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A MORE ACCURATE DETERMINATION OF THE CRYSTAL STRUCTURE OF ANHYDRITE, $CaSO_4$

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A determination of the crystal structure of anhydrite, $CaSO_4$, has been carried out. Once more, by using Patterson, minimization, and electron density functions, a solution to the structure was obtained with the following values of R: $0kl$ – 11.3, $h0l$ – 12.1, $hk0$ – 12.2 and hll – 14.4%. These results must be considered as disproving the structure given in 1926 by Dickson and Binks, although this was featured in the literature as an "anhydrite-type structure," under the designation HO_1. On the other hand, the solution given by Wasastjerna in 1925, almost never quoted in the literature, is verified in principle, although with considerable changes in coordinates and in interatomic distances. For the two S–O distances in the SO_4 tetrahedron which are unrelated by the symmetry, values of 1.47 and 1.48 A were obtained. The four Ca–O distances unrelated by symmetry elements were found to be equal to 2.32, 2.43, 2.52 and 2.58 A.

Introduction

As far back as 1925-26, two different structures had been proposed for anhydrite (Wasastjerna [1, 2], and Dickson and Binks [3]), both of which were reprinted in "Structurbericht" [4] without any arguments in favor of one or the other, although the Dickson-Binks structure was included in a list of typical structures as the H_1 type (anhydrite type). In volume 1/4 of the well-known reference work of Landolt-Börnstein [5], this structure was given as type HO_1.

A new determination of the structure appeared desirable on two counts; first because it was necessary to settle finally the choice between the two structures proposed in 1925-26, and secondly because in both cases the S–O distances in the SO_4 tetahedrons which were given (Dickson and Binks, 1.57 A; Wasastjerna, 1.66 A) are questionable in comparison with the presently accepted values of 1.40-1.50 A for this tetrahedron.

Experimental Results

Using a spherically worked crystal of anhydrite (diam. 130 μ) and MoK_α radiation, Weissenberg photos were taken of the layer lines $0kl$, $h0l$, $hk0$ and hll. A minor absorption effect was calculated from formulas for spherical specimens. All possible reflections within the area of the Mo reflecting sphere were present for the given groups in the list of recorded reflections.

The orthorhombic symmetry of the crystal was again confirmed, and the lattice parameters, given in Table 1, were determined once more.

Systematic extinctions allow for three space groups only: Bbmm, $Bb2_1m$ and Bbm2.

We were not in unconditional agreement with the authors of [1, 3, 6 and 7] in accepting the centrosymmetric group Bbmm, since a statistical analysis of intensities by Howells, Phillips and Rogers [8] supports the noncentrosymmetric group $Bb2_1m$. We nonetheless assumed that the deviation from a centrosymmetric structure was insignificant, and that this could be established from electron density projection derived from calculations based on the centrosymmetric form.

These centrosymmetric methods of calculation, within the space group Bbmm, were used throughout this article.

Structural Analysis

Starting with the Patterson projections $P_0(v, w)$, $P_0(u, w)$ and $P_0(u, v)$ the corresponding minimization functions $M_4(y, z)$, $M_4(x, z)$ and $M_4(x, y)$ were constructed. The atomic positions which emerged from this

TABLE 1. Lattice Parameters of Anhydrite (A)

	Rinne, Hentschel, Schiebold [6]	Wasastjerna [1]	Basche, Mark [7]	Dickson, Binks [5]	Our data
a	6.21	6.24	6.20	6.19	6.23
b	6.95	6.98	6.94	6.94	6.98
c	6.96	6.98	6.97	6.94	6.97

scheme were closer to the initial proposals of Wasastjerna [1] than to those given in the literature as the "anhydrite-type structure" (Dickson and Binks [3]). The calculations of structure factors were initially based on the atomic coordinates given by Wasastjerna, subsequently on the coordinates derived from the minimization functions, and finally on the coordinates which emerged after several cycles of refining. The corresponding values of the coefficient of divergence R are given in Table 2. In the structure factor calculations we used the isotropic temperature factor B, the same for all atoms but differing for the four layer lines: $0kl$ ($B = -0.77$), $h0l$ ($B = -1.17$), $hk0$ ($B = -0.57$), $h1l$ ($B = -0.86$).

Table 2. Values of Divergence Factors R

	Dickson-Binks coordinates, %	Coordinates from minimization functions, %	Coordinates from Table 3, this article, %
0kl	17.0	13.0	11.3 (11.3)
h0l	37.5	17.5	12.1 (15.7)
hk0	53.0	18.4	12.2 (14.6)
h1l	–	–	14.4 (22.8)

Note. In the last column, the first set of numbers were derived using only nonzero values of F_{exp} in the calculations. In the brackets are given the values of all nonobserved values of I, to which are attributed half the minimum observed intensity.

