Zeitschrift für Kristallographie, Bd. 122, S. 175–184 (1965)

The crystal structure of glauberite, $CaNa_2(SO_4)_2$

By G. Cocco, E. Corazza and C. Sabelli

Centro Nazionale di Cristallografia del C.N.R.
Istituto di Mineralogia dell' Università di Firenze, Italia

(Received March 1, 1965)

Auszug

Die Kristallstruktur des Glauberits $CaNa_2(SO_4)_2$ wurde bestimmt mit Präzessions-Daten einer einkristallinen Kugel. Es ergaben sich 4 Moleküle in der monoklinen Zelle C_{2h}^6—$C2/c$; mit $a = 10{,}158$, $b = 8{,}333$, $c = 8{,}551$ Å und $\beta = 112°20'$. Die SO_4-Tetraeder sind „regulär". Ca ist von acht O umgeben (irreguläres quadratisches Antiprisma). Na zeigt Bindungen zu sieben O (in den Ecken und im Mittelpunkt einer Fläche eines stark verzerrten Oktaeders, oktaedrische Umgebung mit einer zentrierten Fläche). Als bester R-Wert ergab sich 9,0%.

Abstract

The crystal structure of glauberite has been determined from precession data taken on a spherical single crystal. The mineral is monoclinic and its space group is C_{2h}^6—$C2/c$. There are four molecules per unit cell. The parameters, determined by diffractometer data and refined by the least-squares method, are: $a = 10.158$ Å, $b = 8.333$ Å, $c = 8.551$ Å, $\beta = 112°20'$. The SO_4^{--} tetrahedra are "regular". Ca atoms are surrounded by eight O atoms placed at the corners of an irregular square antiprism. The Na atoms, binding seven oxygens, form very distorted octahedra with one centered face. The final discrepancy index R is 9.0%.

Introduction

Cardoso, Garrido and García de la Cueva (1931) investigated glauberite essentially from an optical and morphological point of view; they also determined the lattice constants and attributed the mineral to the space group $C2/m$. Later Pardillo (1935) gave new lattice constants: $a = 9.98$ Å, $b = 8.20$ Å, $c = 8.43$ Å, $\beta = 112°11'$, and the space group $C2/c$. This author in a later work (1935) published the crystal structure of glauberite; this trial structure is not satis-

factory both on account of the low accuracy of the experimental data, and of the doubtful atomic arrangement, showing an inexplicably short distance Na—Na of 1.96 Å.

In a recent paper Corazza and Sabelli (1965) have reported the diffractometric data and redetermined the lattice parameters, the space group and the density of glauberite, as a preliminary investigation of the crystal structure of this mineral.

Experimental

The specimen used for the present structure determination, by x-ray technique, comes from Chinchon (Madrid)*. A transparent and well-formed crystal was ground into a nearly-perfect sphere of 1.03 mm in diameter, by a device similar to the one described by Buerger (1960). The sphere obtained was mounted on an integrating precession apparatus, with the two-fold axis (*b*) as rotation axis.

Intensity data were collected, with filtered Mo$K\alpha$ radiation, for two sets of layers, taken within the mechanical limits of the apparatus: *hkn* ($n = 0$ to 4) and *nkl* ($n = 0$ to 5). The lattice constants determined both from precession photographs and from diffractometer data, and refined by the least-squares method, are:

$$a = 10.158 \text{ Å}, \quad b = 8.333 \text{ Å}, \quad c = 8.551 \text{ Å}, \quad \beta = 112°20'.$$

The observed systematic absences suggest the space groups $C2/c$ and Cc. No evidence of a piezoelectric effect was observed. The application of the statistical method of Howells, Phillips and Rogers (1950) yields a curve which fits the theoretical one for centrosymmetrical crystals perfectly, and the subsequent structure analysis gave no contradictory element; the mineral was therefore assigned to the space group $C2/c$.

Since many and different density values are given in the literature (2.73 to 2.85 g · cm^{-3}), it was thought necessary to repeat this determination. The value measured by the floatation method is 2.77 g · cm^{-3}; it agrees with the calculated density, 2.743 g · cm^{-3}, assuming four molecules of $CaNa_2(SO_4)_2$ per cell.

Integrated intensities were measured by a Nonius microdensitometer on the complete set of precession photographs at the above-mentioned eleven levels with differently exposed films (four for each

* Museum of the Mineralogical Institute, University of Florence, N° 8405-315.

level). Lorentz-polarization and absorbtion corrections, though the latter was somewhat low ($\mu R = 0.86$), were made using a program written by CATANI and ZANAZZI (1965) for the IBM 1620 computer. No attempt was made to correct the extinction errors.

The intensity data were placed on a single scale by correlating the common reflections occurring on the films. 957 non-equivalent reflections were recorded; 360 of which are below the observational limit.

Structure determination

Experimental data were elaborated with a set of programs for the IBM 1620 computer, written by ALBANO, BELLON, and POMPA (1963), ALBANO, BELLON, POMPA and SCATTURIN (1963) and by POMPA, ALBANO, BELLON and SCATTURIN (1963), to whom we are indebted.

