Reprinted from *Acta Crystallographica*, Vol. 11, Part 10, October 1958

PRINTED IN DENMARK

Acta Cryst. (1958). **11**, 686

The Crystal Structure of the Anhydrous Magnesium Sulphate

BY P. J. RENTZEPERIS* AND C. T. SOLDATOS†

Department of Mineralogy, University of Thessaloniki, Greece

(*Received* 5 *May* 1958)

The crystal structure of anhydrous magnesium sulphate, $MgSO_4$, has been determined from X-ray powder data, obtained with an X-ray diffractometer. The unit cell is orthorhombic with $a_0 = 5{\cdot}182$, $b_0 = 7{\cdot}893$, $c_0 = 6{\cdot}506$ Å, $Z = 4$; space group D_{2h}^{17}–$Cmcm$. The unknown parameters were determined by trial and error, taking into account the similar structure of $NiSO_4$. $MgSO_4$ and $NiSO_4$ are isostructural. The S atoms lie at the centre of an almost regular tetrahedron of O atoms. The Mg atoms lie at the centre of a distorted octahedron of O atoms.

Introduction

ination of the structure of anhydrous sulphate, $MgSO_4$, was carried out within me concerned with the systematic X-ray n of the anhydrous sulphates of bivalent dertaken at our department. Of these nose containing cations of a radius smaller Ca^{2+} (0·99 Å) are highly hygroscopic and ong tendency to transform to hydrates. erhaps the most hygroscopic of all and cial care in manipulation. All attempts to l developed single crystals seem to have now; the preparations yielded by all the plied are in the form of a fine white crys- ler (Gmelin, 1939).

Experimental

alline powder of $MgSO_4$ was prepared in g way: To a small quantity of chemically E. Merck, pro analysi) in a porcelain dish diluted sulphuric acid in excess and was left to evaporate over a sand bath Bunsen burner. At first well developed nagnesium sulphate containing molecules re formed. After complete evaporation of ulphuric acid, the first formed crystals sed within the dish and the latter was left e Bunsen flame for an hour. Then it was oven and kept there at a constant tem- 450 °C. for two days. Chemical tests for of water and sulphuric acid were negative. y investigations were carried out by in- powder in capillary tubes of Lindemann obtaining Debye–Scherrer photographs. graphs showed a striking similarity to O_4, the structure of which was determined (1957) by means of single crystals. Assuming a similarity of structure and applying the method of Lipson (1949) for indexing powder diagrams, we were able to account for every line appearing in them. Calculation of the intensities of the various reflexions, carried out with the same atomic parameters as those given for $NiSO_4$ (Dimaras, 1957), led to a satisfactory qualitative agreement with those observed. No quantitative comparison was possible owing to the weakness of the majority of the lines on the diagrams.

The desirability of having quantitative intensity measurements led to the use of a Norelco X-ray diffractometer, by means of which the final work was done. A slab of finely powdered $MgSO_4$ was prepared by packing the powder in a hole of dimensions $2 \times 1{\cdot}1 \times 0{\cdot}1$ cm. in a flat aluminium block. In order to render the specimen waterproof the lower opening of the hole was covered with a cover glass and the upper one, facing the X-ray beam, with a piece of cellotape. Using this specimen and employing filtered Cu $K\alpha$ radiation, recordings with various settings of the instrument were obtained. For final indexing and intensity measurements a slow traverse of 0·25° per min. was used. The indexing was effected as for the Debye–Scherrer diagrams by means of the Lipson (1949) method. On applying the method an orthorhombic unit cell was assumed by analogy with $NiSO_4$. The agreement between the observed and calculated values of $\sin^2\theta$ is shown in Table 1. The intensities of the reflexions were obtained by measuring the area under each peak on the charts with a planimeter; the averages of several measurements of the corresponding peaks on various charts obtained with different settings of the diffractometer were taken. The Lorentz-polarization factor and the f_0 values were obtained graphically. No absorption correction was applied.