An attempt to refine the coordinates derived from the structure of Dickson and Binks [3] did not yield a positive result. The values of the coefficients R_{h0l} and R_{hk0} were lowered by only about 1%. On the electron density projections we prepared it was possible to see the maxima close to the points which corresponded to the Dickson-Binks coordinates, but these maxima were of an unusual form and had relative heights which agreed poorly among themselves.

All this leads to the conclusion that the structure proposed by Dickson and Binks [3] does not correspond to the true one. Even the initial electron density projections $\rho_0(y, z)$, $\rho_0(x, z)$ and $\rho_0(x, y)$ constructed from the coordinates we used gave a clear pattern with rounded maxima which corresponded completely with the maxima on the minimization functions. All three projections were refined, and in Figs. 1-4 we give their final form together with a generalized projection $\rho_1(x, z)$.

In the calculations we used the Fourier coefficients, modified by the introduction of a special "calculation temperature factor" ($B = -0.8$).

The values of the R coefficients given in Table 2 relate to these projections.

We have taken this structure to be the final one. The atomic coordinates and their relative distances are given in Tables 3 and 4. Figure 5 represents a model of

TABLE 3. Atomic Coordinates

		x	y	z			x	y	z
Ca:	H	0.346	0.750	0	O_1:	H	0.296	0.080	0
	DB	0.40	0.75	0		DB	0.25	0.07	0
	W	0.35	0.75	0		W	0.31	0.06	0
S:	H	0.154	0.250	0	O_2:	H	0.020	0.250	0.173
	DB	0.10	0.25	0		DB	0.95	0.25	0.18
	W	0.15	0.25	0		W	0.99	0.25	0.19

Note. H = Höhne, our results; DB = Dickson and Binks' results; W = Wasastjerna's results.

TABLE 4. Interatomic Distances (A)

S — O_1:	H	1.48 (2x)	Ca — O_1:	H	2.52 (2x)
	DB	1.57 »		DB	2.52 »
	W	1.66 »		W	2.50 »
S — O_2:	H	1.47 (2x)	Ca — O_2:	H	2.58 (2x)
	DB	1.57 »		DB	2.42 »
	W	1.66 »		W	2.50 »
Ca — O_1:	H	2.32 (2x)	Ca — O_2:	H	2.43 (2x)
	DB	2.42 »		DB	2.52 »
	W	2.18 »		W	2.38 »

Note. H = Höhne, our results; DB = distances, from Dickson and Binks' coordinates; W = distances, from Wasastjerna's coordinates.

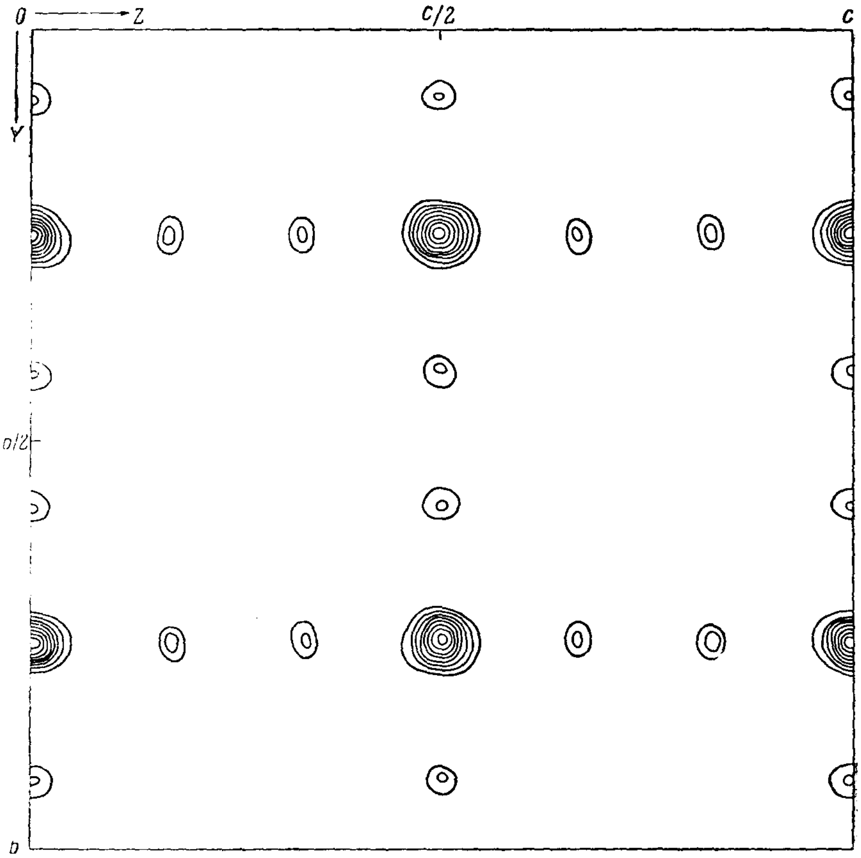

Fig. 1. The electron density projection ρ_0 (y, z).

