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Morphology and Structure of Anhydrous Nickel Sulphate

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The crystal structure of $NiSO_4$ has been determined. The crystals are orthorhombic with $a_0 = 5{\cdot}155$, $b_0 = 7{\cdot}842$, $c_0 = 6{\cdot}338$ Å, $Z = 4$, space group *Cmcm*. 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 Ni atoms lie at the centre of a distorted octahedron of O atoms.

1. Introduction

Among the compounds of the general formula MRO_4 there are some whose structure, notwithstanding their simple composition, is still unknown. Such compounds are, for example, the anhydrous sulphates of the bivalent metals copper, nickel, iron and cobalt.

The reason for our incomplete knowledge of the crystallographic properties of these compounds is that they either form unstable, very hygroscopic crystals which are difficult to handle for X-ray analysis, or do not form single crystals of satisfactory dimensions, but only a fine crystalline powder.

2. Experimental

In order to determine the structure of these compounds we have tried to prepare crystals suitable for X-ray analysis. Up to now we have succeeded, by slow evaporation of a nickel sulphate hydrate solution in sulphuric acid, in obtaining well formed crystals of anhydrous nickel sulphate, $NiSO_4$, suitable for crystallographic measurements and X-ray analysis; the results are given in this paper.

So far as we know from the accessible literature no crystallographic and X-ray data are reported for anhydrous nickel sulphate. According to the literature, good light-yellow crystals can be obtained either by evaporation of a solution of nickel sulphate hydrate in dense sulphuric acid (Etard, 1878), or by co-fusion of nickel sulphate hydrate or nickel oxide with ammonium sulphate (Lepierre & Lachaud, 1892). Two crystal forms are mentioned, one octahedral and one prismatic, depending on the conditions of formation. For these two forms no further crystallographic or optical data are known.

The crystals we have prepared are of various dimensions up to 3 mm. in length. They are thick plates of rhombic habit, with a set of narrow planes parallel to the edges of the rhomb.

Under the polarizing microscope the extinction directions are found to coincide with the diagonals of the rhomb; γ is parallel to the shorter and α to the longer diagonal. Goniometric measurements show that the crystals belong to the orthorhombic bipyramidal class and are bounded by the forms {001}, {110}, {111} and {112}, with {001} dominant. Besides these platy crystals we have also observed some which have a prismatic shape along $[1\bar{1}0]$. Perhaps the supposed dimorphism of the nickel sulphate crystals mentioned in the literature is due to this difference in habit. The following mean values of the angles between the planes were measured goniometrically

Table 1. *Comparison of calculated and observed structure factors*

hkl	F_c	F_o	*hkl*	F_c	F_o	*hkl*	F_c	F
110	71	48	060	84	78	080	97	87
020	92	74	332	32	0	206	35	0
111	−46	45	400	133	142	081	31	45
021	51	45	061	−12	0	226	75	81
002	41	27	224	26	14	443	− 2	0
200	123	122	005	0	0	335	3	0
112	110	109	044	47	47	082	32	39
022	17	0	115	−43	52	046	58	46
220	− 5	18	025	35	39	065	−12	0
221	26	34	062	10	0	083	−30	36
202	105	76	402	22	0	444	41	33
040	106	105	333	31	42	550	55	45
113	0	0	063	10	0	027	−29	26
041	− 4	0	225	33	22	600	71	69
023	−41	39	440	59	58	551	18	24
222	82	89	045	− 1	0	084	75	65
042	100	85	441	− 1	0	227	−27	0
004	129	130	334	79	83	602	47	46
223	−27	33	006	6	0	552	36	39
114	43	42	116	69	64	066	20	0
024	93	71	026	45	47	406	1	0
043	− 1	0	442	76	77	553	−33	41
330	92	88	064	76	77	0,10,0	17	21
331	− 9	0	404	100	107	008	67	94
204	77	55						

$$(111):(001) = 55°\,44',\quad (111):(\bar{1}11) = 87°\,22',$$
$$(112):(001) = 36°\,23'.$$

The zone angle $[\bar{1}10]:[\bar{1}\bar{1}0] = 66{\cdot}5°$ was measured microscopically. The axial ratios calculated from the above measurements are

$$a:b:c = 0{\cdot}6569:1:0{\cdot}8058\,.$$

Anhydrous nickel sulphate remains stable in air for a few days, but after a longer interval the crystals become opaque and green, and are gradually transformed to a fine crystalline powder of nickel sulphate hexahydrate. For this reason the specimens for X-ray examination were protected in capillary glass tubes. Because the platy form of crystals was not suitable for intensity measurements, the crystals were embedded in plexiglass and cut to the shape of small laths of almost equal thickness parallel to the a or b axis. These laths, and also a prismatically developed crystal parallel to $[\bar{1}10]$, were used for rotation and Weissenberg diagrams. The interpretation of these diagrams gave

$$a_0 = 5{\cdot}155\pm0{\cdot}001,\quad b_0 = 7{\cdot}842\pm0{\cdot}001\,,$$
$$c_0 = 6{\cdot}338\pm0{\cdot}002\ \text{Å}\,.$$

From these are calculated the following axial ratios and angles:

$$a:b:c = 0{\cdot}6573:1:0{\cdot}8082\,,$$
$$(111):(001) = 55°\,38',\quad (111):(\bar{1}11) = 87°\,26',$$
$$(112):(001) = 36°\,20',\quad [\bar{1}10]:[\bar{1}\bar{1}0] = 66°\,38'.$$

These values are in satisfactory agreement with those obtained goniometrically.

