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The Crystal Structure of Anhydrite ($CaSO_4$)

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The structure of anhydrite ($CaSO_4$) was determined by Wasastjerna in 1925 and a somewhat different solution for its structure was described by Dickson and Binks in 1926. Redetermination of the structure using Fourier and least-squares refinements of one projection yields a result very similar to that favoured by Wasastjerna. The alternative structure gives markedly poorer agreement between observed and calculated intensities.

Details of the structure of anhydrite were first investigated by Wasastjerna (1925) using powder photograph and spectrometer methods. Eighty-five different types of structure were considered and it was shown that only two structures (in the present work denoted as *A* and *B*) were possibly correct. These two structures are closely related to one another but differ by the translation of atom groups in the direction of one cell axis by 0·05 of the axial repeat (6·24 Å). Wasastjerna chose structure *B* as agreeing better with the observed X-ray data, but noted that better agreement was obtained with structure amplitudes than with their squares. Another determination of the structure of anhydrite was carried out independently by Dickson & Binks (1926), using a single crystal and an ionization spectrometer. Dickson & Binks compared observed and calculated intensities, and their solution was very close to structure *A* and is here denoted as *A'*. Both determinations used trial-and-error methods to place the Ca and S atoms, and an assumed size of SO_4 group for placing the oxygen atoms at the corners of a regular tetrahedron around the sulphur.

The space group of anhydrite was given by the above and by earlier workers as V_h^{17}: if this is taken in the orientation *Amma*, the cell parameters more recently determined by Swanson *et al.* (1955) are $a=6{\cdot}991$, $b=6{\cdot}996$, $c=6{\cdot}238$ Å, and the atomic coordinates for the structures *A'* and *B* are as set out in Table 1.

Table 1. *Atomic coordinates in anhydrite*

(*A'*) according to Dickson & Binks (1926)
(*B*) according to Wasastjerna (1925)

		x	*y*	*z*
(*A'*)	Ca	0·75	0	0·40
	S	0·25	0	0·10
	O_1	0·25	0·18	−0·05
	O_2	0·07	0	0·25
(*B*)	Ca	0·75	0	0·35
	S	0·25	0	0·15
	O_1	0·25	0·19	−0·01
	O_2	0·06	0	0·31

In view of the methods used in both structure determinations, the small differences in *x* and *y* coordinates are unimportant, but the differences in *z* coordinates are substantial. The two structures are illustrated in Fig. 1. Wasastjerna reviewed the two solutions in a later paper (1926) and then appeared

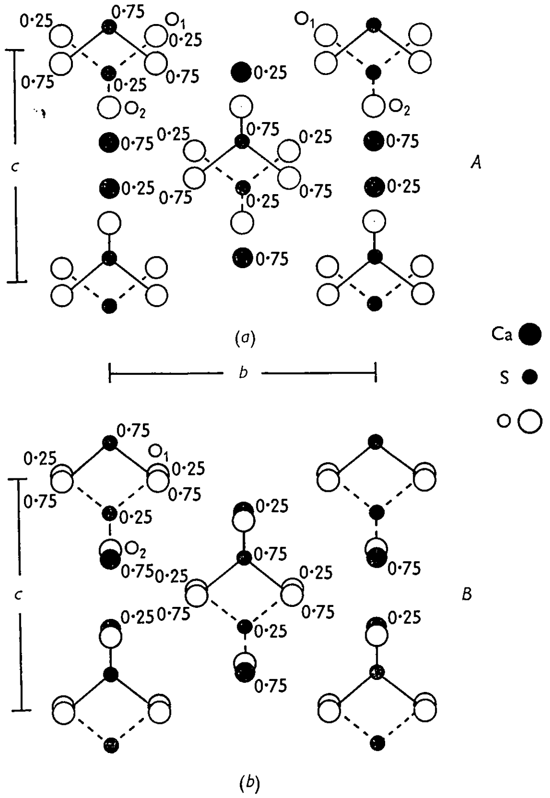

Fig. 1(*a*). Structure of anhydrite *A'*, proposed by Dickson & Binks (1926). This structure has been proved to be incorrect. (*b*). Structure of anhydrite *B*, proposed by Wasastjerna (1925). This structure has been proved to be essentially correct but the linkage of S to O_1 atoms is incorrect (see Fig. 2(*a*) and (*b*)).

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less certain that B was correct. In general, agreement of calculated and observed intensities for the two structures appeared equally good (or bad) and was worse for intermediate structures.