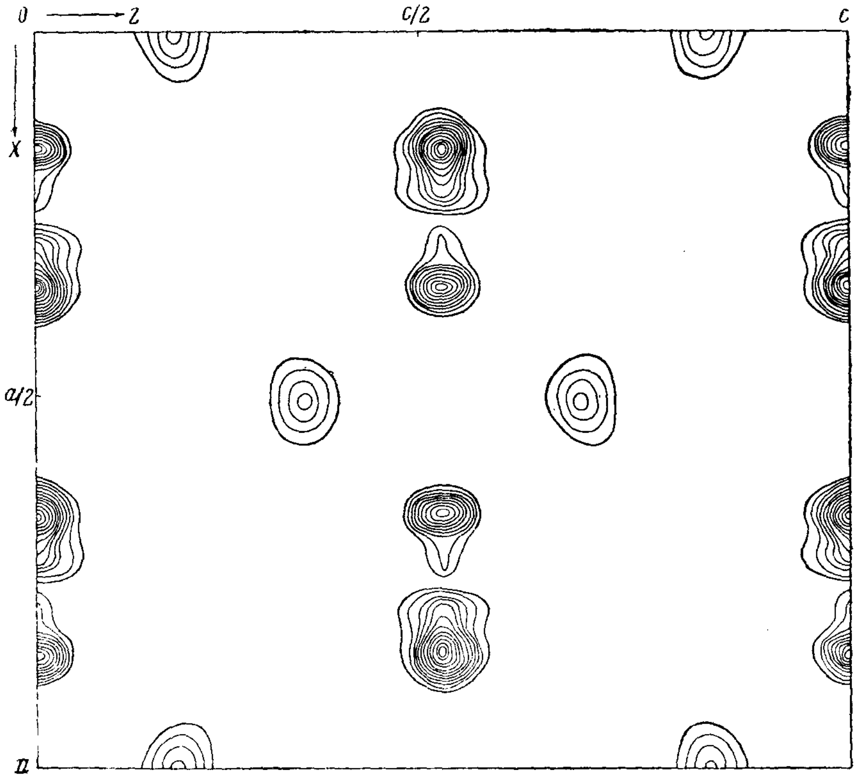

Fig. 2. The electron density projection ρ_0 (x, z).

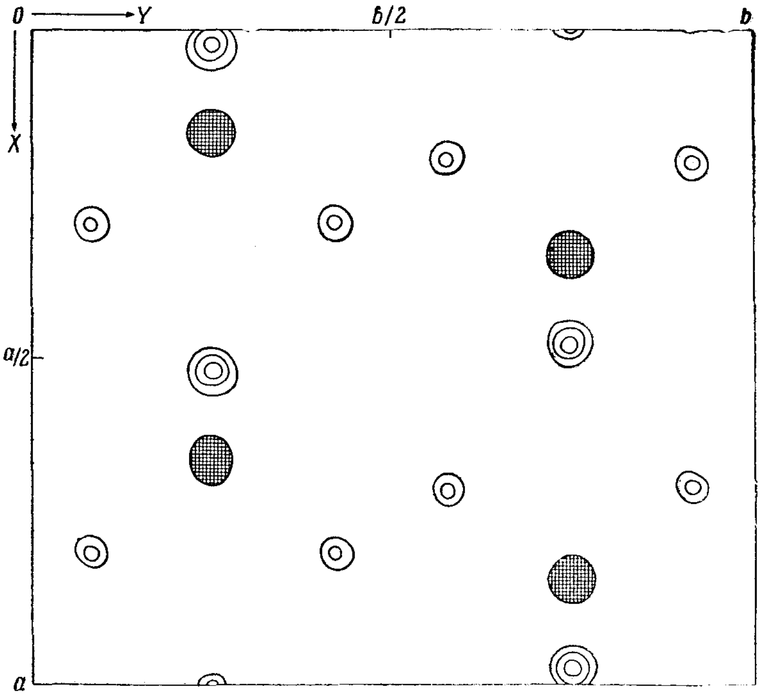

Fig. 3. The electron density projection ρ_0 (x, y).