Lattice constants and space group

The best agreement between the calculated $\sin^2\theta$ values and the corresponding observed ones was obtained with the following values of the coefficients:

The determ magnesium the program investigation metals, unc sulphates, th than that of show a stro $MgSO_4$ is p requires spe prepare well failed up to methods ap talline powd

A fine cryst the following pure MgO (was added the solution heated by a needles of n of H_2SO_4 we the liquid s were pulveri again on the put into an perature of the presence

Preliminar serting the glass and These photo those of NiS by Dimaras

* Now at: Mineralogisches Institut der Universität, Frankfurt a. M., Germany.

† Now at: Mineralogisch-Petrographisches Institut der E.T.H., Zürich, Switzerland.

Table 1. *Comparison between observed and calculated* $\sin^2\theta$ *and* I *values*

$\sin^2\theta_o$	$\sin^2\theta_c$	hkl	I_c		I_o
0·0456	0·0457	111	251		300
0·0520	0·0522	021	167		167
0·0560	0·0561	002	5		7
0·0878	0·0878	112	197	269	250
	0·0885	200	72		
0·0942	0·0943	022	34		19
0·1078	0·1080	130	86		94
0·1264	0·1267	220	34		48
0·1405	0·1407	221	16		10
0·1446	0·1447	202	55		45
0·1526	0·1526	040	24		20
0·1644	0·1642	132	0·5	31·5	33
	0·1645	023	31		
0·1827	0·1828	222	36		45
0·2089	0·2087	310	0·5	41·5	39
	0·2088	042	41		
0·2229	0·2228	311	22	63	63
0·2246	0·2246	004	41		
0·2341	0·2343	133	38		27
0·2530	0·2530	223	8	18	28
0·2552	0·2552	241	10		
0·2646	0·2648	312	37		37
0·2749	0·2747	151	4		4
0·2850	0·2850	330	19		22
0·2973	0·2973	242	116		96
0·3168	0·3168	152	1		3
0·3329	0·3326	134	28	35	28
	0·3332	204	7		
0·3540	0·3541	400	27		22
0·3676	0·3675	243	4		6
0·3828	0·3827	115	20		17
0·3872	0·3870	153	18		24
0·4062	0·4063	421	13		12
0·4462	0·4460	261	18		15
0·4516	0·4517	351	2		4
0·5098	0·5097	334	14		16
0·5187	0·5186	423	9		8
0·5377	0·5371	116	11		9
0·5462	0·5458	172	15		12
0·5632	0·5629	442	17	28	30
	0·5640	353	11		
0·5768	0·5768	511	5	21	13
0·5787	0·5787	404	16		
0·5923	0·5922	245	2		4
0·6167	0·6169	424	7		9
0·6328	0·6321	226	15	15·5	14
	0·6331	443	0·5		
0·6566	0·6566	264	2	10	10
0·6624	0·6623	354	8		
0·6990	0·6991	280	14		8
0·7226	0·7228	372	13		13

$A = 0{\cdot}02213$, $B = 0{\cdot}00954$, $C = 0{\cdot}01404$. These values lead to the following lattice constants (Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å):

$$a_0 = 5{\cdot}182\pm0{\cdot}0015,\quad b_0 = 7{\cdot}893\pm0{\cdot}002,$$
$$c_0 = 6{\cdot}506\pm0{\cdot}0016\text{ Å},\quad V = 266{\cdot}10\text{ Å}^3.$$

The axial ratios calculated from these are:

$$a_0:b_0:c_0 = 0{\cdot}6565:1:0{\cdot}8242\ .$$

A unit-cell content of four molecules $MgSO_4$ requires a density of 2·93 g.cm.$^{-3}$, whereas that given in the literature ranges between 2·63–2·77 g.cm.$^{-3}$ (Gmelin, 1939). The deviation is probably due to incomplete internal development of the single crystals comprising the powder, a fact observed in the single crystals of $NiSO_4$ (Dimaras, 1957) and those of $CuSO_4$ and $ZnSO_4$ (Kokkoros & Rentzeperis, 1958).

