	1	57.018	55.193
2	5	2	32.643	33.518
2	5	3	3.739 *	9.643
2	5	4	21.360	20.600
2	5	5	39.218	41.024
2	5	6	44.188	46.602
2	5	7	22.510	28.110
2	5	8	18.756	18.900
2	6	0	21.701	21.253
2	6	1	18.489	21.420
2	6	2	4.906 *	3.239
2	6	3	4.358 *	8.739
2	6	4	13.364 *	15.114
2	6	5	22.216	23.261
2	6	6	16.775	16.881
2	7	0	31.429	31.099
2	7	1	28.925	27.247
2	7	2	12.517 *	12.876
2	8	0	8.680 *	7.761
2	7	4	10.374 *	14.280
3	0	1	34.486	38.850
3	0	2	50.161	51.233
3	0	3	110.313	108.030
3	0	4	8.063 *	2.658
3	0	5	25.771	25.986
3	0	6	8.720 *	9.665
3	0	7	41.939	41.868
3	0	8	13.783 *	10.298
3	0	9	35.409	38.237
3	1	2	90.421	88.909
3	1	3	50.024	57.174
3	1	4	33.240	35.092
3	1	5	33.253	35.015
3	1	6	17.162	15.680
3	1	7	16.656	13.298
3	1	8	48.491	49.532
3	1	9	20.929	21.018
3	2	1	37.378	36.731
3	2	2	6.553	3.202
3	2	3	99.463	99.213
3	2	4	38.061	40.401
3	2	5	25.508	26.789
3	2	6	30.865	29.662
3	2	7	37.822	38.150
3	2	8	13.697 *	11.682
3	2	9	37.022	36.547
3	3	1	15.075 *	16.647
3	3	2	64.863	64.787
3	3	3	57.907	58.686
3	3	4	26.906	28.144
3	3	5	35.991	38.083
3	3	6	20.523	16.178
3	3	7	15.443 *	8.226
3	3	8	43.133	42.193
3	3	9	21.935	19.938
3	4	1	31.706	29.964
3	4	2	18.115	19.157
3	4	3	68.037	70.299
3	4	4	12.577 *	4.592
3	4	5	21.409	19.748
3	4	6	10.719 *	9.794
3	4	7	30.406	30.303
3	4	8	2.399 *	7.589
3	5	1	12.529 *	8.036
3	5	2	42.649	44.238
3	5	3	25.799	20.335
3	5	4	23.108	22.326
3	5	5	18.633	16.776
3	5	7	7.206 *	9.262
3	6	1	22.664	22.135
3	6	2	4.219 *	3.017
3	6	3	46.894	46.174
3	6	4	19.238	13.872
3	6	5	6.325 *	14.880
3	6	6	18.140	16.419
3	7	1	14.782 *	12.864
3	7	2	23.365	25.276
3	7	3	30.938	39.017
3	7	4	10.089 *	12.418
4	0	0	36.530	35.747
4	0	1	141.056	139.001
4	0	2	6.344 *	8.273
4	0	3	26.154	26.299
4	0	5	98.378	94.968
4	0	6	9.131 *	6.193
4	0	7	62.047	61.904
4	0	8	4.355 *	1.843
4	0	9	11.753 *	6.709
4	1	0	85.719	84.619
4	1	2	7.056 *	9.370
4	1	3	7.085 *	4.494
4	1	4	44.834	47.698
4	1	5	10.347 *	5.208
4	1	6	33.489	34.009
4	1	7	9.900 *	6.093
4	1	8	12.121 *	14.174
4	1	9	2.486 *	3.598
4	2	0	6.872 *	8.262
4	2	1	73.422	71.702
4	2	2	5.097 *	7.524
4	2	3	9.195 *	4.778
4	2	4	11.637 *	9.919
4	2	5	74.389	75.160
4	2	7	44.378	41.920
4	3	0	75.230	73.809
4	3	1	12.268 *	4.804
4	3	3	6.500 *	5.758
4	3	4	38.434	39.466
4	3	5	8.373 *	5.276
4	3	6	32.728	32.909
4	3	7	11.677 *	6.670
4	3	8	10.867 *	8.539
4	3	9	11.411 *	1.651
4	4	0	17.361	16.308
4	4	1	86.806	85.683
4	4	2	4.175 *	4.389
4	4	3	16.500 *	12.751
4	4	4	6.055 *	5.649
4	4	5	64.978	67.339
4	4	6	7.981 *	3.196
4	4	7	43.675	44.658
4	4	8	5.459 *	1.298
4	5	0	29.296	28.644
4	5	1	8.273 *	1.637
4	5	2	13.134 *	8.642
4	5	3	10.813 *	6.903
4	5	4	25.329	28.718
4	5	5	8.130 *	2.749
4	5	6	14.589 *	17.176
4	5	7	9.023 *	2.083
4	6	1	49.134	46.274
4	6	2	7.630 *	1.832
4	6	3	8.695 *	2.651
4	6	5	42.705	43.354
4	6	6	9.427 *	6.600
4	7	0	28.935	28.581
4	7	1	9.385 *	4.378