A three-dimensional Patterson was computed with the actually observed reflections. Since the multiplicity of atoms in general positions in the $C2/c$ space group is eight, and four Ca atoms are contained in the unit cell, Ca atoms must lie in special positions, namely symmetry centers or two fold axes. As in the Patterson synthesis peaks in positions $\frac{1}{2}\ 0\ \frac{1}{2}$ and $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$ are lacking, Ca atoms cannot occupy sites on symmetry centers. Therefore the Ca atoms were located on two-fold axes and their y coordinate was determined from the Patterson synthesis, on which vectors from Ca to the SO_4^{--}-tetrahedron atoms were also found.

A three-dimensional Fourier synthesis was calculated assigning to the F_o's the signs of the F_c's as obtained from the contribution of Ca and SO_4^{--} coordinates only. The Na sites, hardly detectable from the Patterson vectors, were thus recognized. A further Fourier synthesis gave the coordinates used for the refinement. At this stage the reliability index R was 0.16 for the non-zero reflections.

The atomic scattering factors used in computing the structure factors are those given by HANSON, HERMAN, LEA and SKILLMAN (1964)

The refinement was carried out by the least-squares method, assigning a general isotropic temperature parameter B of 1 Å^2. The computer program applies the following weighting scheme to the observed reflections:

$$w(hkl) = 1/(a + F_o + cF_o^2)$$

where a is twice the minimum observed F_o and c is twice the reciprocal of the maximum observed F_o. After some refinement cycles, coupled

Table 1. *Observed and calculated structure factors*
The calculations were made with the atomic coordinates given in Table 2