The present authors decided to determine which of the two structures is correct using modern methods of structure refinement, and this can be done using $0kl$ data alone. These X-ray data were collected using Weissenberg photographs from a single crystal of anhydrite (from Madagascar), and Mo $K\alpha$ radiation: 145 reflexions came within the limiting circle, and of these 92 had measurable intensity. Two separate refinements were carried out (using Fourier F_o and (F_o-F_c) syntheses and also the method of least squares), one starting at structure A' and the other at B. After several cycles of refinement the structure B (with initial $R=40$) gave the coordinates shown in Table 2(C), and an R value of 11% (R', calculated with omission of terms with $F_o=0$, was 8%). Values for the thermal vibration parameter B are also given for each atom. Observed and calculated structure amplitudes are compared in Table 3.

Table 2. *Atomic parameters in anhydrite*

(C) from x axis projection of correct structure, after refinements (Cheng & Zussman, present text)
(D) from three projections, after refinements (Höhne, 1961, 1962)

		x	y	z	B (cm.^{2})
(C)	Ca	0·75	0	0·346	0·7
	S	0·25	0	0·155	0·7
	O_1	0·25	0·171	0·015	0·9
	O_2	0·08*	0	0·298	1·1
(D)	Ca	0·75	0	0·346	
	S	0·25	0	0·154	
	O_1	0·25	0·173	0·020	
	O_2	0·08	0	0·296	

* Calculated assuming equal S–O distances in SO_4 tetrahedron.

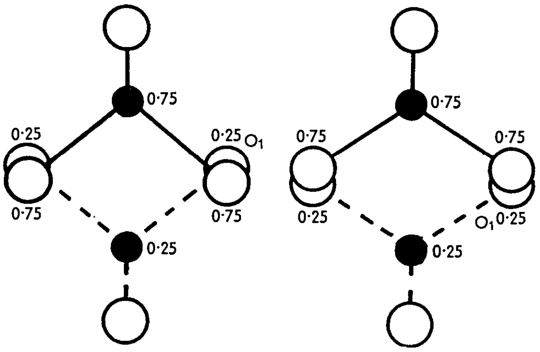
The structure A' gave an initial R of 50%. Using the method of least squares, the oxygen parameters refined slowly with successive cycles towards those of structure B, but the parameters of Ca and S atoms remained virtually unchanged, and R would not improve beyond 30%. Using ϱ_o and $(\varrho_o-\varrho_c)$ syntheses, however, the structure A' refined to give coordinates similar to those obtained by refinement of structure B.

Table 3. *Observed and calculated structure amplitudes for* (100) *projection*

k	l	$\|F_o\|$	F_c
0	2	105	−69
	4	52	−52
	6	176	155
	8	12	7
	10	40	−43
	12	21	21
	14	26	23
	16	21	−20
1	1	0	−15
	3	154	148
	5	21	−24
	7	20	24
	9	0	3
	11	0	7
	13	0	4
	15	0	−7
	17	7	9
2	0	283	314
	2	229	−226
	4	141	−134
	6	112	106
	8	11	−17
	10	50	−54
	12	13	15
	14	23	21
	16	22	−20
3	1	159	−154
	3	0	9
	5	69	−69
	7	7	−7
	9	17	−13
	11	0	−2
	13	0	−4
	15	0	−7
	17	6	9
4	0	235	236
	2	136	−139
	4	123	−108
	6	91	97
	8	9	−14
	10	48	−50
	12	10	13
	14	19	18
	16	20	−20
5	1	7	9
	3	75	64
	5	0	−11
	7	14	19
	9	0	4
	11	0	6
	13	0	−1
	15	0	−6
	17	0	5
6	0	225	218
	2	38	−39
	4	42	−48
	6	101	109
	8	5	7
	10	32	−32
	12	15	18
	14	17	19
	16	14	−17
7	1	0	−1
	3	34	34
	5	0	−11
	7	11	11
	9	0	4
	11	0	6
	13	0	1
	15	0	−4
8	0	125	109
	2	74	−71
	4	71	−73
	6	57	61
	8	0	−10
	10	34	−34
	12	10	11
	14	13	14
	16	8	−13
9	1	30	−31
	3	0	−2
	5	24	−28
	7	0	−9
	9	0	−7
	11	0	−2
	13	0	−3
	15	0	−4
10	0	82	86
	2	42	−43
	4	47	−50
	6	94	49
	8	0	−6
	10	28	−28
	12	6	8
	14	8	10
11	1	0	5
	3	19	23
	5	0	−1
	7	0	7
	9	0	3
	11	0	3
	13	0	0
12	0	84	77
	2	10	−13
	4	19	−21
	6	45	46
	8	0	5
	10	17	−16
	12	10	10
13	1	0	−3
	3	10	12
	5	0	−3
	7	0	3
	9	0	2
	11	0	3
14	0	35	33
	2	23	−25
	4	27	−28
	6	21	21
	8	0	−3
	10	16	−16
	12	5	6
15	1	10	−11
	3	0	−2
	5	8	−9
	7	0	−4
	9	0	−4
	11	0	−1
16	0	29	27
	2	12	−12
	4	17	−16
	6	16	17
	8	0	−2
	10	8	−12
17	1	0	4
	3	7	7
	5	0	2
	7	0	3
18	0	23	22
	2	0	−3
	4	6	−6
	6	15	15
19	1	0	−1
	3	3	2