4	7	4	17.847	18.036
5	0	1	34.584	38.152
5	0	2	28.102	29.463
5	0	3	68.490	74.541
5	0	4	13.390 *	7.880
5	0	6	15.722 *	14.475
5	0	7	34.504	36.618
5	0	8	19.936	20.826
5	0	9	26.816	28.468
5	1	1	24.334	28.022
5	1	2	49.237	54.923
5	1	3	60.097	64.237
5	1	4	34.673	36.365
5	1	5	25.970	26.307
5	1	6	9.863 *	11.262
5	1	7	15.102	14.910
5	1	8	45.742	46.388
5	1	9	24.119	23.446
5	2	1	61.909	67.512
5	2	2	9.674 *	7.333
5	2	3	94.639	93.200
5	2	4	9.371 *	15.099
5	2	5	22.025	23.408
5	2	6	25.201	24.247
5	2	7	28.015	26.575
5	2	8	21.911	19.693
5	2	9	32.847	28.601
5	3	1	27.262	27.316
5	3	2	38.191	39.295
5	3	3	57.555	60.439
5	3	4	26.547	23.695
5	3	5	27.994	28.281
5	3	6	14.555 *	14.109
5	3	7	8.835 *	11.200
5	3	8	44.138	39.847
5	4	1	30.358	27.806
5	4	2	12.273 *	14.990
5	4	3	50.399	53.420
5	4	5	8.100 *	5.815
5	4	6	9.072 *	12.808
5	4	7	27.206	26.829
5	4	8	16.306 *	15.142
5	5	1	17.165	16.776
5	5	2	35.304	35.488
5	5	3	34.700	36.349
5	5	4	25.359	25.628
5	5	5	14.591 *	15.407
5	5	7	8.288 *	10.034
5	6	1	22.941	23.296
5	6	2	12.960 *	2.928
5	6	3	43.456	45.650
5	6	4	13.152 *	8.532
5	6	5	3.971 *	13.483
5	7	1	16.304 *	15.281
5	7	2	11.912 *	15.971
5	7	3	32.813	32.790
6	0	0	19.169	18.832
6	0	1	9.337 *	11.882
6	0	2	9.427	8.223
6	0	3	2.894 *	4.919
6	0	4	26.355	27.272
6	0	5	30.756	32.078
6	0	6	23.578	27.908
6	0	8	18.604	17.331
6	0	9	19.536	20.083
6	1	0	86.806	85.317
6	1	1	69.419	76.880
6	1	2	22.455	24.952
6	1	3	3.661 *	5.444
6	1	4	27.423	28.292
6	1	5	56.049	56.643
6	1	6	41.124	41.404
6	1	7	34.919	31.605
6	1	8	16.014 *	17.623
6	2	0	54.252	54.693
6	2	1	15.074 *	17.116
6	2	2	19.799	14.434
6	2	5	34.097	31.498
6	2	6	40.323	37.483
6	2	7	10.387 *	5.011
6	2	9	4.109 *	2.306
6	3	0	66.911	66.223
6	3	1	92.722	94.409
6	3	2	19.387	20.747
6	3	3	9.492 *	7.212
6	3	4	19.141	23.700
6	3	5	43.763	46.085
6	3	6	36.662	34.968
6	3	7	25.034	23.730
6	3	8	11.428 *	14.503
6	4	0	16.999	16.208
6	4	4	21.356	20.782
6	4	5	23.935	22.421
6	4	6	15.155 *	19.958
6	5	0	52.082	51.243
6	5	1	50.904	52.407
6	5	2	20.715	19.178
6	5	4	13.787 *	17.684
6	5	5	36.812	37.643
6	5	6	27.703	28.754
6	6	0	22.424	22.941
6	6	2	9.870 *	6.733
6	6	4	14.901 *	13.664
6	7	0	30.020	30.226
6	7	1	15.696 *	22.982
7	0	1	5.478 *	2.747
7	0	2	77.149	82.921
7	0	3	9.992 *	9.900
7	0	4	46.086	47.241
7	0	7	7.323 *	12.793
7	0	8	41.121	39.071
7	1	1	18.185	17.832
7	1	2	32.651	36.076
7	1	3	51.857	55.077
7	1	4	23.443	24.193
7	1	6	9.177 *	10.698
7	1	7	37.528	37.903
7	1	8	7.944 *	11.529
7	2	1	14.386 *	13.386
7	2	2	64.913	65.685
7	2	3	13.566 *	15.905
7	2	4	39.130	37.355
7	2	5	21.334	21.319
7	2	6	13.901 *	8.908
7	2	7	18.467	18.679
7	2	8	40.386	37.862
7	3	1	19.802	17.080
7	3	2	13.873	16.470
7	3	3	45.495	47.194
7	3	4	25.541	29.013
7	3	5	8.451 *	3.488
7	3	6	11.574 *	13.357
7	3	7	33.211	31.995
7	4	2	56.533	57.840
7	4	4	36.677	36.262
7	4	5	6.794 *	4.223