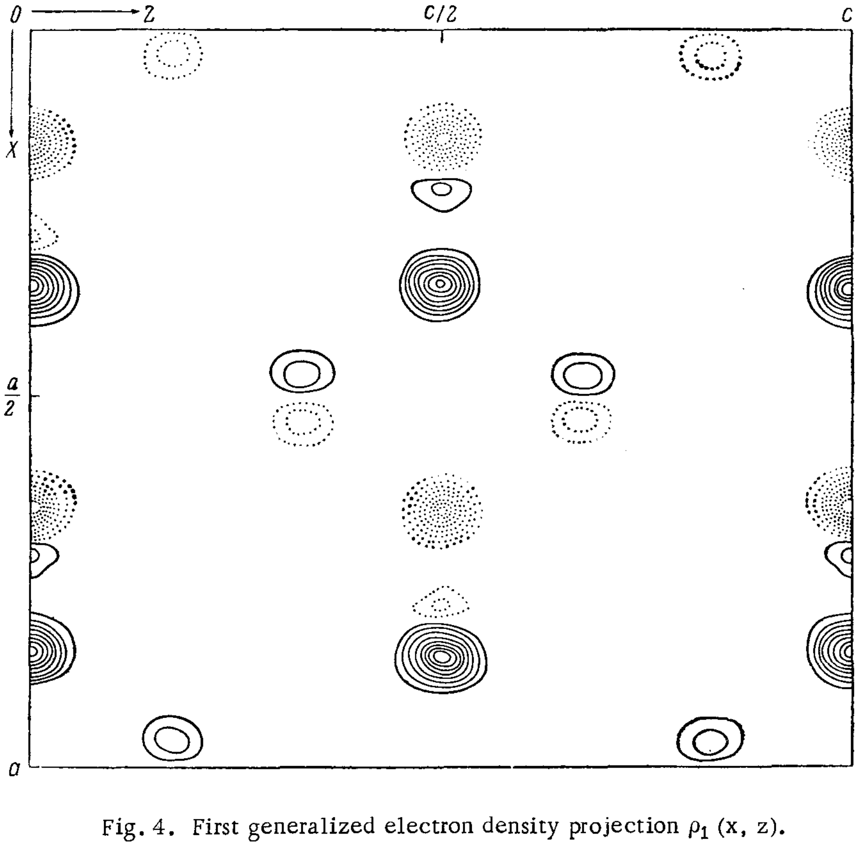

Fig. 4. First generalized electron density projection ρ_1 (x, z).

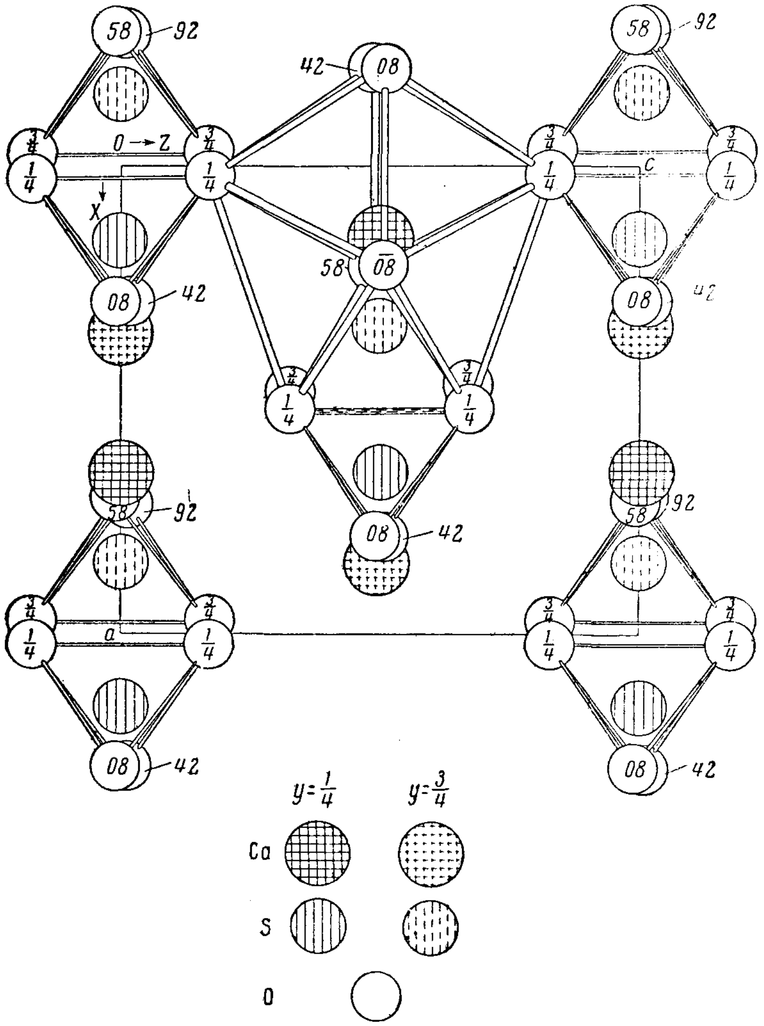

Fig. 5. Model of the structure in a projection on the xz plane. The numbers in the empty circles give the values of the y coordinates (in hundredths of the b cell side). The O atoms which lie on the mirror plane perpendicular to the z axis, and are superimposed, have been slightly separated for clarity (this also applies to Fig. 6).

the structure in a projection on the xz plane, with the coordination polyhedrons picked out.