The different behaviour of least squares and Fourier methods may be related to the fact that intermediate Ca and S positions give worse 'agreement' than either the *A* or *B* positions.

The above refinements showed that the correct approximate structure was undoubtedly *B*, that originally chosen by Wasastjerna (1925, 1926).



(*a*) (*b*)

Fig. 2(*a*) and (*b*). Alternative configurations of SO_4 groups for structure *B*. 2(*a*): as in Wasastjerna's structure. 2(*b*): correct configuration.

In the course of this work it was realized that the structure *B*, as given by Wasastjerna, itself possesses an ambiguity in the (100) projection, since the atoms O_1 have $z \simeq 0$. It is therefore not clear whether the allocation of oxygens to an SO_4 tetrahedron is as shown in Fig. 2(*a*) or 2(*b*). Wasastjerna's structure has configuration 2(*a*), and this results in his obtaining an unusually large mean value for the tetrahedral edge (2·7 Å) and for the S–O distance (1·66 Å). In the refined structure, however, the atoms O_1 have moved further away from $z=0$ and only configuration 2(*b*) results in reasonable O–O and S–O distances as compared with the O–O tetrahedral edge which can be directly determined, and as compared with similar S–O distances in other sulphate structures.

Although the work of Wasastjerna and of Dickson & Binks left some doubt as to which was the correct structure, later literature almost invariably assumes the latter to be correct, *e.g.* *Strukturbericht*, Vol. 1, p. 340, Wooster (1936), Bragg (1937); it now appears that the wrong choice was made. (Wyckoff's 'Crystal Structures' (1948), gives the correct structure). A probable reason for this emerges when the packing of Ca and $(SO_4)^{2-}$ ions is considered, since for the wrong structure, as Dickson & Binks explain 'the calcium atoms are surrounded as uniformly as possible by oxygen atoms ...'. For the wrong structure (*A'*) the calcium atom is surrounded by eight oxygens, four at a distance of 2·55 Å, two at 2·47 Å and two at 2·43 Å: the smallest Ca–Ca distance is 3·68 Å.

From our projection on (100), one S–O distance and one edge of the SO_4 tetrahedron are directly measurable and these are 1·48 Å and 2·39 Å respectively; the smallest Ca–Ca distance is 3·99 Å. The projection leaves one parameter (x of O_2) undefined. Assuming equal S–O distances in the SO_4 tetrahedron this parameter would be $x=0{\cdot}081$, and using this value some approximate interatomic distances can be calculated. For structure *B* the Ca atom is surrounded by eight oxygens, two at 2·55, two at 2·51, two at 2·46 and two at 2·32 Å. Thus the correct structure has a less regular environment of oxygens around each calcium atom, but it has the advantage of a greater Ca–Ca separation.

We intended, before publication of this work, to determine the one remaining unknown coordinate by means of a (010) projection. While preparing to do this, however, we have noticed that Dr E. Höhne has been working on the same problem at the Deutsche Akademie der Wissenschaften, Berlin. Höhne (1961, 1962) reports that he has found, as we have, that the structure *B* is the correct one. The above two publications are very brief but they state that all three projections have been studied, and that a fuller paper is to be published later. In view of this, and in expectation of a full account by Dr Höhne, no further work on anhydrite is contemplated by us, and our work to date is reported here.

For the purpose of comparison the atomic coordinates derived by Dr Höhne are repeated here in Table 2(*D*). Agreement between the two sets of coordinates is very good except for atom O_1. Overlapping of O_1 atoms near the line $z=0$ makes the parameters determined from the (100) projection somewhat less reliable. In a (010) projection these atoms are clearly resolved, so that the values given in Table 2(*D*), derived from all three projections, will be more accurate.

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