7	4	6	10.480 *	9.717
7	5	1	14.941 *	12.743
7	5	2	19.261	19.164
7	5	3	32.200	31.731
7	5	4	13.930 *	13.324
7	5	5	14.397 *	3.214
7	6	1	9.813 *	6.037
7	6	2	36.727	36.771
8	0	0	106.697	105.443
8	0	2	39.780	40.598
8	0	3	8.218 *	7.500
8	0	4	32.360	32.365
8	0	5	12.810 *	10.230
8	0	6	64.056	62.332
8	0	7	13.282 *	11.612
8	0	8	27.001	27.066
8	1	0	16.276	16.003
8	1	1	25.437	26.891
8	1	3	15.505 *	13.020
8	1	4	11.389 *	9.783
8	1	5	44.765	44.241
8	1	6	2.856 *	3.797
8	2	0	79.209	78.130
8	2	2	24.669	25.658
8	2	3	9.142 *	6.987
8	2	4	32.429	30.329
8	2	6	54.503	50.251
8	2	7	4.880 *	2.412
8	3	0	18.084	17.805
8	3	1	28.250	27.177
8	3	2	3.671 *	4.452
8	3	3	10.182 *	9.033
8	3	4	10.334 *	7.814
8	3	5	40.072	38.909
8	3	6	2.667 *	5.282
8	3	7	4.736 *	5.751
8	4	0	75.953	75.297
8	4	1	10.162 *	9.890
8	4	2	30.330	30.614
8	4	4	25.042	24.409
8	4	5	6.185 *	7.351
8	4	6	47.886	46.802
8	5	0	5.787 *	5.488
8	5	1	9.993 *	11.722
8	5	2	4.236 *	1.661
8	5	3	13.598 *	10.917
8	6	0	47.019	46.144
8	6	2	16.111 *	17.852
9	0	1	8.520 *	12.110
9	0	2	37.944	39.266
9	0	3	15.620 *	16.699
9	0	4	27.826	26.197
9	0	5	12.014 *	12.158
9	0	6	8.105 *	7.395
9	0	7	20.739	18.180
9	1	1	19.942	19.943
9	1	2	34.371	37.022
9	1	3	39.720	41.095
9	1	4	38.680	37.835
9	1	5	2.891 *	1.989
9	1	6	7.123 *	6.008
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
9	2	2	45.337	50.492
9	2	4	43.172	41.537
9	2	5	18.836	15.583
9	2	6	6.836 *	4.856
9	3	1	14.229 *	14.944
9	3	2	33.417	34.415
9	3	3	29.150	29.868
9	3	4	34.693	35.351
9	4	1	11.721 *	7.766
9	4	2	29.189	30.178
9	4	3	9.593 *	10.193
9	4	4	24.216	20.853
9	4	5	9.031 *	10.297
9	5	1	12.532 *	14.282
9	5	2	26.619	24.074
9	5	3	27.498	28.834
10	0	0	27.488	25.621
10	0	1	13.506 *	13.655
10	0	3	16.599 *	13.391
10	0	4	14.243 *	15.801
10	0	5	27.911	26.422
10	0	6	9.627 *	7.769
10	1	0	58.954	56.636
10	1	1	29.976	30.375
10	1	2	24.990	23.521
10	1	3	7.182 *	9.065
10	1	4	25.411	22.914
10	1	5	31.587	30.639
10	1	6	40.313	39.752
10	2	0	19.169	19.307
10	2	1	29.709	28.590
10	2	2	3.545 *	6.473
10	2	4	22.235	15.720
10	2	5	29.569	28.856
10	3	0	47.019	45.134
10	3	1	28.210	27.282
10	3	2	17.677	16.894
10	3	3	8.902 *	7.903
10	3	4	20.706	19.991
10	3	5	29.323	26.317
10	4	0	18.086	17.142
10	4	1	14.677 *	10.403
10	4	2	10.533 *	3.060
10	4	3	10.204 *	10.026
11	0	1	22.606	15.009
11	0	2	5.763 *	1.292
11	0	3	52.829	53.113
11	0	4	13.536 *	5.939
11	0	5	19.044	15.863
11	1	1	6.791 *	7.993
11	1	2	37.111	37.781
11	1	3	23.707	21.675
11	1	4	14.270 *	14.977
11	2	1	11.488 *	15.248
11	2	2	8.057 *	9.468
11	2	3	42.495	41.248
11	2	4	18.031	16.384
11	3	1	4.680 *	8.799
11	3	2	36.280	33.748
11	3	3	25.043	22.726
12	0	0	18.084	17.237
12	0	1	48.161	42.665
12	0	2	9.788 *	7.378
12	0	3	9.737 *	1.210
12	1	0	21.701	22.526
12	1	1	3.492 *	6.784
12	2	0	3.617 *	3.574
12	2	1	40.552	35.880
12	2	2	10.953 *	2.511
12	3	0	21.339	21.028

