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The crystal structure of syngenite, $K_2Ca(SO_4)_2 \cdot H_2O$

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Auszug

Syngenit hat die Raumgruppe $P2_1/m$; die Elementarzelle mit $a = 9{,}77$ Å, $b = 7{,}15$ Å, $c = 6{,}25$ Å, $\beta = 104{,}0°$ enthält $2K_2Ca(SO_4)_2 \cdot H_2O$.

Die Struktur ist aus parallel (100) liegenden Netzen von Sauerstoff-Polyedern um K-Atome aufgebaut. Die Polyeder sind sehr unregelmäßige Würfel, denen eine Ecke fehlt und dafür eine Fläche zentriert ist. Die Ca-Atome sind von neun Sauerstoffatomen umgeben; die Polyeder bilden über gemeinsame Kanten Ketten parallel y. Durch diese Polyeder um Ca und durch die SO_4-Gruppen werden die K-Netze miteinander verbunden.

Abstract

Syngenite crystallizes in the space group $P2_1/m$, with two molecules in the unit cell of dimensions $a = 9.77$, $b = 7.15$, $c = 6.25$ Å, $\beta = 104.0°$.

Intensities of ten layers were recorded by the precession method from a spherical specimen. Corrections for absorption and secondary extinction were applied.

The structure consists of a two-dimensional net of K polyhedra, each K being surrounded by eight oxygen atoms at the vertices of a very irregular cube lacking one corner, and with one face centered. K polyhedra form a chain parallel to y by the alternate sharing of a quadrangular face and a triangular one. These chains, two per cell, are linked together by edges and corners to form a sheet parallel to (100). The Ca atom binds nine oxygen atoms, and the Ca polyhedra share one edge to form a chain in the y direction. Each Ca polyhedron shares three corners on one side and two on the opposite one with K polyhedra, and in this way bridges the K sheets to each other. Additional bridges among the Ca chains, and among the Ca chains and the K sheets, are provided by the regular SO_4 tetrahedra. The only oxygen not belonging to SO_4 is the water molecule.

Introduction

The crystal structure of syngenite has been investigated as a part of a series of studies on sulphate minerals. ARUJA (1957) determined the lattice constants of syngenite in several ways, both on synthetic and

natural specimens. The parameters measured by us on the Weissenberg and precession photographs agree with ARUJA's ones. In the determination of the present crystal structure the following lattice constants were then assumed:

$$a = 9.77, \quad b = 7.15, \quad c = 6.25 \text{ Å}, \quad \beta = 104.0°.$$

The space group $P2_1/m$ given by ARUJA was confirmed by the negative result of a piezoelectric test, and the solution of the structure gave no element in favour of the acentric space group $P2_1$.

The specific gravity measured by ARUJA (2.579 g · cm^{-3}) agrees well with the calculated one (2.575 g · cm^{-3}).

Experimental

The crystals used for this structure investigation come from Kalusz, Galicia. A transparent and colorless fragment was ground to the spherical shape (radius 0.52 mm) for a proper absorption correction.

Crystal data:

chemical formula: $K_2Ca(SO_4)_2 \cdot H_2O$

monoclinic, $a = 9.77$, $b = 7.15$, $c = 6.25$ Å, $\beta = 104.0°$

$V = 423.5$ Å^3

$D_m = 2.579$ g · cm^{-3}, $Z = 2$, $D_x = 2.575$ g · cm^{-3}, $F(000) = 328$

space group: $P2_1/m$

absorption coefficient for x-rays [λ (Mo$K\alpha$) = 0.7107 Å]:

$$\mu = 21.72 \text{ cm}^{-1}, \quad \mu R = 1.13$$

Intensity data were collected at room temperature, using a zirconium filtered Mo$K\alpha$ source, on an integrating Buerger precession camera, for two sets of reciprocal-lattice levels *hkl* ($l = 0$ to 3) and *hkl* ($h = 0$ to 5). Intensities deduced from the optical densities were measured by a microdensitometer for all the ten levels, each recorded with a series of five differently exposed films.

Lorentz-polarization and absorption corrections were made by a program written for the I.B.M. 1620 computer by CATANI and ZANAZZI (1965). The $|F_o|^2$'s were converted to an appropriate relative scale by the correlation of the common reflections. 1364 independent reflections were recorded, 343 of which were below the observational limit.

Structure determination

A three-dimensional Patterson function was computed from the corrected intensity data. The general position in $P2_1/m$ being fourfold, Ca atom and the oxygen atom of the water molecule had to lie in special positions; O could lie only on a mirror plane because of the symmetry of the water molecule.

In this Patterson synthesis vectors due to the contribution of K, two sulphur atoms, Ca and four oxygen atoms were recognized, taking into account the main cleavages of syngenite. This could be explained only by admitting the existence of a chain of Ca polyhedra along the y direction.

By means of a three-dimensional Fourier synthesis the remaining atoms were placed. An outstanding feature was that, among 11 non-hydrogen atoms in the asymmetric unit, only K and two oxygen atoms [O(5) and O(7)] lay off the mirror planes. So, the number of atoms in special positions rose from two, as expected before the solution of the structure, to eight. The atomic scattering factors used for the calculations of the structure factors are the ones given by HANSON *et al.* (1964).

