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The Crystal Structure of the Anhydrous Sulphates of Copper and Zinc

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The crystal structure of $CuSO_4$ and $ZnSO_4$ has been determined from X-ray single-crystal data. The crystals are isostructural. They are orthorhombic with $a_0 = 8{\cdot}39$, $b_0 = 6{\cdot}69$, $c_0 = 4{\cdot}83$ Å for $CuSO_4$ and $a_0 = 8{\cdot}58$, $b_0 = 6{\cdot}73$, $c_0 = 4{\cdot}77$ Å for $ZnSO_4$, $Z = 4$, space group *Pnma*. The unknown parameters were determined by trial and error. The S atoms lie at the centre of an almost regular tetrahedron of O atoms. The metal atoms lie at the centre of a distorted octahedron of O atoms.

1. Introduction

Of the normal anhydrous sulphates of bivalent metals only those of Ca, Sr, Ba and Pb form well developed stable crystals, the morphology and structure of which have been fully investigated. The corresponding compounds, containing bivalent cations of a radius smaller than that of Ca (1·06 Å), are unstable and only with great difficulty form comparatively large single crystals, usually yielding a very fine crystalline powder. Most of them are highly hygroscopic and when left in air they absorb moisture and transform to hydrous compounds. But also without the influence of moisture, originally clear crystals of anhydrous Cu, Zn and Fe sulphates become opaque after some time and transform to non-crystalline powders. For this reason, the structure of these compounds and the morphology of several of them have been, notwithstanding their simple composition, only incompletely or not at all investigated.

In the course of the systematic X-ray investigation of these compounds undertaken by us, we investigated the structure of anhydrous copper and zinc sulphates, $CuSO_4$ and $ZnSO_4$. Crystallographic measurements on $CuSO_4$ were made by Scacchi (1873) on natural crystals, formed by very hot fumaroles of Vesuvius. To this mineral Scacchi gave the name hydrocyanite. As regards the dimensions of the unit cell and the space group, nothing is mentioned, so far as we know, in the literature accessible to us. Of $ZnSO_4$, which is mentioned in the literature as a mineral under the name zinkosite but the existence of which is very doubtful, having only once been observed, Schiff (1934) determined the lattice constants $a_0 = 8{\cdot}58$, $b_0 = 6{\cdot}73$, $c_0 = 4{\cdot}76$ Å and the space group *Pnma*. No new data on its structure have been given in the literature up to now.

The single-crystal X-ray photographs of $CuSO_4$, obtained by us, yielded lattice constants approximately the same as those of $ZnSO_4$ and the same space group *Pnma*. The intensities of the corresponding reflexions of the two compounds are very close to each other. After ascertaining that the two compounds are isostructural, we first examined the structure of $CuSO_4$ and then, using the atomic coordinates found for it, we proceeded to the determination of the structure of $ZnSO_4$.

2. Experimental

Well formed, colourless, transparent single crystals of $CuSO_4$, of a length up to 1 mm., were prepared by slow evaporation of an aqueous copper sulphate pentahydrate solution, to which a small quantity of dense sulphuric acid was added. The solution was put into a retort of Jena glass and kept at a constant temperature of about 250° C. until complete evaporation took place. From the crystals thus formed, were chosen those with almost equidimensional cross-section normal to the rotation axis and of a diameter less than 0·4 mm. To protect them from the humidity of the air the crystals were enclosed in capillary tubes of Lindemann glass. By using these crystals and employing unfiltered Cu K radiation, rotation diagrams round the three crystallographic axes and zero-layer and equiinclination Weissenberg diagrams of the first and second layers were obtained. The blackness of the $K\alpha$ reflexions was measured by means of a non-recording Hilger photometer. From this the intensity of the reflexions was calculated, after allowing for the influence of the continuous radiation, estimated by measuring the blackness of the background at the immediate neighbourhood of each reflexion. For the very strong reflexions the blackness of the corresponding $K\beta$ reflexions was also taken into account. The ratio of the intensities of $K\alpha$ and $K\beta$ reflexions of the same plane was taken as $K\beta:K\alpha = 1:7$. The final value of the I_{hkl} was considered to be the average of several intensity measurements of the corresponding reflexion on various diagrams obtained with different exposures. A slight correction for absorption was applied by using approximate absorption factors estimated graphically, after taking into account the shape and dimensions of the crystals used. The relative values of F_{hkl} were obtained in the usual way, after correcting for the polarization and Lorentz factors. By multiplication by a suitable coefficient the F_o values were derived.