Hammel (1936) gives the following values for the lattice constants of $MgSO_4$, prepared by dehydration of its hydrates in a stream of hot air of 300 °C.:

$$a_0 = 4{\cdot}8_2,\quad b_0 = 6{\cdot}7_2,\quad c_0 = 8{\cdot}3_5\text{ Å}\ .$$

He derived these values after indexing the diagram of $MgSO_4$ by assuming an analogy between three strong lines on the diagrams of $MgSO_4$ and $CoSO_4$, the lattice constants of which were found by Hocart and Serres (1931) by means of single crystals. We have also observed an analogy between certain reflexions, but the two diagrams do not coincide, as do those of $MgSO_4$ and $NiSO_4$. Considering the excellent agreement between $\sin^2\theta_o$ and $\sin^2\theta_c$ obtained in this investigation and also the satisfactory agreement of I_o and I_c (Table 1), one is led to the conclusion that either the analogy assumed by Hammel was not really there and consequently his values are incorrect or his material was of a different structure from that examined by us.

Examination of the observed reflexions shows the following conditions: (hkl): $h+k = 2n$; $(h0l)$: $l = 2n$. From these it follows that the probable space groups are: C_{2v}^{12}–$Cmc2_1$, C_{2v}^{16}–$C2cm$ and D_{2h}^{17}–$Cmcm$. The similarity, however, of $MgSO_4$ with $NiSO_4$ and the fact that the structure is well explained by means of the space group D_{2h}^{17}–$Cmcm$, render this as the most probable space group for $MgSO_4$.

Determination of the structure and discussion

The unit cell of $MgSO_4$ contains four molecules; thus we have to find the parameters of four Mg, four S and sixteen O atoms. Based upon the similarity of the $MgSO_4$ diagram with that of $NiSO_4$, we assumed a similar spatial arrangement in the unit cell, namely that the Mg atoms occupy the fourfold position

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

the S atoms occupy the fourfold position

$$(c)\quad (0,y,\tfrac{1}{4};\ 0,\bar{y},\tfrac{3}{4};\ \tfrac{1}{2},\tfrac{1}{2}+y,\tfrac{1}{4};\ \tfrac{1}{2},\tfrac{1}{2}-y,\tfrac{3}{4})\ ,$$

the sixteen O atoms, which form pairs occupying the vertices of an almost regular tetrahedron round the S atoms, are divided into two groups, O_I and O_{II}, occupying eightfold positions

O_I at (f) $(0,y,z;\ 0,\bar{y},\bar{z};\ 0,y,\tfrac{1}{2}-z;\ 0,\bar{y},\tfrac{1}{2}+z;$
$\tfrac{1}{2},\tfrac{1}{2}+y,z;\ \tfrac{1}{2},\tfrac{1}{2}-y,\bar{z};\ \tfrac{1}{2},\tfrac{1}{2}+y,\tfrac{1}{2}-z;$
$\tfrac{1}{2},\tfrac{1}{2}-y,\tfrac{1}{2}+z)$

and

O_{II} at (g) $(x,y,\tfrac{1}{4};\ \bar{x},y,\tfrac{1}{4};\ x,\bar{y},\tfrac{3}{4};\ \bar{x},\bar{y},\tfrac{3}{4};$
$\tfrac{1}{2}+x,\tfrac{1}{2}+y,\tfrac{1}{4};\ \tfrac{1}{2}-x,\tfrac{1}{2}+y,\tfrac{1}{4};$
$\tfrac{1}{2}+x,\tfrac{1}{2}-y,\tfrac{3}{4};\ \tfrac{1}{2}-x,\tfrac{1}{2}-y,\tfrac{3}{4})\ .$

A preliminary calculation of the intensities of the various reflexions by employing the atomic parameters found for $NiSO_4$ showed that the above assumption was correct but a slight shift of the S and O atoms was necessary. The best agreement between the observed and calculated intensities was obtained with the atomic parameters listed in Table 2.

Table 2. *Atomic parameters in* $MgSO_4$

Atom	x	y	z
4 Mg	0	0	0
4 S	0	0·37	0·25
8 O_I	0	0·25	0·06
8 O_{II}	0·25	0·47	0·25

The intensities calculated with the above values are given in Table 1 in comparison with the observed ones. Although the indexing of the reflexions was quite satisfactory up to $\sin^2\theta = 0{\cdot}8600$, we did not include in this table those with $\sin^2\theta$ greater than 0·7226, because of the uncertainties in the intensity measurements caused by frequent overlapping and the separation of the α_1 and α_2 reflexions.