h	k	l	F_o	F_c
0	0	2	136.0	-128.6
		4	26.4	27.8
		6		-16.0
		8	48.0	-39.4
		10	30.3	-36.2
0	2	0	53.6	-50.0
		1	16.3	11.2
		2	122.9	126.2
		3		- 4.6
		4	18.4	22.6
		5	40.8	-36.8
		6	92.8	-81.8
		7	53.6	57.4
		8	37.2	32.2
		9	43.0	-40.6
		10	47.1	-46.0
0	4	0		6.4
		1	147.8	-162.0
		2	56.9	-54.6
		3	60.3	60.0
		4	50.7	53.2
		5	30.2	-28.6
		6		- 1.0
		7		-15.4
		8	26.5	-30.4
		9		1.6
		10	31.0	31.4
0	6	0	71.5	-72.6
		1	49.3	51.2
		2		11.0
		3	31.3	-33.4
		4	54.3	-56.0
		5	67.7	-65.4
		6	47.7	52.2
		7	36.7	35.8
		8		7.4
		9	37.8	-32.8
0	8	0	44.5	-53.2
		1	58.1	-58.8
		2		11.0
		3		9.8
		4	36.2	-34.4
		5		-20.2
		6	29.2	26.0
		7	31.8	-29.0
		8		9.4
0	10	0		-10.4
		1	45.8	44.4
		2		- 2.0
		3	48.7	-51.8
		4		- 5.4
		5	20.6	28.0
1	1	0	56.1	45.4
		1	80.4	83.6
		2	91.9	-96.0
		-2	51.6	-45.0
		3		- 1.2
		-3	139.5	154.4
		4		- 3.8
		-4	121.9	118.4
		5	15.2	15.4
		-5	107.2	-112.4
		6	60.6	-74.0
		-6	38.5	37.2
		7	12.8	10.8
		-7	86.7	85.4
		8	18.2	26.4
		-8	13.2	10.2
		9		-12.2
		-9	26.7	-27.6
		10		- 3.0
		-10	35.0	-32.6
		11		16.8
		-11		-11.2
1	3	0	15.3	-12.4
		1	41.9	-44.0
		-1	13.0	12.8
		2	50.9	-51.6
		-2		5.8
		3	128.3	141.4
		-3	60.3	52.0
		4	23.3	-23.0
		-4	58.4	54.6
		5	44.7	-49.0
		-5	68.0	65.8
		6	10.9	11.8
		-6	65.2	-62.6
		7	46.8	53.8
		-7	16.1	-16.6
		8	16.2	14.2
		-8	61.2	65.0
		9		- 2.4
		-9	19.2	-12.4
		10		-16.2
		-10		- 1.8
		11		-11.6
		-11	23.1	23.6
h	k	l	F_o	F_c
1	5	0		- 2.0
		1	63.7	-62.6
		-1	45.0	-44.8
		2	33.6	-32.0
		-2	30.6	27.2
		3	11.6	9.8
		-3	109.8	111.6
		4	38.0	34.8
		-4	109.8	-112.2
		5	40.2	45.0
		-5	47.9	-38.6
		6	17.8	17.4
		-6	68.9	65.6
		7	36.1	37.0
		-7	44.8	45.8
		8		- 5.8
		-8	35.5	-29.2
		9	36.6	-40.0
		-9	43.1	-40.0
		10	21.8	21.8
		-10		13.2
		-11		6.4
1	7	0	48.5	-46.0
		1	38.7	-39.6
		-1	32.0	34.6
		2	112.7	117.6
		-2	38.6	-41.6
		3	18.9	16.6
		-3		- 4.6
		4	53.4	-54.8
		-4	24.1	25.8
		5		- 4.2
		-5		- 5.2
		6	48.1	47.2
		-6	32.6	-34.4
		7		15.6
		-7		5.6
		8		- 7.2
		-8	16.9	-15.0
		9		2.2
		-9	26.5	-18.8
		-10	30.0	26.6
1	9	0		-13.0
		1		- 3.4
		-1	32.8	21.4
		2		5.2
		-2	60.9	63.6
		3		- 2.4
		-3	19.3	-17.4
		4	34.2	38.8
		-4	76.9	-77.4
		5	24.6	-17.4
		-5	14.1	11.4
		6		- 3.2
		-6	46.2	43.8
		7		- 5.8
		-7	39.6	-32.8
		8	35.6	-37.4
		-8	43.6	-42.8
1	11	0	13.4	13.2
		1	50.8	47.2
		-1		4.8
		2	30.0	27.4
		-2		1.6
		3	59.0	-61.2
		-3		5.6
		4	31.5	-31.6
		-4	15.4	17.8
		5	36.8	34.8
		-5	12.2	- 9.4
		6	13.2	15.8
		-6	30.9	-29.0
2	0	0	75.4	-66.0
		2	22.9	-24.2
		4	87.0	77.2
		-4		4.2
		6	48.1	-52.6
		-6	80.7	-83.0
		8	47.6	53.2
		-8	77.1	77.4
		-10	48.8	-52.8
2	2	0	122.7	126.4
		1	59.2	-55.8
		-1	125.8	-136.4
		2	64.7	-64.4
		-2	136.1	-149.2
		3	94.5	113.2
		-3	34.5	-28.6
		4	29.7	34.6
		-4	47.2	39.2
		5		- 1.6
		-5	15.9	-12.4
		6	24.8	25.0
		-6	34.0	-26.0