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 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 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	0.00269(11)	0.01022(32)	0.00334(16)	0	0.00010(18)	0
S	0.00264(27)	0.00444(64)	0.00182(44)	0	0.00009(30)	0
O(1)	0.00325(95)	0.01042(348)	0.00814(164)	0	0.00320(94)	0
O(2)	0.00496(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)
S-O(1)		1.470(8)Å	Sr-O(2)	x2	2.987(4)
S-O(2)		1.456(9)	Sr-O(2)		2.622(8)
S-O(3)	x2	1.483(6)	Sr-O(3)	x2	2.685(6)
			Sr-O(3)	x2	2.651(6)
<S-O>		1.473	Sr-O(3)	x2	2.816(6)
			<Sr-O>		2.827
O(1)-O(2)		2.426(14)	O(1)-S-O(2)		112.0(5)°
O(1)-O(3)	x2	2.406(9)	O(1)-S-O(3)	x2	109.1(3)
O(2)-O(3)	x2	2.495(9)	O(2)-S-O(3)	x2	109.1(3)
O(3)-O(3)		2.403(11)	O(3)-S-O(3)		108.2(4)
<O-O>		2.405	<O-S-O>		109.5

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)

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

		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

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

TABLE 7. BOND STRENGTH TABLE* FOR CELESTITE

	S	Sr	Σ†
O(1)	1.512	0.325 $0.054^{x2}_{\downarrow\rightarrow}$	1.945 (1.837)†
O(2)	1.589	0.244 $0.098^{x2}_{\downarrow\rightarrow}$	2.029
O(3)	$1.469^{x2}_{\downarrow}$	$0.206^{x2}_{\downarrow}$ $0.226^{x2}_{\downarrow}$ $0.148^{x2}_{\downarrow}$	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 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+} = Sr, Pb and Ba). The copper sulphate group (M^{2+} = 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 1.07Å. 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^{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 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 2.10Å. An ionic radius for tetrahedrally coordinated Ca

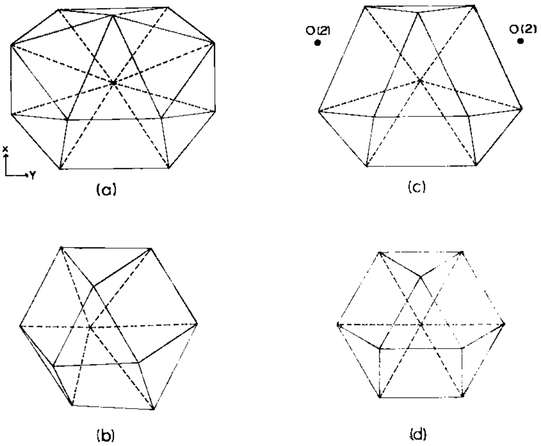

FIG. 2. (a) the [12]-coordinated Sr site in celestite; (b) the [10]-coordinated Ca(2) site in merwinite; (c) the coordination of Sr in celestite, treated as [10] + [2] (note that the O(2) atoms in the figure are not the furthest anions from Sr); (d) the ideal Ca(2) coordination polyhedron in merwinite.