3. Lattice constants and space group

In the following description a mutual change of the axes *a* and *b*, as these are given in the literature, has been found necessary in order to bring the orientation of $CuSO_4$ in agreement with that of its isostructural $ZnSO_4$. The interpretation of the diagrams obtained gave:

$$a_0 = b_{\text{lit.}} = 8{\cdot}39,\ b_0 = a_{\text{lit.}} = 6{\cdot}69,\ c_0 = c_{\text{lit.}} = 4{\cdot}83\ \text{Å}\,.$$

The axial ratios calculated from these are:

$$b_0 : a_0 : 2c_0 = 0{\cdot}797 : 1 : 1{\cdot}151$$

whereas the goniometrically obtained values, given in the literature (Hintze, 1930) are:

$$a : b : c = 0{\cdot}7971 : 1 : 1{\cdot}130\,.$$

For a unit cell content of four molecules $CuSO_4$ was deduced a density of 3·90 g.cm.$^{-3}$, whereas that given in the literature is 3·65 g.cm.$^{-3}$ (Dana, 1952). Density measurements carried out by us gave also a low value, 3·57 g.cm.$^{-3}$, due to imperfect internal development of the crystals, many of which show cavities when viewed through a microscope.

Examination of the crystals under the polarizing microscope showed that the optical orientation of the axes is different from that given in the literature (Posnjak & Tunnel, 1929). We found the following orientation:

$$X \| c_0,\ \Psi \| b_0,\ Z \| a_0\,.$$

The observed reflexions are: *hkl*: no conditions; 0*kl*: $k+l = 2n$; *h*0*l*: no conditions; *hk*0: $h = 2n$. From these conditions, taking also into account the holohedral appearance of the crystals, it follows that V_h^{16}–*Pnma* is the most probable space group.

4. Determination of the structure, and discussion

As the unit cell contains four molecules $CuSO_4$, we have to arrange in it four Cu, four S and sixteen O atoms, the last ones in tetrahedral arrangement round the S atoms at a distance not less than 1·40 Å, according to the data given in the literature for the numerous sulphates with known structures. The space group V_h^{16} contains three fourfold positions. Two of these,

$$(a)\quad (0,0,0;\ 0,\tfrac{1}{2},0;\ \tfrac{1}{2},0,\tfrac{1}{2};\ \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2})$$

and

$$(b)\quad (0,0,\tfrac{1}{2};\ 0,\tfrac{1}{2},\tfrac{1}{2};\ \tfrac{1}{2},0,0;\ \tfrac{1}{2},\tfrac{1}{2},0)$$

coincide with symmetry centres, while the third,

$$(c)\quad (x,\tfrac{1}{4},z;\ \bar{x},\tfrac{3}{4},\bar{z};\ \tfrac{1}{2}-x,\tfrac{3}{4},\tfrac{1}{2}-z;\ \tfrac{1}{2}+x,\tfrac{1}{4},\tfrac{1}{2}-z)\,,$$

with two degrees of freedom, lies on the symmetry plane *m*. Because of the tetrahedral symmetry of the SO_4 group, the first two positions are not allowed for the S atoms and thus we have to put them on position (*c*), whereas the Cu atoms must occupy one of the fourfold positions (*a*) or (*b*). At the same time the symmetry of the tetrahedron SO_4 renders it necessary to bring one of its symmetry planes in coincidence with the plane (*m*), on which the S atoms lie. In this way, two O atoms of the tetrahedral group SO_4, designated O_{I} and O_{II}, lie on the plane (*m*), whereas the remaining two, designated O_{III}, form a pair lying symmetrically on both sides of the plane (*m*) and occupying an eightfold position with three degrees of freedom. The parameters to be determined are nine: *x* and *z* for the S, O_{I} and O_{II} atoms and *x*, *y*, *z* for the O_{III} atom.

To determine the unknown parameters we considered several structure models satisfying the symmetry requirements of the space group *Pnma* and the space demands of each atom in the unit cell. These models were tested by the trial-and-error method by comparing the F_o values of the reflexions *hk*0, *h*0*l*, 0*kl* with those of F_c. The best agreement between F_o and F_c values was obtained with the coordinates of the atoms listed in Table 1.

Table 1. *Atomic parameters in* $CuSO_4$

Atom	*x*	*y*	*z*
4 Cu	0	0	0
4 S	0·186	0·250	0·444
4 O_{I}	0·130	0·250	0·736
4 O_{II}	0·367	0·250	0·444
8 O_{III}	0·130	0·053	0·305

Comparison of the F_o and F_c values, given in Table 2, shows that the agreement is satisfactory. The reliability index ($R = \Sigma \| F_o| - |F_c\| \div \Sigma |F_o|$), in the calculation of which all the missing reflexions with $F_o = 0$ were also included, without applying the Hamilton correction (Hamilton, 1955), has, for a total of 108 reflexions, the value $0{\cdot}16_8$. Thus the correctness of the model proposed should be considered as certain.