The Symmetry Group of Anhydrite

We must assume even now that the space group is undecided. The hope that a final decision could be taken on whether or not the structure deviated from centrosymmetric was not realized, and we intend to examine this question in detail in a later article. In the description of the structure which follows we will not dwell on this point further, since there is no doubt that the change in coordinates involved would be very minute. However, the certain lowering in symmetry of the basic masonry of the structure must be borne in mind.

Analysis of the Structure

From the above results we must reiterate that the structure proposed by Wasastjerna [1], although hardly ever quoted, is much closer to the true one than that of Dickson and Binks [3]. Nonetheless, the structure we propose makes appreciable changes in Wasastjerna's coordinates, which are particularly apparent in the interatomic distances (see Tables 3 and 4).

Figure 6 represents a projection of a model of Dickson and Binks' structure on the xz plane, and Fig. 5 represents the model corresponding to our coordinates. The two models differ, particularly, in the quite different positions of the coordination polyhedrons with respect to the

TABLE 5. Experimental and Theoretical Structure Factors

hkl	F_{exp}	F_{theor}
0 0 2	159.8	140.6
4	117.5	101.7
6	112.8	93.8
8	47.0	45.5
10	37.6	39.1
12	32.8	34.6
14	14.0	14.2
16	14.0	14.0
18	9.4	10.7
0 2 0	145.7	—142.1
2	61.1	— 54.2
4	49.4	— 48.7
6	75.2	— 61.4
8	30.5	— 26.1
10	23.5	— 25.0
12	28.1	— 23.7
14	11.7	— 6.1
16	9.4	— 8.1
18	9.4	— 6.5
0 4 0	112.8	99.5
2	51.6	46.1
4	49.4	44.2
6	63.4	55.1
8	28.1	24.8
10	21.1	23.2
12	25.7	22.5
14	9.4	7.4
16	7.0	8.0
18	9.4	6.5
0 6 0	108.1	—94.2
2	68.1	—61.1
4	56.4	—56.4
6	58.7	—61.4
8	35.2	—33.6
10	25.7	—29.4
12	23.5	—27.0
14	9.4	—12.1
16	7.0	—11.1
18	7.0	— 8.7
0 8 0	51.6	46.7
2	30.5	27.0
4	25.7	26.7
6	32.8	34.4
8	18.7	15.0
10	14.0	14.8
12	16.4	14.1
14	4.6	4.5
16	4.6	5.2
0 10 0	37.6	—37.5
2	23.5	—23.0
4	21.1	—22.1
6	25.7	—28.1
8	14.0	—13.1
10	14.0	—10.8
12	11.7	—13.0
14	4.6	— 4.1
16	4.6	— 4.7
0 12 0	37.6	35.1
2	25.7	24.1
4	23.5	23.4
6	23.5	27.5
8	14.0	14.0
10	11.7	14.3
12	9.4	13.7
14	4.6	5.8
0 14 0	14.0	—15.0
2	11.7	— 6.7
4	9.4	— 8.1
6	9.4	—12.8
8	7.0	— 4.5
10	4.6	— 5.2
12	4.6	— 5.8
0 16 0	11.7	13.0
2	9.4	7.1
4	7.0	7.2
6	7.0	10.2
8	4.6	4.1
10	2.2	4.5
0 18 0	9.4	—11.1
2	9.4	— 6.8
4	9.4	— 7.0
6	7.0	— 9.1
1 0 1	—	5.3
3	58.0	—53.6
5	—	4.0
7	—	— 2.6
9	10.1	—12.2
11	—	1.2
13	—	— 2.4
15	—	— 3.9
17	—	0.3
19	—	— 0.5
2 0 0	30.8	—33.6
2	91.3	—91.5
4	55.2	—55.6
6	12.4	—15.9
8	26.8	—27.9
10	13.3	—15.1
12	—	— 5.5
14	9.0	— 8.4
16	—	— 3.2
18	—	— 1.2
3 0 1	54.6	51.4
3	—	4.0
5	23.4	29.2
7	—	14.4
9	—	2.6
11	8.5	11.4
13	—	5.1
15	—	1.6
17	—	3.5
19	—	1.1
4 0 0	21.4	—18.2
2	51.0	—51.1
4	43.7	—38.0
6	15.1	—15.4
8	23.5	—24.5
10	15.4	—13.9
12	6.4	— 5.4
14	8.7	— 7.5
16	—	— 2.7
18	—	— 0.6