The observed reflexions are hkl: $h+k = 2n$; $0kl$: $k = 2n$; $h0l$: $l = 2n$, $h = 2n$; $hk0$: $h+k = 2n$. From these it follows that D_{2h}^{17}–*Cmcm* is the most probable space group, *Cmc* and *C2cm* being excluded because of the holohedrical appearance of the crystals.

3. Determination of the structure

From the above lattice constants and a unit cell containing four molecules we calculate a density of 4·01 g.cm.$^{-3}$, whereas that given in the literature is 3·643 g.cm.$^{-3}$. We did not make a density measurement because our crystals showed incomplete internal development due to large cavities.

As the unit cell contains four molecules $NiSO_4$, we have to arrange in it four Ni, four S, and sixteen O atoms. Space-group symmetry *Cmcm* contains three fourfold positions. Two of these, position (*a*) $(0,0,0;\ 0,0,\frac{1}{2};\ \frac{1}{2},\frac{1}{2},0;\ \frac{1}{2},\frac{1}{2},\frac{1}{2})$ and position (*b*) $(0,\frac{1}{2},0;\ 0,\frac{1}{2},\frac{1}{2};\ \frac{1}{2},0,0;\ \frac{1}{2},0,\frac{1}{2})$, coincide with symmetry centres while the third, position (*c*) $(0,y,\frac{1}{4};\ 0,\bar{y},\frac{3}{4};\ \frac{1}{2},\frac{1}{2}+y,\frac{1}{4};\ \frac{1}{2},\frac{1}{2}-y,\frac{3}{4})$, with one degree of freedom, lies on a twofold axis. Because of the tetrahedral arrangement of the O atoms around the S atoms, the only possible position of the latter is the position (*c*). At the same time the SO_4 tetrahedron is oriented by the symmetry so that its twofold axis coincides with the $[0,y,\frac{1}{4}]$ axis. In this way the O atoms occupy eightfold positions, and, in particular, the O atoms of one pair, designated O_I, lie on the $(0,y,z)$ plane and those of the other pair, O_{II}, lie on the $(x,y,\frac{1}{4})$ plane. The N atoms must occupy one of the fourfold positions (*a*) or (*b*). Thus only five parameters remain to be determined, y for the S atom, y and z for the O_I atoms and x and y for the O_{II} atoms.

We attempted to determine the unknown parameters by the trial-and-error method, taking account

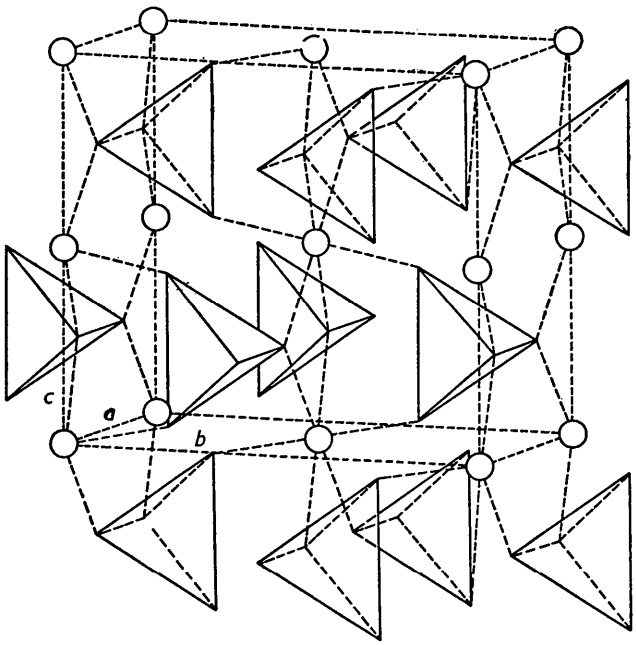

Fig. 1. The structure of $NiSO_4$, showing the spatial arrangement of the SO_4 tetrahedra and the Ni atoms.

of the space demands of the Ni and O atoms. The coordinates of the atoms listed in Table 2 are those

Table 2. *Atomic parameters*

	x	y	z
4 Ni	0	0	0
4 S	0	0·36	¼
8 O_I	0	0·25	0·05
8 O_{II}	0·25	0·48	¼

which give the best agreement between the observed and calculated $F(hkl)$ values (Table 1). Fig. 1 shows the spatial arrangement of the SO_4 tetrahedra and the Ni atoms.

Table 3. *Coordination in* $NiSO_4$

Atom	Point position	Neighbour	Coordination number	Interatomic distance (Å)
Ni	(*a*)	O_I	2	1·99
		O_{II}	4	2·06
S	(*c*)	O_I	2	1·53
		O_{II}	2	1·60
O_I	(*f*)	O_I	1	2·53
		O_I	1	2·58
		O_{II}	2	2·55
		O_{II}	2	2·79
		O_{II}	2	2·92
O_{II}	(*g*)	O_{II}	1	3·18
		O_{II}	1	2·58

4. Description and discussion of the structure

The S atoms have nearest to them four O atoms at the vertices of an almost regular tetrahedron. The Ni atoms are surrounded by six O atoms occupying the vertices of a distorted octahedron. The distances of the atoms in the polyhedra are given in Table 3. These distances are in agreement with those known from other structures.

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