		7	34.5	-46.2
		-7	76.0	74.0
		8		2.8
h	k	l	F_o	F_c
2	2	-8		-13.8
		9	23.2	-30.6
		-9	17.3	13.0
		-10	32.1	30.6
		-11		- 0.6
2	4	0	44.0	-43.2
		1	83.8	86.4
		-1	67.0	-68.0
		2	46.9	47.2
		-2	12.9	10.8
		3	54.3	61.2
		-3		- 2.4
		4	28.0	30.2
		-4	67.4	-59.6
		5	63.6	-75.4
		-5		-13.0
		6		-12.2
		-6		0.6
		7	32.3	39.4
		-7	83.2	77.6
		8		4.6
		-8	30.2	25.2
		9	43.6	-50.4
		-9	27.1	-25.2
		-10	40.6	40.2
		-11	59.8	58.2
2	6	0	23.8	-19.6
		1		- 7.2
		-1	114.8	-125.0
		2	42.0	40.4
		-2		0.2
		3		9.2
		-3	97.6	93.4
		4	25.4	-21.8
		-4		- 4.2
		5		1.6
		-5	26.4	-24.2
		6	15.6	15.0
		-6	20.0	15.6
		7		- 5.2
		-7		- 5.0
		8		- 4.6
		-8	42.1	-42.4
		9	29.0	-16.4
		-9	34.0	36.6
		-10	43.0	41.0
		-11	21.1	-12.4
2	8	0	17.3	-16.6
		1		5.0
		-1	64.5	63.6
		2		4.2
		-2	51.0	52.2
		3		18.2
		-3	58.2	-61.6
		4	41.3	-46.2
		-4		-13.4
		5	24.1	-16.4
		-5	28.5	24.0
		6	30.7	40.0
		-6	22.8	19.6
		7		10.0
		-7	18.6	22.2
		8	27.9	-36.6
		-8	20.2	-16.6
		9		10.4
		-9	51.0	-51.0
		-10	24.5	22.0
		-11	26.3	29.2
2	10	0		-26.4
		1		-12.6
		-1		3.0
		2		- 4.8
		-2	58.0	59.6
		3	25.8	-24.2
		-3		14.2
		4		-12.4
		-4	22.4	-18.6
		5	37.4	35.6
		-5		- 3.4
		6	20.9	-17.6
		-6	32.8	30.4
		7	20.7	-18.4
		-7	31.1	-32.8
		8		- 6.8
		-8		6.0
		-9	37.5	40.0
3	1	0	66.8	60.6
		1	105.7	-101.6
		-1	127.6	-137.0
		2	27.1	-25.8
		3		-15.2
		4		- 3.6
		-4	107.1	114.2
		5		11.0
		-5	68.7	73.0
		6	81.0	-77.8
		-6	36.5	-30.6
h	k	l	F_o	F_c
3	1	7	40.1	-39.0
		-7	73.0	-79.0
		8	24.9	33.8
		-8	31.7	34.6
		9	24.7	24.2
		-9	19.9	14.2
		10	17.7	-15.2
		-10	38.9	-41.6
		-11	23.8	32.6
3	3	0	98.4	97.8
		1	47.8	-43.6
		-1	91.5	-92.6
		2	67.2	-65.6
		-2	19.3	18.6
		3	38.3	-34.4
		-3	26.4	18.8
		4		7.6
		-4	20.1	-12.4
		5	80.9	-77.8
		-5	111.7	-120.0
		6	16.8	20.8
		-6	22.8	26.2
		7	54.1	54.0
		-7	51.9	54.4
		8	33.9	-36.0
		-8	34.8	-32.6
		9	52.6	-53.6
		-9	50.8	-53.0
		10		- 1.2
		-10		- 8.4
		-11	36.1	40.2
3	5	0	62.4	-60.6
		1	60.6	-51.6
		-1		3.4
		2	64.5	62.2
		-2	39.2	37.2
		3	17.3	16.6
		-3	13.3	-12.6
		4		10.2
		-4		10.0
		5	56.8	-53.0
		-5	69.8	-74.2
		6		-10.6
		-6	67.4	-70.0
		7		- 2.4
		-7		- 2.4
		8	20.5	17.4
		-8	21.2	21.2
		9		11.0
		-9		5.2
		10	20.5	-22.6
		-10		5.0
		-11		15.2
3	7	0		-10.2
		1	56.1	-52.8
		-1		- 7.8
		2	17.6	22.8
		-2		- 6.2
		3		12.4
		-3		12.8
		4		-10.8
		-4	77.6	-73.4
		5		- 4.4
		-5	21.9	-18.8
		6	46.1	44.8
		-6	64.8	68.8
		7		5.8
		-7		- 2.4
		8	43.9	-43.4
		-8	54.0	-60.0
		9		- 2.2
		-9		-16.4
		10	42.5	44.6
		-10	39.2	36.6
		-11		5.8
3	9	0	45.2	-46.6
		1	32.6	26.8
		-1	26.4	26.6
		2	42.0	32.8
		-2		- 1.8
		3	30.5	-33.0
		-3		0.0
		4	35.8	-28.0
		-4	21.3	-17.6
		5	28.6	23.6
		-5	17.5	19.0
		6		14.2
		-6		2.6
		7		13.6
		-7		- 4.8
		8	20.2	21.8
		-8	25.0	23.0
		9		- 2.6
		-9		-14.4
		10		- 8.8
		-10		0.4
		-11		- 6.2