The spatial arrangement of the SO_4 tetrahedra and the Mg atoms is shown in Fig. 1 in clinographic

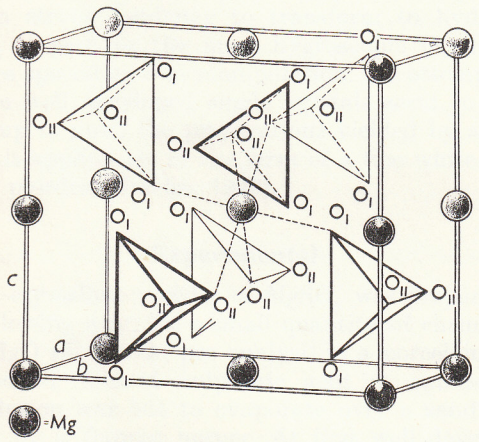

Fig. 1. The structure of $MgSO_4$, showing the spatial arrangement of the SO_4 tetrahedra and the Mg atoms.

projection. The orientation of the SO_4 tetrahedra within the unit cell is such that one of their symmetry planes is parallel to (100).

Table 3 gives the interatomic distances between the nearest atoms in the unit cell obtained from the values of the atomic parameters listed in Table 2. The values are in agreement with those known from the structures of other sulphates.

The SO_4 tetrahedron appears only slightly distorted with an average S–O distance 1·54 Å and O–O distances ranging between 2·47 and 2·59 Å. The six nearest O atoms surrounding each Mg atom occupy the vertices of a strongly distorted octahedron. They are arranged in two groups centrosymmetrically round the Mg atoms: one pair at a distance 2·01 Å from it and the remaining four at a distance 2·09 Å. The distances between the O atoms of the octahedron range between 2·59 and 3·29 Å.

Table 3. *Interatomic distances in* $MgSO_4$

Atom	Point position	Neighbour	Coordination number	Interatomic distance (Å)
Mg	(α)	O_I	2	2·01
		O_{II}	4	2·09
S	(c)	O_I	2	1·56
		O_{II}	2	1·52
		O–O distances in SO_4 tetrahedron		
O_I	(f)	O_I		2·47
		O_{II}		2·49
O_{II}	(g)	O_{II}		2·59
		O–O distances in MgO_6 octahedron		
O_I	(f)	O_{II}		2·96
		O_{II}		2·84
O_{II}	(g)	O_{II}		3·29
		O_{II}		2·59

Note added in proof.—After this paper had been sent to press, Prof. J. Zemann, Göttingen, kindly drew our attention to the fact that $NiSO_4$, and consequently $MgSO_4$, is isostructural with $CrVO_4$ and several chromates of bivalent metals (*Structure Reports*, vol. 9, 1955).

We wish to express our thanks to Prof. P. A. Kokkoros, Head of the Department, for suggesting the subject of this investigation. The part of this research concerned with the intensity measurements was carried out at the Mineralogical Institute of the University of Frankfurt/Main, Germany. Our thanks are due to the Head of the Institute Prof. H. O'Daniel for his kindness of putting the necessary apparatus at our disposal, especially those supplied by the Deutsche Forschungsgemeinschaft, to which we are greatly indebted. One of us, P. J. R., wishes to thank the Alexander von Humboldt-Stiftung, Bonn, for a stipent in Germany that made the work at the Mineralogical Institute of the University of Frankfurt possible.

References

Dimaras, P. I. (1957). *Acta Cryst.* **10**, 313.
Gmelin's (1939). *Handbuch der anorg. Chemie*, **27**, II, 212.
Hammel, F. (1936). *C. R. Acad. Sci., Paris*, **202**, 57.
Hocart, R. & Serres, A. (1931). *C. R. Acad. Sci., Paris*, **193**, 1180.
Kokkoros, P. A. & Rentzeperis, P. J. (1958). *Acta Cryst.* **11**, 361.
Lipson, H. (1949). *Acta Cryst.* **2**, 43.
Structure Reports for 1942–1944. (1955). **9**, pp. 181 and 183. Utrecht: N. V. A. Oosthoek's Uitgevers Mij.

Printed in Denmark at Fr. Bagges kgl. Hofbogtrykkeri, Copenhagen