The refinement was carried out by two more Fourier syntheses. At this stage, the R index being 0.14, the refinement was continued by the least-squares, block-diagonal, method, using CRUICKSHANK's weighting formula, and individual thermal parameters, as derived from the difference Fourier map. After 8 cycles of refinement the R index dropped to the value of 0.075 for all the observed reflections, and to 0.096 including the non-observed ones, which were given an intensity one

Table 1. *Fractional atomic coordinates and isotropic thermal parameters with their standard deviations*

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
K	.3357	.0002	.0068	.0002	.1947	.0002	1.35 Å²	.02 Å²
Ca	.9679	.0002	.2500		.3327	.0002	.47	.02
S(1)	.9897	.0002	.2500		.8396	.0003	.38	.02
S(2)	.6373	.0002	.2500		.2697	.0003	.66	.03
O(1)	.1191	.0008	.2500		.0167	.0011	1.26	.10
O(2)	.2244	.0007	.2500		.5015	.0011	1.05	.09
O(3)	.5322	.0007	.2500		.0586	.0011	1.12	.09
O(4)	.5650	.0008	.2500		.4493	.0012	1.49	.11
O(5)	.7296	.0005	.0842	.0007	.2837	.0008	1.47	.07
O(6)	.8687	.0008	.2500		.9421	.0011	1.20	.10
O(7)	.9813	.0005	.0840	.0006	.6959	.0007	.89	.06
H	.243		.354		.597			

Table 2. *Observed and calculated structure factors* ($\times 10$)
The calculations were made with the atomic coordinates given in Table 1