TABLE 5. (continuation)

hkl	F_{exp}	F_{theor}
5 0 1	8.5	—12.5
3	26.0	—29.4
5	—	— 5.9
7	—	— 7.2
9	9.0	—11.6
11	—	— 1.6
13	—	— 3.2
15	—	— 3.6
17	—	— 0.3
6 0 0	63.7	55.0
2	40.9	36.4
4	36.6	33.4
6	39.2	35.5
8	19.1	18.5
10	14.5	15.0
12	14.3	12.4
14	5.9	5.0
16	—	4.0
18	—	2.7
7 0 1	9.8	10.1
3	—	—0.2
5	—	7.9
7	—	3.9
9	—	—1.1
11	—	3.0
13	—	0.7
15	—	—0.3
17	—	1.0
8 0 0	—	2.4
2	5.5	—4.7
4	—	—3.4
6	—	1.5
8	—	—3.4
10	—	—1.4
12	—	3.5
14	—	—1.4
16	—	—0.4
9 0 1	—	0.4
3	—	—3.4
5	—	1.1
7	—	0.2
9	—	—1.4
11	—	1.0
13	—	0.0
15	—	—0.4
10 0 0	17.5	—12.1
2	18.6	—14.2
4	16.6	—12.2
6	11.1	— 8.5
8	11.6	— 8.0
10	10.3	— 5.2
12	—	— 2.6
14	—	— 2.4
16	—	— 1.1
11 0 1	—	1.2
3	—	0.0
5	—	1.1
7	—	0.4
9	—	0.0
11	—	0.2
13	—	0.2
15	—	0.0
12 0 0	8.2	3.7
2	—	3.2
4	—	2.4
6	—	2.4
8	—	1.6
10	—	1.1
12	—	0.7
14	—	0.4
13 0 1	—	0.4
3	—	0.1
5	—	—0.4
7	—	—0.2
9	—	—0.1
11	—	0.0
13	—	0.0
14 0 0	9.2	4.9
2	8.5	5.4
4	7.6	4.7
6	6.4	3.5
8	5.0	3.3
10	—	2.2
15 0 1	—	—1.2
3	—	—0.7
5	—	—1.2
9	—	—0.9
9	—	—0.4
16 0 0	8.6	—4.1
2	8.2	—3.1
4	7.6	—2.7
6	6.3	—2.9
8	—	—1.6
17 0 1	—	1.2
3	—	2.0
2 0 0	34.1	—34.1
1	106.1	—102.7
2	28.2	—24.1
3	127.4	108.6
4	11.7	10.6
5	66.0	—58.1
6	21.1	17.5
7	51.8	46.7
8	—	3.0
9	49.5	—44.6
10	—	0.6
11	28.2	26.2
12	11.7	—7.7
13	21.1	—20.7
14	—	—3.4
15	18.8	20.4
16	—	0.6
17	9.4	—9.1
18	4.6	2.5
19	4.6	7.4
4 0 0	22.6	—19.6
1	28.2	23.7
2	37.7	35.6
3	61.2	—53.0
4	35.4	—30.2
4 5 0	23.5	18.7
6	25.8	18.0
7	21.1	—18.8
8	28.2	—22.5

TABLE 5. (continuation)