The spatial arrangement of the SO_4 tetrahedra and

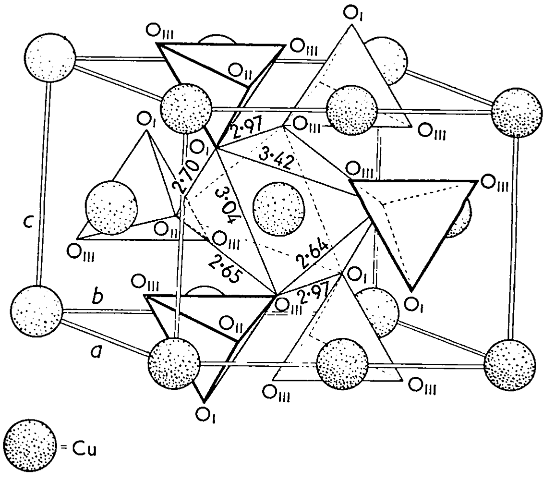

Fig. 1. The structure of $CuSO_4$, showing the spatial arrangement of the SO_4 tetrahedra and the Cu atoms.

Table 2. *Comparison of the observed and calculated structure factors of* $CuSO_4$

0kl reflexions

	F_o	F_c		F_o	F_c		F_o	F_c		F_o	F_c
011	13	−12	042	91	+91	062	40	+39	073	46	+38
020	51	+53	033	53	+57	044	64	+67	064	30	+33
002	74	+78	051	25	−25	015	26	−26	006	29	+31
031	26	−28	004	80	+79	071	0	− 5	082	72	+69
022	29	+33	024	33	+44	035	33	+27	055	26	−20
040	113	+140	060	14	+ 3	080	81	+72	026	66	+69
013	61	−56	053	38	−31						

h0l reflexions

	F_o	F_c		F_o	F_c		F_o	F_c		F_o	F_c
101	54	+93	600	90	+104	404	44	+42	902	0	− 2
200	47	+62	303	58	+56	800	54	+57	704	37	+26
201	29	−23	502	39	−27	801	0	− 2	505	55	+62
301	87	+115	601	0	− 1	504	0	− 8	1000	45	+50
102	50	+50	403	30	+25	105	32	+36	1001	0	+ 3
202	55	+65	602	69	+77	703	56	+74	903	52	+58
400	0	+ 4	104	29	+23	802	12	+17	106	42	+29
401	17	+18	204	50	+54	205	0	− 1	605	32	−30
302	21	+ 7	503	28	+31	305	59	+64	206	48	+54
103	79	+88	701	54	+64	604	51	+56	804	43	+50
402	85	+95	304	12	−15	901	54	+58	1002	63	+60
501	45	+48	702	0	+ 9	405	30	+22	306	0	+ 2
203	0	− 8	603	23	−24	803	0	+ 2			

hk0 reflexions

	F_o	F_c		F_o	F_c		F_o	F_c		F_o	F_c
210	36	−46	420	73	+82	640	68	+81	1010	20	+13
220	95	+114	240	40	+42	810	0	− 2	850	0	− 7
630	40	+41	430	25	−30	820	65	+79	280	23	+29
450	34	+33	610	11	−13	460	75	+77	1020	30	+32
470	35	−23	440	35	+33	650	0	− 4	670	21	+26
660	11	+27	620	28	+37	830	0	− 3	1030	32	−28
410	35	+36	250	48	−45	270	18	− 9	480	32	+41
230	0	− 4	260	72	+78	840	26	+39			

the Cu atoms is shown in Fig. 1 in clinographic projection. In this figure the tetrahedra drawn with bold lines are those perspectively nearest. The orientation of the SO_4 tetrahedra within the unit cell is such that one of its planes is parallel to (100).

Table 3. *Interatomic distances in* $CuSO_4$

Atom	Point position	Neighbour	Coordination number	Interatomic distance (Å)
Cu	(*a*)	O_I	2	2·36
		O_{II}	2	2·15
		O_{III}	2	1·87
S	(*c*)	O_I	1	1·48
		O_{II}	1	1·51
		O_{III}	2	1·53
O–O distances in tetrahedron				
O_I	(*c*)	O_{II}	—	2·43
		O_{III}	—	2·45
O_{II}	(*c*)	O_{III}	—	2·46
O_{III}	(*d*)	O_{III}	—	2·58
O–O distances in octahedron				
O_I	(*c*)	O_{II}	—	2·70
		O_{II}	—	3·42
		O_{III}	—	2·97
		O_{III}	—	3·04
O_{II}	(*c*)	O_{III}	—	2·64
		O_{III}	—	2·65

The interatomic distances between the nearest atoms in the unit cell, calculated by using the values of the parameters listed in Table 1, are given in Table 3. The distances are in agreement with those known from the structures of other compounds.