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	h k l	F_o	F_c
0 2 0	589	-638	11 4 0		- 18	-5 3 1	255	246	-10 3 1	187	-172	2 9 2	208	218
4	1057	1246	5	171	180	2	194	-196	2		20	-3 9 2	228	240
6	569	-600	12 0 0		36	1	119	120	1	312	290	8	219	-220
8	637	634	1	273	276	0	835	-802	0	412	378	7	287	-296
1 0 0	318	326	2	311	290	5 0 1	106	128	10 0 1	233	-256	6	131	142
1	431	374	3	134	-140	1	63	48	1	176	196	5	263	250
2	523	-548	4		10	2	392	412	2	238	-276	4	366	-392
3	57	- 32	13 0 0	161	-174	3	182	188	3	121	-138	3	551	-594
4		- 10	1	75	54	4	84	86	4	100	- 64	2	162	-160
5	169	150	0 0 1	238	124	5		46	5	135	174	3 0 2	1782	-1260
6	468	-436	1	424	-408	6	243	234	6	86	- 90	1	354	350
7	231	-214	2	73	70	7		26	7	122	-128	2	383	372
8		50	3	241	244	8		50	8		- 28	3	303	-310
9		- 8	4	215	212	9		- 18	-11 8 1	92	- 72	4	752	-806
2 0 0	290	302	5	298	-282	-6 9 1	63	- 72	7		- 12	5	171	190
1	303	-282	6	118	124	8		- 42	6	223	-216	6	293	308
2	736	-812	7	92	86	7	152	-134	5		6	7	213	-206
3	260	254	8	88	84	6	127	112	4	159	-124	8	452	-460
4	223	224	9	161	-182	5	60	58	3		- 18	9	88	104
5	80	- 70	-1 9 1		42	4		- 46	2	250	-226	-4 9 2	169	174
6	443	-440	8	94	88	3	78	80	1		- 10	8	293	296
7	150	150	7	79	- 76	2	345	340	0	97	- 84	7	279	-292
8	145	144	6	338	334	1	160	138	11 0 1	137	154	6	221	218
9		- 12	5	222	220	0	215	214	1		26	5	297	330
3 0 0	1367	1248	4	293	276	6 0 1	296	302	2		6	4	499	548
1	560	552	3	207	188	1		26	3		- 68	3	320	-328
2	389	336	2	290	296	2	324	-356	4	192	224	2	123	120
3	562	-558	1	344	374	3	126	128	5		40	4 0 2	479	-456
4	556	556	1 1 1	419	428	4	376	436	6	68	64	1	131	-108
5	320	304	2	727	-826	5		- 32	7			2	71	64
6	120	-120	3	51	- 26	6	92	-410	-12 7 1	255	-246	3	51	- 54
7	214	-230	4	200	-194	7	66	- 60	6	120	80	4	136	-124
8	376	368	5	185	186	8	224	266	5	249	232	5		10
9	204	200	6	492	-470	9	120	-120	4	111	32	6	207	198
4 0 0	192	242	7	117	-116	-7 9 1	167	174	3	301	-260	7		80
1	260	254	8	76	- 60	8	101	84	2	158	128	8	100	- 96
2	244	-240	9		36	7	144	-140	1	333	300	9	126	114
3	68	- 62	-2 9 1	111	- 96	6		28	0		44	-5 9 2	158	162
4	217	-188	8		- 54	5	249	256	12 0 1	138	134	8		- 78
5	152	134	7		- 34	4	154	136	1	75	92	7	93	-102
6	382	-374	6	458	-462	3	227	-200	2	86	-102	6		30
7	220	-212	5		58	2	196	184	3	133	-142	5	236	244
8		- 46	4	169	-164	1	293	276	4	122	138	4	163	-150
9		20	3	432	462	0	353	334	5	79	64	3	123	-122
5 0 0	163	178	2	776	-890	7 0 1	151	-222	6	81	- 72	2		
1	293	280	2 0 1	186	138	1	199	198	-13 6 1	125	-120	1	297	286
2	478	-460	1	212	218	2	508	-572	5	170	158	0	257	-244
3	109	82	2	366	400	3	205	-198	4	214	180	5 0 2		- 32
4	114	116	3	394	388	4	36	34	3		- 64	1	237	210
5	211	208	4	215	196	5	154	178	2		- 60	2	599	606
6	363	-344	5	133	136	6	219	-238	1	176	168	3	544	-506
7		- 60	6	281	292	7	129	-120	0	311	286	4		- 30
8	114	106	7		- 14	8		32	0 0 2	736	-822	5	168	162
9	71	56	8	95	80	9	104	122	1	481	514	6	403	420
6 0 0	638	630	9		- 38	-8 9 1		44	2	561	-558	7	145	-174
1	268	250	-3 9 1	112	- 94	8		- 42	3	535	-540	8	58	- 62
2	141	120	8	100	- 98	7		- 90	4	234	-222	9	203	210
3	254	-246	7	71	- 68	6	279	-276	5	307	300	-6 9 2	227	274
4	496	484	6	231	230	5	126	116	6		42	8	67	- 74
5	238	220	5	46	- 36	4	88	- 74	7	311	-310	7	305	-366
6		4	4	203	-204	3	64	- 68	8	184	-192	6	112	-110
7	207	-198	3		8	2	472	-454	9	199	198	5	333	360
8	323	302	2	603	676	1	169	166	-1 9 2	247	258	4	176	-156
7 0 0		62	1	113	96	0	156	-136	8	188	194	3	565	-634
1	338	334	0		- 8	8 0 1	229	308	7	400	-392	2	263	-276
2	191	-190	3 0 1	176	-134	1	79	- 76	6	234	236	1	522	522
3	318	-308	1	335	-376	2		28	5	479	448	0	422	-366
4	150	-134	2	88	- 76	3		56	4	421	416	6 0 2	537	-590
5	193	214	3	367	370	4	260	276	3	556	-580	1	217	-198
6	252	-254	4	291	278	5		- 30	2	351	370	2	194	192
7	238	-244	5	272	-260	6		46	1	707	802	3		50
8	103	- 68	6	137	130	7	88	74	0	506	582	4	549	-564
8 0 0	210	280	7	79	88	8	140	178	1 0 2	646	-634	5	151	-150
1	281	278	8	158	156	9		6	1	49	24	6	89	106
2	351	-330	9	218	-212	-9 9 1		- 10	2	121	102	7		66
3		- 24	-4 9 1	137	160	8		- 26	3	380	-372	8	332	-364
4	110	116	8		12	7	189	-166	4	191	-188	9	57	- 50
5	237	244	7	127	-134	6	149	134	5	120	114	-7 9 2		94
6	340	-332	6	326	316	5	123	106	6	187	194	8	290	330
7	131	-128	5	277	268	4		- 26	7		12	7	117	-132
8	93	98	4	41	42	3		- 14	8	113	-116	6	112	110
9 0 0	365	404	3	182	-166	2	261	248	9	209	218	5	116	126
1	435	428	2	471	504	1	175	168	-2 9 2	238	246	4	494	552
2		36	1	352	360	0		32	8	77	- 62	3	182	-172
3	261	-272	0	144	-118	9 0 1	264	254	7	82	- 84	2	67	- 66
4	359	360	4 0 1	540	-562	1	151	160	6		2	1	165	158
5	338	340	2	394	-440	2	188	-204	5	256	250	0	390	370
6	65	40	3	65	- 50	3	92	- 96	4	100	- 90	7 0 2		-116
7	287	-300	4	261	-252	4	242	272	3	446	-448	1	178	158
10 0 0	211	-196	5	60	52	5	87	94	2	123	- 92	2		24
1	84	82	6	232	-230	6	122	-134	1	309	328	3	122	-120
2	52	- 52	7		- 28	7	119	-150	2 0 2	235	238	4		- 54
3	100	- 90	8	111	-100	8	157	194	1	253	272	5	146	142
4	170	-178	9	55	50	9		8	2	738	718	6		72
5		52	-5 9 1	85	- 66	-10 9 1	143	154	3	469	-482	7		- 32
6	62	- 46	8	213	-202	8	123	118	4	88	76	8	58	- 58
11 0 0	67	68	7		- 44	7	166	-166	5	237	212	9	108	120
1	161	182	6	131	-112	6	109	-108	6	372	372	-8 9 2	79	92
2	107	-100	5	84	76	5	261	262	7	223	-226	8		52
3	84	- 76	4	416	-438	4	205	180	8		10	7	74	- 84