Table 1. *(Continued)*

h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c
3 11 0		-19.8	4 10 2	42.5	41.0	5 9 -4		16.4	7 5 -4	63.2	-60.4
1		8.8	-2		-11.8	5	26.8	29.8	7 7 0		4.0
-1		6.8	3	24.5	29.8	-5	25.9	23.6	1		8.8
2	23.5	-18.8	-3	38.8	-32.6	6	49.1	46.6	-1		- 4.6
-2		7.4	4	45.7	-41.8	-6	37.3	34.4	2	35.1	30.6
3		0.2	-4		4.6	7		-19.2	-2		-12.4
-3		-10.2	5		-14.6	-7		- 6.4	3		14.0
4		- 4.2	-5	25.5	22.6	8	29.3	-30.2	-3		- 0.2
-4		-16.0	-6		0.6	-8	38.1	-35.2	4	56.9	-63.2
5	20.5	15.6	5 1 0	90.1	83.8	9		- 0.8	-4	46.0	44.4
-5	36.7	36.6	1		7.8	-9	24.8	25.2	7 9 0	27.6	-32.0
6	24.0	25.0	-1	21.7	21.4	-10	39.3	37.8	1		7.8
-6	28.6	27.8	2	28.0	-30.0	-11	24.9	-22.6	-1	25.1	21.2
7	22.8	-21.0	-2	90.1	-90.4	-12		-17.8	2		7.4
-7	34.3	-33.8	3		7.6	5 11 0	42.1	-36.0	-2	80.4	89.2
8	19.0	-20.0	-3	48.1	-51.0	1	27.1	20.2	3		10.2
-8	16.5	-14.0	4	69.9	56.0	-1	56.2	52.0	-3	44.2	-42.4
-9	34.2	32.6	5	69.2	-65.2	2		1.0	4		20.6
-10	27.5	23.4	6	17.9	21.4	-2	23.5	17.4	-4	64.6	-63.4
4 0 0	156.5	-144.4	7	56.6	69.2	3		- 6.2	7 11 1	21.9	15.6
2	71.0	-71.6	-7	29.6	34.0	-3	49.2	-48.8	-1		- 6.0
-2	81.9	-82.4	8		13.4	4		17.0	2	31.4	27.8
4		8.0	-8	24.9	36.6	-4		-11.0	-2	19.4	-23.8
-6	55.8	-48.2	9	45.2	-50.6	5		7.2	3	46.0	-41.8
-8	71.2	63.0	-9	29.6	-35.0	-5	33.4	31.6	-3		5.4
-10	45.7	48.2	-10		- 9.2	-6		10.8	4	21.1	-19.6
-12	21.0	-24.8	-11	24.5	21.8	-7		2.4	-4		19.2
4 2 0	19.9	17.6	-12		24.6	6 0 0	172.5	168.2	8 0 0	22.9	30.0
1	53.0	-45.8	5 3 0	38.8	-38.6	2	106.2	-104.6	2	61.3	70.4
-1	24.3	-22.0	1	76.9	-79.0	-2	86.2	-94.4	-2		2.8
2	114.7	-123.8	-1	118.6	-124.8	4	53.5	66.2	4		13.0
-2	70.5	-73.4	2	45.0	44.4	6 2 0	34.4	-39.6	-4	23.0	23.8
3	50.6	51.6	-2	17.2	-12.2	1		3.6	8 2 0	101.1	105.4
4	52.0	55.2	3		- 6.8	-1	39.3	44.6	1	54.2	-53.6
5		-41.0	-3	38.9	30.8	2	49.9	53.2	-1	67.8	-76.2
-5	29.2	-32.4	4	50.9	47.8	-2	35.6	32.6	2	40.6	-40.8
-6	43.0	32.0	5		6.4	3	28.9	-36.2	-2	47.6	-45.2
-7		- 7.0	6	54.2	-56.2	-3	85.7	79.0	3	28.6	33.2
-8	50.0	55.6	-6	31.5	-34.6	4	21.1	-27.6	-3		10.0
-9		-14.6	7	25.7	-30.4	6 4 0	40.8	42.2	4	26.2	33.2
-10	47.6	-42.2	-7	17.8	19.2	1	155.1	-154.4	-4		3.8
-11	39.4	38.0	8	35.3	37.6	-1	42.9	-45.8	8 4 0	49.0	-53.8
-12	56.1	55.2	-8		- 2.2	2	64.5	-69.2	1	28.2	30.2
4 4 0	16.5	29.2	9		2.4	-2	18.1	20.0	-1		- 9.4
1	22.1	-18.2	-9		1.2	3	44.2	50.4	2		9.4
-1		- 7.6	-10		-14.4	-3	32.4	33.8	-2	36.8	38.4
2	52.0	51.4	-11		15.0	4		21.6	3		4.6
-2	22.7	-25.2	-12		24.8	-4		6.8	-3		14.4
3		12.0	5 5 0	30.6	29.2	6 6 0	33.1	-32.0	4		11.0
-3	91.5	78.2	1		- 7.8	1		5.6	-4		- 2.0
4	56.8	-66.8	-1	37.2	-33.2	-1	29.2	34.3	8 6 0	29.2	-30.2
-4		0.6	2		3.4	2	31.5	28.0	1	52.4	-48.2
5		6.4	-2		- 9.4	-2	28.7	25.8	-1	65.2	-65.8
-5	60.7	-60.4	3	43.2	50.0	3	35.8	-36.6	2		6.4
-6		13.4	-3	21.2	-20.6	-3		2.4	-2		-13.6
-7	55.3	50.4	4	46.5	-45.0	4	35.1	-44.4	3	27.0	32.4
-8		-14.6	-4	38.9	36.2	-4	38.6	-30.4	-3	23.4	23.6
-9	24.6	-21.2	5	74.9	-69.6	6 8 0	37.5	-44.6	4	25.8	-23.2
-10		11.8	-5	27.3	-28.2	1	34.2	-31.0	-4		- 6.2
-11		-18.4	6	39.1	39.6	-1	28.8	-30.0	8 8 0		-17.4
-12	31.1	-26.2	-6	30.7	29.0	2	45.1	42.6	1	32.8	24.6
4 6 0		2.0	7	21.5	24.0	-2		- 1.6	-1	33.4	32.6
1	66.6	-63.2	-7	41.3	37.6	3	38.6	41.0	2		6.0
-1	12.8	-13.8	8	55.6	-55.6	-3		- 1.2	-2		8.0
2	27.2	25.8	-8	41.3	-47.8	4		-13.8	3		-19.4
-2	67.1	70.0	9		-23.2	-4		-16.0	-3	43.9	-46.8
3	71.4	78.0	-9	22.3	-23.6	6 10 1	69.0	64.4	4		-35.4
-3		10.8	-10	25.2	21.4	-1	25.3	23.0	-4	30.6	-25.4
4		14.2	-11	35.0	37.6	2		0.6	8 10 1	13.2	-10.8
-4	31.7	-26.4	-12		-17.2	-2		1.8	-1	18.5	-20.4
5		-27.8	5 7 0	51.9	-47.4	3	44.3	-47.4	2		11.6
-5	47.2	49.6	1	34.1	33.8	-3		-14.6	-2	35.1	40.6
-6		-15.0	-1	23.2	-28.0	4		15.4	3	20.0	-17.8
-7		18.8	2		- 0.8	-4	44.9	-40.4	-3		- 0.6
-8	25.7	-20.6	-2	100.7	108.2	7 1 0		11.2	4		- 6.0
-9	54.9	-55.8	3		3.2	1	23.5	-20.8	-4		-14.6
-10		- 3.6	-3	25.9	21.8	-1	27.2	-20.8	9 1 0		12.0
-11	41.1	39.0	4		-15.0	2	47.1	-41.6	1	42.7	-35.4
-12		-13.2	-4	58.0	-52.2	-2	49.9	-48.8	-1		- 2.0
4 8 0		-18.6	5		-11.4	3		15.6	2	28.2	-22.4
1	35.1	36.6	-5		-16.0	-3	110.6	100.0	-2		- 1.4
-1		- 2.0	6	23.1	-22.6	4	36.4	45.4	3	41.3	44.4
2	41.0	40.2	-6	28.9	32.8	-4		- 1.6	-3	23.3	-21.8
-2	53.3	53.4	7		2.0	7 3 0		2.6	4		6.2
3	35.9	-38.4	-7		17.0	1	25.5	-21.8	-4	104.1	103.2
-3	60.7	58.2	8		11.0	-1	44.4	50.2	9 3 0	38.2	45.6
4		- 1.6	-8	25.2	22.2	2		- 4.2	1		- 6.0
-4	36.6	-33.4	9		- 9.0	-2	62.5	-65.2	-1		-18.8
5	24.5	54.4	-9		12.4	3	75.5	88.6	2	50.8	-48.4
-5		- 5.6	-10		-18.6	-3		4.8	-2		8.8
-6	18.5	17.6	-11		14.2	4		- 7.8	3		11.6
-7		- 2.8	-12	25.9	-29.0	-4	57.3	48.8	-3	92.3	87.4
-8	50.4	-50.2	5 9 0		- 1.6	7 5 0	31.3	-33.8	4		3.2
-9	25.1	25.6	1		1.6	1	18.7	-17.4	-4	36.8	-37.8
-10		16.6	-1	16.6	-17.8	-1	64.3	-73.4	9 5 0	22.5	-27.4
-11	33.1	-34.8	2		14.8	2		- 5.8	1	43.4	-35.0
-12		- 6.6	-2	21.2	-17.4	-2	57.3	52.2	-1		2.6
4 10 0		- 2.6	3		- 3.8	3		8.2	2	41.7	38.0
1		7.2	-3		- 0.6	-3	113.5	113.4	-2		-21.0
-1	38.2	36.0	4	62.8	-59.2	4		6.4	3		23.0