hkl	F_{exp}	F_{theor}
9	33.0	27.2
10	21.1	16.1
11	14.1	— 8.7
12	11.7	— 8.4
13	11.7	8.4
14	14.1	9.6
15	11.7	—12.4
16	9.4	— 5.1
17	4.6	2.0
18	—	1.8
6 0 0	70.1	63.1
1	25.8	21.1
2	56.6	—56.2
3	—	1.7
4	51.8	50.4
5	23.5	18.7
6	49.5	—45.7
7	16.5	—13.6
8	37.7	35.2
9	—	— 0.6
10	28.2	—28.1
11	11.7	—10.4
12	23.5	22.6
13	7.0	5.2
14	16.5	—17.7
15	—	1.7
16	9.4	11.8
17	—	4.2
18	7.0	—8.8
8 0 0	—	3.0
1	57.8	—53.5
2	16.5	—14.4
3	40.0	39.1
4	14.1	12.4
5	44.7	—46.0
6	—	— 2.1
7	37.7	38.1
8	7.0	10.4
9	23.5	—24.0
10	7.0	— 7.0
11	25.8	24.3
12	—	1.4
13	14.1	—20.1
14	—	— 5.6
15	9.4	10.6
16	—	3.1
17	7.0	—11.2
10 0 0	20.6	—17.6
1	—	0.2
2	30.6	29.8
3	—	2.8
10 4 6	28.2	—26.7
5	—	0.2
6	14.1	14.0
7	—	0.2
8	21.1	—21.0
9	—	— 3.0
10	16.5	17.0
11	—	— 0.1
12	7.0	— 6.0
13	—	— 0.6
14	11.7	10.4
15	—	1.8
16	—	— 6.2
12 0 0	11.1	6.5
1	14.1	11.7
2	16.5	—15.6
3	11.7	— 8.2
4	16.5	13.1
5	11.7	8.4
6	7.0	— 4.5
7	14.1	— 9.5
8	11.7	13.0
9	7.0	4.7
10	9.4	— 8.1
11	7.0	— 5,5
12	—	2.2
13	4.6	3.5
14	7.0	— 6.1
14 0 0	11.1	11.5
1	18.8	—20.4
2	7.0	— 6.1
3	11.7	13.2
4	7.0	5.4
5	16.5	—16.5
6	7.0	— 8.4
7	14.1	14.2
8	4.6	3.4
9	7.0	— 8.1
10	4.6	— 3.1
11	7.0	10.8
16 0 0	10.2	—11.0
1	—	— 3.6
2	9.4	10.5
3	4.6	8.7
4	11.7	— 9.7
5	—	— 2.8
6	9.4	9.3
7	—	3.4
8	—	— 7.7
1 1 1	16.5	—22.0
3	4.0	— 5.6
5	4.8	— 6.0
7	—	— 3.4
9	—	0.0
11	—	0.0
13	—	0.4
15	—	0.7
17	—	0.0
19	—	0.1
2 1 0	119.5	—101.6
2	86.1	—73.0
4	63.1	—56.6
6	50.0	—47.8
8	31.0	—31.5
10	23.9	—24.4
12	16.7	—18.2
14	9.8	—8.7
16	6.9	—7.2
18	4.7	—4.5
3 1 1	10.8	7.1
3	19.5	20.2
5	3.6	2.5
7	3.1	3.6
9	3.6	6.7
11	—	1.0
13	—	2.2
15	—	2.7

TABLE 5. (continuation)

hkl	F_{exp}	F_{theor}
17	—	0.4
19	—	0.9
4 1 0	25.0	23.0
2	43.8	40.5
4	33.2	32.0
6	20.3	17.7
8	22.2	22.0
10	13.7	14.0
12	4.2	7.2
14	4.2	8.0
16	4.0	3.7
18	—	1.5
5 1 1	12.1	—12.7
2	—	3.7
5	6.5	— 9.6
7	—	— 6.0
9	—	— 0.2
11	—	— 6.5
13	—	— 1.5
15	—	— 0.6
17	—	— 2.6
6 1 0	22.5	19.6
2	38.4	34.5
4	27.5	28.1
6	14.6	14.4
8	17.5	20.4
10	11.9	12.9
12	—	5.9
14	4.0	8.4
16	—	4.0
18	—	1.7
7 1 1	7.6	—4.7
3	—	10.0
5	—	—4.6
7	—	—1.1
9	—	5.0
11	—	—2.5
13	—	0.4
15	—	2.0
17	—	—1.0
8 1 0	55.4	—41.1
2	38.8	—33.1
4	35.6	—31.2
6	36.5	—34.7
8	19.9	—19.0
10	16.5	—16.7
12	13.7	—15.5
14	4.7	—6.4
16	4.2	- 5.9
9 1 1	—	2.5
3	12.8	12.7
5	—	1.2
7	—	3.5
9	4.2	8.1
11	—	0.5
13	—	2.5
15	—	3.4
10 1 0	—	0.2
2	9.4	10.5
4	7.2	8.2
6	—	0.2
8	4.2	7.5
10	—	3.7
12	—	0.1
14	—	3.5
16	—	1.0
11 1 1	—	—8.9
3	—	—0.6
5	4.2	—8.7
7	—	—4.4
9	—	—0.7
11	—	—5.6
13	—	—2.5
15	—	—0.4
12 1 0	14.6	8.9
2	20.3	16.2
4	16.2	12.9
6	9.8	6.6
8	13.1	11.2
10	8.5	7.0
12	—	3.0
14	—	5.0
13 1 1	—	—0.2
3	—	5.5
5	—	—0.9
7	—	0.5
9	—	3.5
11	—	—0.6
13	—	0.6
14 1 0	15.3	—12.7
2	10.3	—7.4
4	9.4	—7.4
6	9.7	—9.9
8	4.7	—4.1
10	4.2	—4.5
15 1 1	—	0.1
3	—	3.7
5	—	—0.1
7	—	0.5
9	—	2.4
16 1 0	—	—2.2
2	—	0.9
4	—	0.5
6	—	—1.7
8	—	1.0
17 1 1	—	—1.6
3	—	0.5