Table 2. *(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	h k l	F_o	F_c
-8 6 2	67	- 70	-13 2 2		42	5 3 3	179	-172	10 5 3		- 6	2 2 4	47	- 32
5	186	196	1		- 60	4		54	6	180	160	3	604	616
4	67	78	0	269	252	5		76	7		18	4	453	-438
3		- 4	0 0 3		20	6	77	- 88	8		- 30	5	405	-368
2	218	-248	1	134	156	7	156	-150	9		4	6	72	56
1	210	200	2	383	-388	8		36	-11 9 3		44	7	282	280
0	77	- 54	3	62	- 48	9		40	8		0	8	300	-272
8 0 2	131	-148	4	258	-248	-6 9 3		6	7		8	9	373	-342
1		50	5	141	136	8		- 48	6	163	180	-3 9 4	195	-182
2	471	472	6	366	-378	7	121	126	5		38	8	164	-152
3	206	-214	7		- 60	6	204	-234	4		30	7	257	252
4		- 80	8	113	-114	5	97	-108	3		- 28	6	117	110
5		38	9	91	94	4	90	- 84	2	233	240	5	207	-188
6	389	400	-1 9 3	57	- 54	3		16	1		24	4	227	-228
7	55	- 58	8		58	2	498	-468	0	73	58	3	483	496
8	70	- 86	7		44	6 0 3	264	-242	11 0 3	78	- 76	2	345	360
9	103	90	6	256	-234	1	259	260	1	107	110	1	284	-282
-9 9 2	110	126	5	192	-180	2		- 36	2	108	118	0		- 6
8		112	4	100	98	3	299	-298	3		- 48	3 0 4		- 20
7	223	-246	3	179	-170	4	315	-330	4	145	-150	1	259	-254
6	317	-326	2	132	-112	5	206	226	5		70	2	108	64
5	213	226	1	193	-188	6	99	- 92	6		36	3	314	304
4	123	136	0	514	544	7	147	-140	7	112	-114	4	67	58
3	264	-272	1 0 3	353	332	8	208	-210	8	111	-110	5	185	-172
2	458	-472	1	248	220	9	181	194	-12 9 3		30	6	92	74
1	311	306	2	443	428	-7 9 3	147	-156	8	185	-182	7	237	232
0	175	154	3	149	-136	8	113	-110	7		56	8		40
9 0 2	263	-248	4	184	184	7	84	106	6		4	9	131	-130
1	189	-178	5	128	140	6	144	156	5		- 42	-4 9 4	131	-114
2		- 22	6	270	266	5	196	-230	4	274	-268	8	423	-436
3		4	7		- 46	4	157	-162	3		- 40	7	98	96
4	277	-282	8		68	3	170	174	2		- 2	6	114	116
5	168	-156	9		82	2	256	236	1		- 56	5	170	-170
6		- 40	-2 9 3		52	1	274	-262	0	291	-288	4	667	-698
7	97	98	8	129	128	0	190	-164	12 0 3	359	-328	3	170	154
8	188	-196	7	119	116	7 0 3	334	342	1		- 18	2	265	238
9		- 40	6	178	180	1		26	2	147	140	1	233	-222
-10 9 2		44	5	93	- 98	2	265	276	3	94	100	0	747	-734
8	280	294	4	321	326	3		40	4	302	-294	4 0 4	164	156
7		- 52	3	79	- 48	4	112	102	5		- 2	1	246	-230
6		- 14	2	229	240	5		30	6	132	118	2	316	300
5		42	1	264	-258	6	86	78	7		26	3	271	254
4	420	444	0	477	526	7		2	-13 8 3	169	-162	4	57	50
3	91	- 92	2 0 3	187	176	8		50	7		- 20	5	175	-202
2	87	- 86	1	236	-218	9		10	6	275	274	6	176	166
1		52	2	64	- 68	-8 9 3	111	126	5		- 26	7	133	112
0	449	416	3	113	-106	8		36	4	224	-208	8		22
10 0 2	104	-110	4	59	48	7		- 30	3	122	-106	9	177	-198
1		- 44	5	152	-158	6	126	140	2	283	274	-5 9 4		- 52
2	151	164	6	131	-130	5	88	102	1		- 12	8		- 42
3		48	7		22	4	75	90	0	311	-298	7	74	- 62
4	152	-158	8		42	3	195	-202	-14 7 3		- 44	6	367	342
5		- 20	9		- 32	2	283	290	6	220	216	5		16
6		82	-3 9 3	93	88	1	124	110	5	103	88	4		- 18
7		82	8	102	- 96	0	289	270	4		- 26	3		6
8		-114	7	56	- 56	8 0 3		2	3	103	- 90	2	531	492
9		14	6	273	-272	1	192	188	2	221	204	5 0 4	212	-188
-11 9 2	88	76	5	136	148	2		6	1	115	92	1	302	-288
8		10	4	228	-212	3	105	-102	0		- 90	2	284	-290
7		- 68	3	152	-146	4		- 56	0 0 4	214	266	3	404	458
6		14	2	408	-428	5	112	126	1	322	-332	4	137	-142
5	160	148	1	205	216	6		- 34	2		30	5	247	-268
4		- 4	0	271	-288	7	180	-176	3	387	394	6	172	-184
3		- 46	3 0 3	112	- 94	8		- 44	4	76	64	7	166	210
2	91	-110	1	177	178	9		30	5	223	-220	8	72	- 72
1	160	152	2	124	-132	-9 9 3		- 20	6		- 46	9	257	-286
0	181	-162	3	215	-204	8	117	-128	7	293	278	0 0 5	57	- 50
11 0 2	122	-120	4	363	-352	7	167	176	8		24	1	180	-192
1		- 94	5	182	174	6	120	-108	-1 9 4	196	-180	2	305	330
2	367	364	6	269	-260	5	152	-174	8	350	-326	3	117	112
3		40	7	93	- 96	4	180	-194	7	129	130	4	156	164
4		-100	8	200	-192	3		48	6	67	62	5	133	-132
5	95	- 90	9	152	156	2	195	-198	5	202	-190	6	390	384
6	292	296	-4 9 3	168	-160	1	268	-250	4	486	-498	7	137	122
7		56	8		- 52	0	263	-260	3	253	242	8	108	76
8	70	- 88	7	133	134	9 0 3	289	-392	2	54	- 66	-1 9 5	114	124
-12 8 2		84	6		- 42	1	111	110	1	196	-202	8	80	- 72
7	131	-132	5	297	-300	2	93	112	0	589	-704	7	127	-130
6	209	-212	4	112	-106	3		- 82	1 0 4	110	118	6		- 24
5	116	104	3	179	172	4	335	-350	1	154	-128	5	237	244
4	91	92	4 0 3	116	124	5		112	2	514	496	4	121	-108
3		- 54	1	48	- 34	6	85	88	3	383	346	3	146	-130
2	315	-304	2	652	616	7		- 64	4		- 24	2	219	-234
1	164	148	3	191	176	8	231	-238	5	145	-136	1	297	310
0		58	4	64	- 58	9	82	84	6	297	260	0	212	-338
12 0 2	279	-252	5		- 12	-10 9 3		- 60	7	85	50	1 0 5	69	- 68
1	172	-174	6	280	288	8	102	-112	8		- 32	1		46
2		20	7	48	44	7		32	9	255	-210	2	212	-186
3		60	8		- 38	6	210	228	-2 9 4	160	-140	3	209	-192
4	227	-228	9		- 36	5	110	-110	8		- 10	4		6
5	178	-160	-5 9 3	88	88	4	135	-136	7		- 44	5		0
6		20	8		- 92	3		0	6	308	302	6	99	- 96
7	101	114	7	96	94	2	197	196	5		- 2	7	67	- 72
8	156	-154	6	395	388	1	113	-100	4		38	8		6
-13 8 2	165	158	5	57	- 60	0	263	-244	3	211	196	9		34
7		36	4	159	-150	10 0 3	85	88	2	416	464	-2 9 5	89	- 88
6		14	3	167	-148	1		- 24	1	100	88	8	111	104
5		- 56	5 0 3	76	86	2	303	300	0	86	90	7		- 4
4	212	222	1	153	150	3		28	2 0 4	648	-692	6	222	-230
3		82	2	112	-110	4		- 20	1	455	-454	5	88	- 92