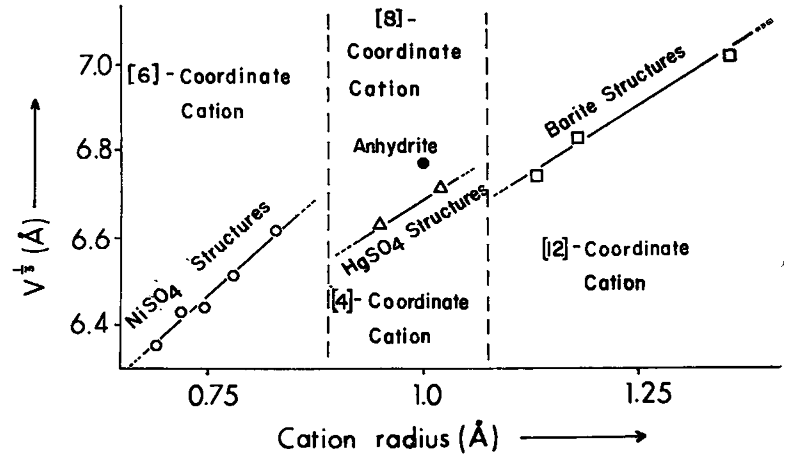

FIG. 3. Type I stability diagram for the divalent metal sulphates $M^{2+}SO_4$. The copper sulphate structures have been omitted for clarity.

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[1] high-temperature modification.

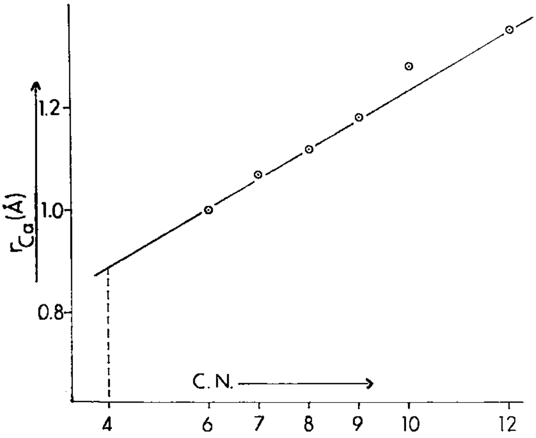

FIG. 4. Ionic radius of Ca^{2+} versus cation coordination number.

may be obtained by extrapolation in Figure 4, giving a value of 0.88Å, and an expected $Ca\text{-}O^{IV}$ 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:

$CdSO_4$ 0.80Å + 1.35Å = 2.15Å
Observed $Cd\text{-}O^{IV}$ = 2.17Å

$HgSO_4$ 0.96Å + 1.35Å = 2.31Å
Observed $Hg\text{-}O^{IV}$ = 2.28Å

$CaSO_4$ 0.88Å + 1.35Å = 2.23Å
Interpolated $Ca\text{-}O^{IV}$ = 2.25Å

Based solely on an ionic radius criterion, the agreement here is quite good. However, it was shown above that the anions require a $Ca\text{-}O^{IV}$ 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^{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.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the cooperation of the Materials Research Institute, McMaster University, Hamilton, in the collection of the intensity data. Financial assistance was provided by the National Research Council of Canada and the University of Manitoba.

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[1] 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

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[1] 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 FOR THENARDITE

	x	y	z	$B_{\text{equiv.}}$
Na	0.4416(1)	1/8	1/8	1.51(2)Å
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-Oa	x2	2.538(1)Å			
Na-Ol	x2	2.426(1)	S-Oa	x4	1.479(1)Å
Na-Od	x2	2.334(1)			
Na-O 6		2.432			
O-Ob	x2	2.415(2)	O-S-Ob		109.41(9)°
O-Of	x2	2.389(2)[a]	O-S-Of		107.67(9)
O-Oe	x2	2.444(2)	O-S-Oe		111.36(8)
O-O		2.416	O-S-O		109.48
O-Of	x1	2.389(2)[a]	O-Na-Of		56.15(6)
O-Og	x2	3.397(2)	O-Na-Og		86.35(5)
O-Oj	x2	3.944(1)	O-Na-Oj		108.05(5)
O-Oc	x2	3.189(1)	O-Na-Oc		81.67(4)
O-Oh	x2	3.119(2)	O-Na-Oh		81.88(5)
O-Oi	x2	3.481(1)	O-Na-Oi		93.99(4)
O-Ok	x1	4.481(1)	O-Na-Ok		134.93(8)
		3.428	O-Na-O		91.25

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

[a] denotes edge shared between SO_4 and NaO_6 polyhedra

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

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

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Manuscript received November 1974, emended February 1975.