Table 1. *(Continued)*

h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c
9 5 -3		11.8	10 4 -3	56.6	48.4	11 5 0	22.6	27.4	12 8 1		-11.6
4	25.9	-23.0	4		-16.8	1	21.5	-21.4	-1	13.8	11.2
-4		13.8	-4		9.6	-1		- 6.6	2	30.1	22.2
9 7 0		-35.0	10 6 0		-18.0	2		-14.8	-2		19.2
1	38.4	-40.4	1		5.6	-2		- 0.2	-3		- 5.2
-1		-11.2	-1		5.8	-3		-21.4	-4		- 8.6
2		10.2	2		11.8	-4	30.8	-25.4	12 10 -1		19.2
-2	28.1	26.4	-2	30.8	33.0	11 7 1		- 4.8	-2	21.9	13.4
3		3.0	3	34.2	39.0	-1		- 2.8	-3		- 3.6
-3		7.2	-3		3.8	2	45.1	39.6	-4	35.2	-27.0
4	22.4	20.0	4		7.8	-2	33.1	33.0	13 1 -1	40.5	-49.6
-4	69.7	-65.4	-4	25.5	-25.8	-3		12.0	-2	30.2	-35.8
9 9 1	23.3	19.0	10 8 1		- 7.6	-4	27.1	-26.8	-3	36.6	40.0
-1	16.6	20.6	-1	21.4	-20.4	11 9 -1		- 1.8	-4		-13.2
2	47.5	34.4	2	23.2	15.4	-2		-15.6	13 3 -1		9.4
-2		- 5.2	-2	43.4	44.8	-3		9.4	-2	27.4	-27.4
3	24.0	-27.0	3	24.0	-27.2	-4		- 7.6	-3	23.3	-23.0
-3		0.6	-3	34.7	31.0	11 11 -2	18.3	18.0	-4	26.2	29.2
4	25.1	-22.8	4		-19.2	-3		-20.8	13 5 -1	40.4	-47.2
-4		2.2	-4	36.0	-34.2	-4		- 3.4	-2	47.5	51.8
9 11 -2	20.0	22.6	10 10 -1	31.7	37.6	12 0 0	27.1	28.0	-3	44.0	46.2
-3	28.5	-27.2			14.4	2	67.3	-90.6	-4	23.2	-20.2
-4	33.1	-31.2	-2		- 5.0	-2		-12.4	13 7 -2		-15.6
10 0 0	23.7	23.2	3		5.4	-4		- 2.2	-3		0.4
2	25.7	-37.0	-3	41.0	-36.6	12 2 1		0.4	-4		12.2
-2	54.4	-46.8	4	21.8	-32.8	-1		8.2	13 9 -2	52.5	54.8
4		- 5.0	-4		17.2	2		15.0	-3		-18.4
-4	34.7	37.6	11 1 0	47.1	42.8	-2	24.9	-28.4	-4	31.3	-35.6
10 2 0		- 1.0	1	36.1	38.8	-3	39.7	32.8	14 0 -4	54.2	59.2
1		-11.6	-1		4.2	-4	62.5	59.4	14 2 -3		11.2
-1	28.6	-37.2	2	22.5	-25.6	12 4 1	56.9	-59.0	-4		-12.0
2	32.3	-31.6	-2		-22.8	-1		-21.2	14 4 -3	32.3	30.6
-2	15.6	-12.4	3	19.8	-25.0	2		-13.8	-4		6.0
3	29.6	33.8	-3		5.4	-2		3.8	14 6 -3		- 5.4
-3		- 3.6	-4	24.7	24.0	-3		2.6	-4		- 4.0
4	32.6	40.2	11 3 0		-11.4	-4		-15.4	14 8 -3		- 5.8
-4		- 4.6	1	49.2	-42.4	12 6 1		5.8	-4		-14.6
10 4 0		2.0	-1	64.0	-74.2	-1	13.2	-13.4	14 10 -3		- 6.4
1		- 0.4	2	21.1	18.0	2	30.7	26.2	15 1 -4		26.8
-1	52.4	-53.4	-2		11.6	-2	24.0	23.4	15 3 -4		-18.8
2	21.9	27.6	-3		14.0	-3	50.7	45.4	15 5 -4		28.8
-2	36.1	-43.0	-4	21.1	22.8	-4	23.2	-23.4	15 7 -4	38.2	-39.0
3	23.4	25.0									

with proper rescalings, the R index reached a final value of 9.0% for all the observed reflections and 14.8% including the non-observed reflections, which were given an intensity one half the minimum observable in each level.

Table 1 lists the observed and calculated structure factors for glauberite after the last cycle of refinement. The final coordinates of the asymmetric unit and the isotropic thermal parameters for each atom, together with their standard deviations, are listed in Table 2.