Table 2. *(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	h k l	F_o	F_c
-2 4 5	177	166	5 9 5		36	-4 2 6	230	-210	-3 7 7	120	-110	-2 5 8	286	304
3	69	72	0 0 6	312	328	1	301	-300	6	205	-218	4	199	116
2	353	-376	1		54	0	323	448	5	73	74	3	208	-216
1	85	- 78	2	98	- 78	4 0 6	113	98	4		- 28	2	85	98
0	126	184	3	89	- 86	1		20	3		- 30	1	243	344
-2 0 5	418	-426	4	259	266	2	434	-432	2	170	-194	0	62	98
1		- 12	5		12	3		- 16	1	101	126	2 0 8	294	-284
2	70	62	6	126	- 94	4	72	80	0	74	68	1	128	110
3	72	70	7	68	- 70	5		20	3 0 7		54	2	254	240
4	323	-314	-1 8 6	330	334	6	331	-346	1		24	3	83	- 76
5		22	7		44	7		- 16	2	207	-212	4	214	-190
6	95	80	6	336	-344	8	77	80	3		- 22	5	113	84
7		38	5		28	-5 9 6		- 86	4		6	6	279	254
8	209	-198	4	447	478	8		- 62	5		2	-3 9 8	96	106
9		24	3	66	- 58	7	188	172	6	209	-202	8		- 46
-3 9 5		60	2	320	-318	6	262	-240	7		- 40	7	139	-124
8	117	90	1		14	5	230	-202	8		20	6	113	-132
7		- 12	0	593	708	4	130	-140	9		- 26	5	167	162
6	291	302	1 0 6		26	3	108	100	-4 9 7		- 40	4		- 84
5		46	1	227	-220	2	259	-262	8		10	3	142	-140
4	179	170	2	477	-474	1	255	-242	7		38	2	165	-198
3	120	-130	3	89	84	0		-102	6	103	128	1	152	178
2	289	328	4	67	60	5 0 6	379	360	5	62	- 34	0	82	-102
1	61	62	5	210	-168	1	212	184	4		38	3 0 8	184	-258
0		98	6	391	-342	2	134	-130	3	62	54	1		68
3 0 5	51	54	7	133	136	3	212	-234	2	279	324	2		- 86
1	222	-214	8	92	70	4	262	286	1	54	- 60	3	65	- 66
2	234	222	-2 9 6	51	- 40	5	160	180	0	193	206	4	104	-128
3	226	218	8		0	6	112	-140	4 0 7		- 46	5		72
4	190	198	7	154	166	7	92	-104	1		- 32	6		30
5	176	-176	6	311	-314	8	171	204	2		24	7	77	- 48
6	303	280	5	194	-190	9	164	180	3	136	154	-4 8 8		18
7	173	152	4	47	- 44	0 0 7		32	4	84	- 94	7	208	-210
8	121	100	3		32	1		18	5		- 16	6	75	84
9	102	-110	2	347	-388	2	117	-132	6		- 30	5	198	182
-4 9 5	94	92	1	216	-238	3		30	7		60	4		26
8		4	0	46	- 38	4	83	- 86	-5 9 7	105	104	3	216	-234
7	67	- 64	2 0 6	425	442	5		- 8	8	131	-122	2		38
6	83	- 90	1		28	-1 7 7	81	76	7		- 38	1	174	226
5	144	146	2	124	-106	6	85	84	6		10	0		- 54
4		0	3	135	-136	5	86	-100	5	96	110	-5 9 8	157	140
3	73	- 70	4	303	296	4	141	152	4	187	-178	8	194	180
2	350	-356	5	60	60	3	95	88	3	102	-104	7	208	-198
1	154	158	6	206	-182	2	172	188	2		56	6		- 16
0	254	-280	7		8	1	92	-110	1	92	96	5	278	266
4 0 5	293	-270	8	226	216	0	199	256	0	150	-160	4	258	268
1	118	-110	9	148	122	1 0 7	105	-104	5 0 7	309	326	3	187	-172
2		- 48	-3 9 6		- 6	1	61	54	1		24	2		- 80
3	60	- 54	8	247	234	2		26	2	84	- 78	1	236	302
4	103	-104	7		- 8	3	105	102	3		78	0	198	226
5	116	-112	6	106	- 82	4	131	-118	4	256	306	-2 3 9		- 26
6		60	5		- 54	5	71	62	5		6	2		26
7		30	4	342	352	6	60	- 8	6		- 60	1		- 64
8	77	- 68	3	93	- 90	-2 9 7	31	36	7		- 12	-4 7 9	42	- 44
9		- 22	2	184	-162	8	62	- 60	8	164	210	6	78	- 76
-5 9 5	171	-160	1		- 36	7		- 22	0 0 8	211	-246	5		30
8		- 2	0	299	330	6		- 32	1	115	106	4		- 32
7		24	3 0 6	254	266	5	82	94	2	87	-108	3	76	- 78
6		- 14	1	79	66	4	72	- 82	3	143	-120	2	149	-166
5	146	-124	2		40	3		4	-1 6 8	168	150	1		56
4		- 32	3	122	-104	2	49	- 50	5	224	216	0		-106
3	237	220	4	124	122	1	74	88	4		- 26	-5 8 9	78	54
2	92	- 86	5		38	0		- 88	3	235	-234	7	126	88
1	120	-106	6	96	- 78	2 0 7	219	230	2	78	74	6		86
0	188	-174	7	86	- 90	1	178	-166	1	194	276	5	126	-126
5 0 5	258	-246	8	113	100	2	85	80	0	132	-138	4	86	86
1		- 62	9		30	3	214	196	1 0 8		40	3	122	102
2		6	-4 9 6	111	-118	4	222	216	1	212	200	2	98	120
3		- 6	8	279	262	5	149	-142	2	177	168	1	157	-136
4	187	-214	7	242	244	6	64	60	3	170	-156	0		100
5		- 28	6	211	-194	7	116	110	4	58	42			
6		26	5	217	-208	8	156	142	5	234	186			
7		78	4	376	368	-3 9 7		- 22	-2 7 8	215	-230			
8	123	-146	3	279	288	8		- 16	6	100	98			