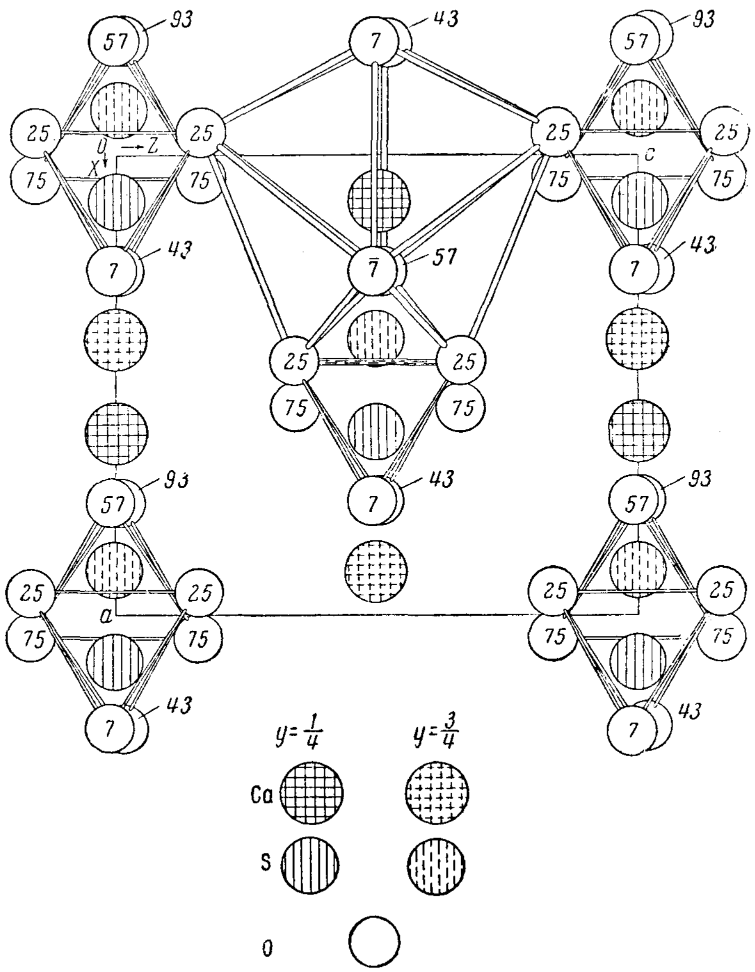

Fig. 6. Model of the Dickson-Binks structure in the projection on the xz plane.

glide plane b (the plane yz). According to Dickson and Binks' results, and also to those of Wasastjerna, this glide plane b cleaves the SO_4 tetrahedrons as in Fig. 6, which does not happen in our structure (Fig. 5). In addition, there are marked changes in all the Ca—O, S—O and O—O distances, and this changes the appearance of the coordination polyhedrons and their relative arrangement.

The coordination numbers and method of linking the coordination polyhedrons are unchanged, so our structure should not be considered as changing the "structure type" as given in reference works.

The sulfur atom is surrounded by eight oxygen atoms, along the tetrahedron. The symmetry of this tetrahedron is only mm2.

The calcium atom is surrounded by eight oxygen atoms, which are situated in the peaks of two tetrahedrons cutting through one another.

Each SO_4 tetrahedron is connected to four Ca polyhedrons by a peak and to a fifth and sixth by a common edge. There are no common O atoms between SO_4 tetrahedrons. Each coordination polyhedron around Ca has a common peak with four SO_4 tetrahedrons, and also common edges with two more. Each Ca polyhedron has a common peak with four other Ca polyhedrons, and a common with two more.

All the calculations of structure factors (Table 5) and electron density projections were made using a Ural-1 electronic computer. The programs were prepared by our colleagues at the Institute, S. Bähr, Ch. Krause and H. G. Weiss, and by a colleague at the Institute of Applied Mathematics and Mechanics, H. Schemmel [9]. I am also indebted to them for helping me to carry out the more elementary calculations on automatic calculators. I am also very grateful to Prof. Dr. Boll-Dornberger-Schiff for his continued interest in this work and for his critical examination of the manuscript. I am also greatly indebted to E. Umlauf for his rapid execution of all the experimental work, and for work on the automatic calculator.

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