The SO_4 tetrahedron appears slightly distorted with an average S–O distance 1·51 Å and O–O distances ranging between 2·58 and 2·43 Å. Each Cu atom is surrounded by six O atoms occupying the vertices of a stronlgy distorted octahedron. The O atoms are arranged in pairs centrosymmetrically round the Cu atom at distances 1·87, 2·36 and 2·15 Å. The edges of the CuO_6 octahedron, which represent the distances between the centres of neighbouring O atoms, range between 2·64 and 3·42 Å.

5. The structure of $ZnSO_4$

After ascertaining that $CuSO_4$ and $ZnSO_4$ were isostructural, there remained only the estimation of the

Table 4. *Atomic parameters in* $ZnSO_4$

Atom	*x*	*y*	*z*
4 Zn	0	0	0
4 S	0·186	0·250	0·458
4 O_I	0·130	0·250	0·750
4 O_{II}	0·367	0·250	0·458
8 O_{III}	0·130	0·072	0·319

Table 5. *Comparison of the observed and calculated structure factors of* $ZnSO_4$

$0kl$ reflexions

	F_o	F_c		F_o	F_c		F_o	F_c		F_o	F_c
011	12	−12	042	97	+96	062	40	+44	073	51	+29
020	37	+39	033	53	+48	044	76	+81	064	0	+28
002	84	+87	051	20	−16	015	19	−20	006	45	+52
031	38	−34	004	90	+88	071	0	+ 2	082	71	+74
022	32	+39	024	0	+29	035	39	+32	055	0	−14
040	128	+133	060	26	− 8	080	92	+76	026	51	+59
013	48	−46	053	27	−31						

$hk0$ reflexions

	F_o	F_c		F_o	F_c		F_o	F_c		F_o	F_c
200	63	+67	610	0	−11	810	0	− 3	1000	57	+55
210	50	−52	440	44	+47	820	72	+79	1010	23	−12
220	84	+120	620	29	+38	460	86	+86	850	20	− 4
400	8	+ 8	250	61	−40	650	7	− 5	1020	38	+36
410	38	−38	630	37	+42	830	0	− 4	280	26	+31
230	13	− 9	450	26	+31	270	23	+20	1030	49	−30
420	79	+90	260	81	+81	840	35	+38	670	0	+14
240	44	+46	640	80	+84	660	0	+26	480	42	+45
430	44	−33	800	69	+63	470	51	+25	860	39	+46
600	99	+105									

atomic parameters of the latter for the complete investigation of its structure. To do this a detailed and complete X-ray examination of this compound was carried out. In preparing the crystals and obtaining the X-ray diagrams the same procedure was followed as for $CuSO_4$. Owing to the fact that the crystals of $ZnSO_4$ did not show suitable development along [010] the intensities of the reflexions were greatly influenced by the non-equidimensional form of the crystals. For this reason we limited ourselves to rotation and zero-layer Weissenberg diagrams round the other two axes, parallel to which the crystals show prismatic development and are of almost equidimensional cross section.

The lattice constants obtained from Weissenberg diagrams are:

$$a_0 = 8{\cdot}58,\ b_0 = 6{\cdot}73,\ c_0 = 4{\cdot}77\ \text{Å}$$

in close agreement with those found by Schiff (1934).

To obtain satisfactory agreement between the F_o and the F_c values the parameters of the atoms, which were originally taken equal to the corresponding parameters of $CuSO_4$, had to be slightly altered. The final atomic parameters in $ZnSO_4$ are given in Table 4.

The observed and calculated structure factors are given in Table 5.

With the exception of three reflexions (024, 064, 660), which have a considerable F_c value but do not appear in the diagrams, the agreement between the F_o and F_c values is on the whole satisfactory. This can also be seen from the reliability index, which has the value $R = 0{\cdot}18_6$. Just as in the case of $CuSO_4$, the reliability index was calculated without omitting the values F_c corresponding to $F_o = 0$ or applying the Hamilton correction.

The interatomic distances, calculated by using the parameters listed in Table 4, are given in Table 6.

Table 6. *Interatomic distances in* $ZnSO_4$

Atom	Point position	Neighbour	Coordination number	Interatomic distance (Å)
Zn	(*a*)	O_{I}	2	2·35
		O_{II}	2	2·13
		O_{III}	2	1·95
S	(*c*)	O_{I}	1	1·47
		O_{II}	1	1·55
		O_{III}	2	1·45
	O–O distances in tetrahedron			
O_{I}	(*c*)	O_{II}	—	2·46
		O_{III}	—	2·38
O_{II}	(*c*)	O_{III}	—	2·45
O_{III}	(*d*)	O_{III}	—	2·39
	O–O distances in octahedron			
O_{I}	(*c*)	O_{II}	—	2·66
		O_{II}	—	3·51
		O_{III}	—	2·97
		O_{III}	—	3·14
O_{II}	(*c*)	O_{III}	—	2·77
		O_{III}	—	2·89

As can be seen from this table, the distances of the atoms lie within the usual limits.

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