half the minimum observable in each level. During the later stages of refinement the correction for secondary extinction was applied, according to HALL and MASLEN's (1965) method:

$$F_o^2 = F_{o1}^2 \exp(\varepsilon \cdot I_c)$$

where F_o and F_{o1} are the corrected and uncorrected observed structure factors and I_c is the calculated intensity; the coefficient of secondary extinction, ε, was 3.3×10^{-5}.

Towards the end of the refinement the hydrogen atom was recognized on a three-dimensional difference Fourier map, and its coor-

dinates were included in the last two cycles of refinement, but its thermal parameter was kept at the reasonable value of 5 Å^2. In Table 1 are reported the final coordinates of the asymmetric unit and the individual thermal parameters, together with their standard deviations. Table 2 lists the observed and calculated structure factors for syngenite after the last cycle of refinement.

Description of the structure

The K atom, in the general position, is surrounded by eight oxygen atoms at the seven corners of a very irregular cube lacking one corner, and on the center of one face. Each K atom is connected to eight more neighbouring K atoms in the following way: by a quadrangular face (K—K distance 3.48 Å) and a triangular one (K—K distance 3.67 Å) to its two symmetrical K atoms through the mirror planes; by one edge to each of its two centrosymmetrical ones (shortest K—K distance 4.48 Å); and by one corner to the four K atoms related by the screw axis.

The projection of the crystal structure along the *c* axis, with exclusion of Ca atoms, is shown in Fig. 1. In this projection the connec-