Table 2. *Atomic coordinates and isotropic temperature parameters with their standard deviations*

Atom	x	$10^3\,\sigma(x)$	y	$10^3\,\sigma(y)$	z	$10^3\,\sigma(z)$	B(Å²)	$\sigma(B)$
Ca	.0000	.0	.0640	.3	.2500	.0	.55	.03
S	.3153	.2	.2858	.2	.3126	.3	.55	.03
Na	.3621	.5	.0550	.6	.0597	.6	1.63	.08
O_1	.1618	.8	.2743	.8	.2735	.9	.42	.09
O_2	.3371	.8	.3379	.8	.1579	.9	.48	.10
O_3	.3843	.9	.1305	1.0	.3644	1.0	.74	.11
O_4	.3741	.9	.4122	1.0	.4411	1.0	.81	.11

Discussion

Distances and bond angles with their standard deviations were calculated using a program written by the authors for the IBM 1620 computer; the results are listed in Tables 3 and 4.

The projection along the *b* axis is shown in Fig. 1.

Table 3. *Interatomic distances and their standard deviations*

Ca—O_1(VII)	2.358 Å	± .007 Å	Na—O_1(I)	2.797 Å	± .009 Å
—O_2(I)	2.432	.007	—O_2(IV)	2.343	.008
—O_4(IV)	2.466	.008	—O_2(VII)	2.547	.009
—O_4(I)	2.737	.010	—O_3(V)	2.486	.010
S—O_1(I)	1.468	.008	—O_3(VI)	2.348	.010
—O_2(I)	1.486	.009	—O_3(VII)	2.605	.010
—O_3(I)	1.458	.008	—O_4(I)	2.675	.010
—O_4(I)	1.474	.008			

Table 4. *Bond angles and their standard deviations*

Ca			Na		
O_1(V)	O_1(VII)	84.0° ± .5°	O_1(I)	O_2(IV)	120.5° ± .3°
O_1(VII)	O_2(I)	100.5 .2	O_1(I)	O_2(VII)	124.5 .3
O_1(VII)	O_2(III)	165.8 .1	O_1(I)	O_3(V)	111.1 .3
O_1(V)	O_4(I)	139.6 .2	O_1(I)	O_3(VI)	82.1 .3
O_1(VII)	O_4(I)	85.7 .3	O_1(I)	O_3(VII)	71.5 .3
O_1(VII)	O_4(II)	95.3 .3	O_1(I)	O_4(I)	51.5 .2
O_1(VII)	O_4(IV)	77.8 .3	O_2(IV)	O_2(VII)	75.2 .3
O_2(I)	O_2(III)	78.5 .5	O_2(IV)	O_3(V)	127.4 .3
O_2(I)	O_4(I)	54.6 .2	O_2(IV)	O_3(VI)	88.5 .3
O_2(I)	O_4(II)	114.9 .3	O_2(IV)	O_3(VII)	115.0 .3
O_2(I)	O_4(IV)	72.8 .3	O_2(VII)	O_3(V)	84.4 .3
O_2(III)	O_4(I)	82.2 .3	O_2(VII)	O_3(VI)	153.1 .2
O_4(I)	O_4(II)	64.4 .5	O_2(VII)	O_3(VII)	55.1 .2
O_4(I)	O_4(III)	125.0 .5	O_2(IV)	O_4(I)	70.4 .3
O_4(I)	O_4(IV)	120.4 .2	O_2(VII)	O_4(I)	102.2 .3
O_4(II)	O_4(IV)	170.8 .2	O_3(V)	O_3(VI)	89.0 .6
			O_3(V)	O_3(VII)	89.5 .6
S			O_3(VI)	O_3(VII)	151.0 .2
			O_3(V)	O_4(I)	162.2 .2
O_1(I)	O_2(I)	108.7° ± .4°	O_3(VI)	O_4(I)	91.9 .3
O_1(I)	O_3(I)	110.9 .4	O_3(VII)	O_4(I)	81.2 .3
O_1(I)	O_4(I)	108.1 .5			
O_2(I)	O_3(I)	108.2 .5			
O_2(I)	O_4(I)	107.4 .5			
O_3(I)	O_4(I)	113.3 .4			

The sulphur of the SO_4^{--} group shows the usual tetrahedral coordination; distances and bond angles fall within the limits reported in the literature. The four S—O distances do not differ significantly from the average value, according to the Cruickshank test.

Calcium atoms bind eight oxygens lying at the corners of a distorted square antiprism, its bases being nearly parallel to (100). The