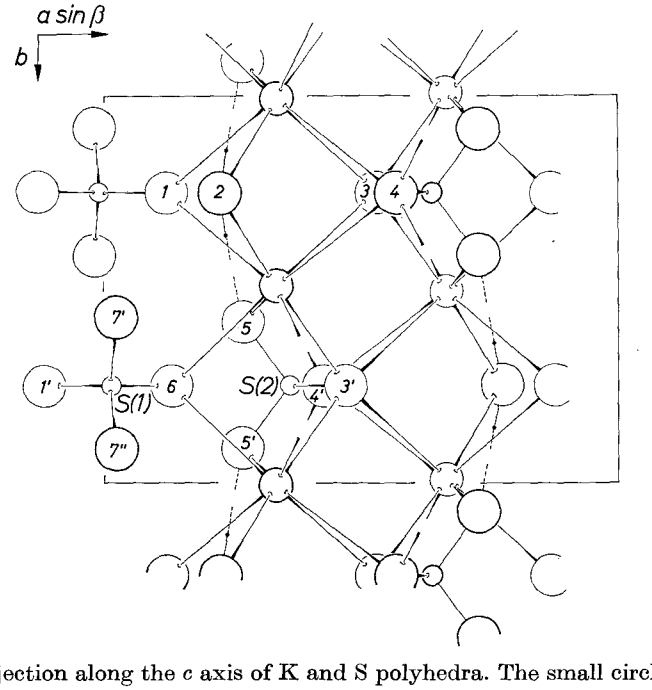

Fig. 1. Projection along the *c* axis of K and S polyhedra. The small circles are S atoms, the larger ones are O atoms, while the medium-sized are K atoms. The solid dots are H atoms

tion, parallel to the b axis, of K polyhedra, linked to each other by four-sided and three-sided faces alternatively, is evident. These K polyhedra, repeated by mirror planes on which are lying the common oxygens O(1), O(2) (water oxygen), O(3), O(4) and O(3′), O(4′), O(6′), build up a straight chain in the y direction. This chain is connected to the correspondent chains of the adjacent unit cells, *i.e.* at a distance c, by two symmetrical chains, these also running parallel to b at intermediate heights. All these chains (two per unit cell) are linked to each other by edges O(3)—O(3) and O(4)—O(4) to form a sheet parallel to (100), are wavy in the c direction, and have a thickness of about $\frac{3}{4}\,a$.

The Ca atom, lying on the mirror plane, binds nine oxygen atoms (mean distance Ca—O = 2.512 Å), three of which also lie on the mirror plane, and six more are symmetrically placed on both sides of the same plane. These Ca polyhedra are arranged along the y direction into an infinite zig-zag chain by the sharing of O(7)—O(7) edges among each

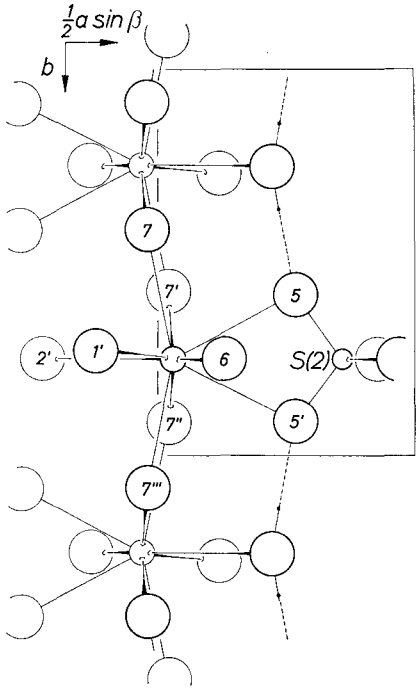

Fig. 2. Projection along the c axis of Ca and S(2) polyhedra. The medium-sized circles are Ca atoms, the remaining ones as in Fig. 1. For a clearer drawing the O(1) atoms are slightly off the mirror planes

polyhedron and its neighbours. Each Ca polyhedron shares three corners of one side and two corners of the opposite side with K polyhedra, bridging the K sheets to each other. These independent Ca chains (one per unit cell) form waves approximately in the *bc* plane. Figure 2 shows the arrangement of Ca polyhedra.

The sulphur atoms, two in special position, instead of one in general position as could be expected, have a regular tetrahedral coordination with a mean S—O distance of 1.473 Å; the bond angles O—S—O range from 107° to 112°.

The S(1) tetrahedron, shown in Fig. 1 only, shares its O(7)—O(7) edge with a Ca polyhedron belonging to a chain and the opposite O(1)—O(6) edge with a Ca polyhedron of another chain. The complex of S(1) tetrahedra, with Ca chains, makes up a sheet parallel to (100); this fills the quarter of cell lacking of K sheets. The strong bonding between S(1) and Ca polyhedra explains the {100} cleavage. Besides, S(1) tetrahedra make additional bridges among the K sheets.

Each S(2) tetrahedron shares one edge with each of its surrounding K polyhedra and the O(5)—O(5) edge with a Ca polyhedron (Figs. 1 and 2) to form further bonds between the K sheets and the Ca chain. Bond lengths and bond angles are given in Tables 3 and 4 respectively.

Cleavages parallel to {110} and {010} are explained by the strong bonds of S(1) tetrahedra with Ca polyhedra in the z direction, and by the linkages of S(2) tetrahedra with K polyhedra in the same direction. In fact, both cleavages break the Ca—O—Ca and K—O—K connections.

Table 3. *Interatomic distances and their standard deviations*

Bond	Length	σ	Bond	Length	σ
K—O(1)	2.756 Å	.005 Å	Ca—O(1′)	2.738 Å	.006 Å
—O(2)	2.981	.004	—O(2′)	2.472	.007
—O(3)	2.867	.005	—O(5)	2.563	.005
—O(3′)	2.920	.004	—O(6)	2.398	.005
—O(4)	2.975	.006	—O(7)	2.453	.004
—O(4′)	2.866	.004	—O(7′)	2.536	.003
—O(5)	2.974	.004			
—O(6)	2.694	.005			
S(1)—O(1′)	1.464	.006	S(2)—O(3′)	1.462	.006
—O(6)	1.474	.006	—O(4′)	1.464	.006
—O(7′)	1.478	.004	—O(5)	1.478	.005

Table 4. *Bond angles and their standard deviations*

Atoms	Angle	σ	Atoms	Angle	σ
O(1)—K—O(2)	61.8°	.2°	O(1′)—Ca—O(5)	123.2°	.2°
—O(3)	90.1	.2	—O(6)	54.6	.2
—O(3′)	125.0	.2	—O(7)	78.1	.1
—O(4)	104.6	.1	—O(7′)	136.5	.2
—O(4′)	143.1	.2	O(2′)—Ca—O(1′)	68.9	.2
—O(5)	77.0	.1	—O(5)	148.0	.1
—O(6)	82.2	.1	—O(6)	123.5	.2
O(2)—K—O(3)	102.3	.1	—O(7)	80.2	.1
—O(3′)	173.1	.2	—O(7′)	77.9	.2
—O(4)	70.1	.2	O(5)—Ca—O(5′)	55.0	.3
—O(4′)	88.9	.1	—O(6)	75.3	.2
—O(5)	138.7	.2	O(7)—Ca—O(5)	74.7	.2
—O(6)	104.1	.2	—O(5′)	129.4	.2
O(3)—K—O(3′)	78.7	.2	—O(6)	88.0	.1
—O(4)	48.2	.2	—O(7′)	69.1	.2
—O(4′)	119.6	.2	—O(7″)	123.6	.1
—O(5)	80.2	.1	—O(7‴)	153.3	.3
—O(6)	144.8	.2	O(7′)—Ca—O(5)	74.9	.1
O(3′)—K—O(4′)	84.7	.1	—O(5′)	99.9	.1
—O(5)	48.2	.2	—O(6)	146.3	.1
—O(6)	77.9	.2	—O(7″)	55.8	.3
O(4)—K—O(3′)	106.4	.2	O(1′)—S(1)—O(6)	107.9	.3
—O(4′)	83.6	.3	—O(7′)	111.7	.2
—O(5)	128.0	.2	O(7′)—S(1)—O(6)	109.4	.2
—O(6)	166.5	.2	—O(7″)	106.7	.4
O(4′)—K—O(5)	126.2	.1	O(3′)—S(2)—O(4′)	109.2	.4
—O(6)	84.0	.2	O(5)—S(2)—O(3′)	109.8	.2
O(5)—K—O(6)	64.5	.2	—O(4′)	110.8	.2
			—O(5)	106.5	.6

Table 5. *Electrostatic valency table*

Anion	Balancing cations	Charges of cations	Total charges surrounding anion
O(1)	S(1), 2K, Ca	3/2 + 2/8 + 2/9	1.972
O(2) (H_2O)	2K, Ca, 2H	2/8 + 2/9 + 110/72	2.000
O(3)	S(2), 4K	3/2 + 4/8	2.000
O(4)	S(2), 4K	3/2 + 4/8	2.000
O(5)	S(2), K, Ca, H	3/2 + 1/8 + 2/9 + 17/72	2.083
O(6)	S(1), 2K, Ca	3/2 + 2/8 + 2/9	1.972
O(7)	S(1), 2Ca	3/2 + 4/9	1.945

The electrostatic charge balance is reported in Table 5; it can be seen that the water oxygen is O(2), a result also noted from the differ-

ence map. The hydrogen atom makes a bridge O(2)----H · · · O(5) of 2.74 Å [distances O(2)—H = 0.94 Å and H—O(5) = 1.80 Å]. The water angle H—O(2)—H is 104°.

All the calculations were carried out on the I.B.M. 1620 computer. We are indebted to Prof. V. SCATTURIN, Dr. V. ALBANO, Dr. P. L. BELLON and Dr. F. POMPA who supplied us the program for the least-squares refinement.

Note added in proofs. This work was presented at the Seventh International Congress of the Union of Crystallography, Moscow, USSR, July 12—19, 1966.

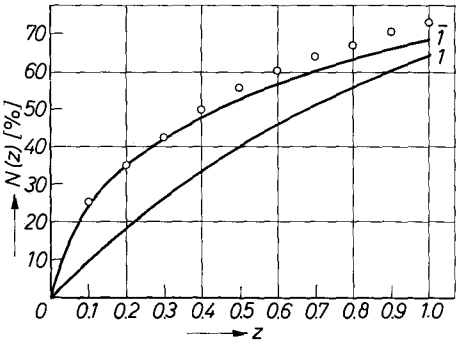

Fig. 3

During the discussion of the paper G. B. BOKIJ informed us that from a crystal structure investigation, made by L. I. GOROGOTZKAYA in 1964 (Doklady Akad. Nauk SSSR, **157**, 1373—1375), syngenite resulted to be acentric. The structure was solved from three-dimensional data, and refined on the *xz* and *xy* projections (R = 18.2 and 17.9 %$_0$ respectively), in the $P2_1$ space group.

A statistical test was then carried out by us, with the contribution of all reflections, as a check of centrosymmetry, according the method of HOWELLS, PHILLIPS and ROGERS [Acta Crystallogr. **3** (1950) 210—214]. The test (Fig. 3) confirmes the space group assumed in this paper.

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