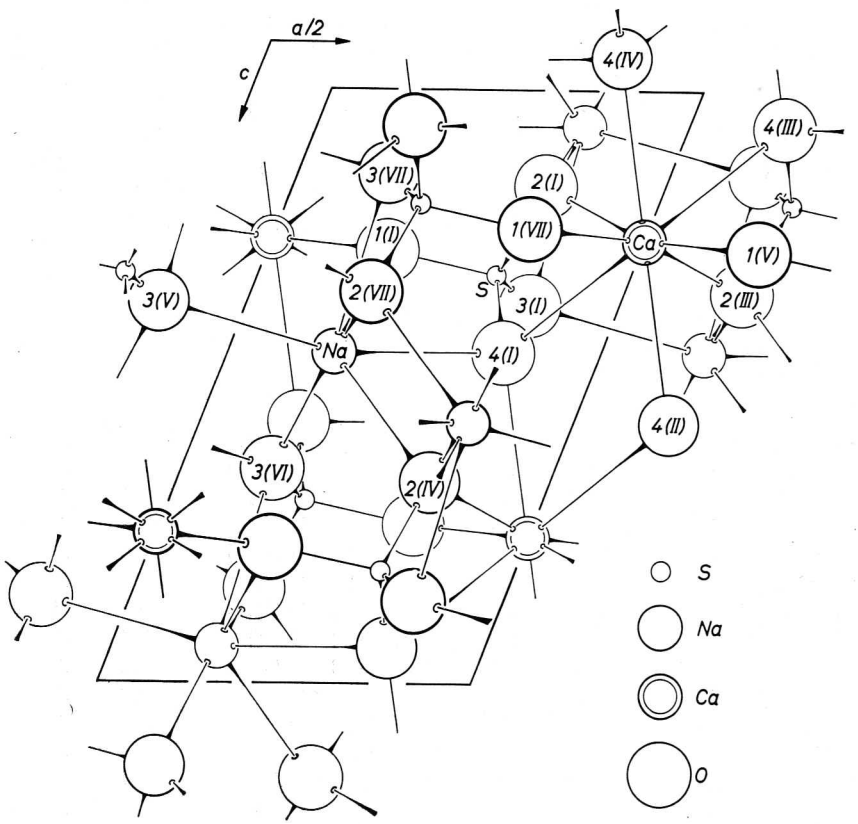

Fig. 1. Projection along the *b* axis of the structure of glauberite

distances are within the limits given in the literature for the eightfold coordination, but two of them (2.737 Å) are rather greater than the 2.50 Å average value. Sodium atoms bind seven oxygens arranged at the corners of a polyhedron similar to an octahedron having one face centered. The average distance is 2.54 Å; the highest value (2.797 Å) is close to the maximum one reported in the literature.

Three oxygen atoms have four neighbours in a nearly tetrahedral arrangement respectively with the following atoms:

O_2 has S + Ca + 2Na
O_3 has S + 3Na
O_4 has S + 2Ca + Na.

The remaining oxygen atom O_1 has only three linkages, namely with S, Ca, Na.

The structure of glauberite, as could be foreseen from its high density, is very compact. The almost homogeneous distribution of the oxygens on layers nearly parallel to (100) makes the two major axes of the optical indicatrix almost equal in magnitude ($n_\beta = 1.535$; $n_\gamma = 1.536$) and lying nearly parallel to this plane: $n_\gamma \equiv b$ and $\widehat{n_\beta c} = 12°$. As $n_\alpha = 1.515$, the negative optical character of the mineral is explained.

The layers formed by oxygens have a high cohesion since they are bound in turn by sulphur and calcium atoms; on account of being divalent and linked to eight oxygens, calcium exerts on each oxygen a bond strength equal to $\frac{1}{4}$ of its valency. Structurally weak points are localized on layers formed by Na atoms, each Na being surrounded by seven oxygen atoms with a bond strength of only $\frac{1}{7}$ of the valency: these layers are parallel to (001) and along them the mineral shows the main cleavage {001}.

It may be concluded that the crystal structure of glauberite shows the following general configuration: each Na polyhedron shares three edges with the surrounding Na polyhedra, forming three types of zig-zag chains, one along the *c*-axial direction, another along the *a*,*b*-diagonal direction, the third along the *a*,*c* diagonal. The straight Ca polyhedra, connected to each other by one edge, are placed along the voids of the sodium-oxygen framework, parallel to the *c* axis.

References

V. Albano, P. L. Bellon and F. Pompa (1963), Programmi cristallografici per l'elaboratore IBM 1620. Nota I: Correzione delle intensità, calcolo dei fattori di struttura e di sintesi di Fourier bidimensionali. La Ricerca Scientifica **3** A, 285—290.

V. Albano, P. L. Bellon, F. Pompa and V. Scatturin (1963), Programmi cristallografici per l'elaboratore IBM 1620. Nota IV: Affinamento di una struttura cristallina col metodo dei minimi quadrati. La Ricerca Scientifica **3** A, 1067—1072.

M. J. Buerger (1960), Crystal structure analysis. J. Wiley, New York.

G. M. Cardoso, J. Garrido y J. García de la Cueva (1931), El grupo estereocristalino de la glauberita. Bol. Soc. Esp. de Hist. Nat. **31**, 547—552.

A. Catani and P. F. Zanazzi (1965), Un programma per la correzione delle intensità dei fotogrammi di precessione. La Ricerca Scientifica, in press.

E. Corazza and C. Sabelli (1965), Dati diffrattometrici sulla glauberite. Rend. Acc. Naz. Lincei **38**, 223—226.

H. P. Hanson, F. Herman, J. D. Lea and S. Skillman (1964), HFS atomic scattering factors. Acta Crystallogr. **17**, 1040—1044.

E. R. Howells, D. C. Phillips and D. Rogers (1950), The probability distribution of x-ray intensities, II. Experimental investigation and the x-ray detection of centers of symmetry. Acta Crystallogr. **3**, 210—214.

F. Pardillo (1935), La distribución atómica en la estructura cristalina de $(SO_4)_2CaNa_2$ (glauberita). Bol. Soc. Esp. de Hist. Nat. **35**, 333—350.

F. Pompa, V. Albano, P. L. Bellon and V. Scatturin (1963), Programmi cristallografici per l'elaboratore IBM 1620. Nota V: Sintesi di Fourier tridimensionale. La Ricerca Scientifica **3** A, 1151—1154.