The Crystal Structure of Nickel Sulphate Heptahydrate $NiSO_4 \cdot 7H_2O$.

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(With 5 figures.)

1. Introduction.

Nickel sulphate heptahydrate is a member of an iso-dimorphous group of crystals which includes the following:

$MgSO_4 \cdot 7H_2O$	Orthorhombic	$MgSO_4 \cdot 7H_2O$	Monoclinic
$MgCrO_4 \cdot 7H_2O$		$VSO_4 \cdot 7H_2O$	
$NiSO_4 \cdot 7H_2O$		$MnSO_4 \cdot 7H_2O$	
$ZnSO_4 \cdot 7H_2O$		$FeSO_4 \cdot 7H_2O$	
		$FeSeO_4 \cdot 7H_2O$	
		$CoSO_4 \cdot 7H_2O$	
		$CoSeO_4 \cdot 7H_2O$	
		$NiSO_4 \cdot 7H_2O$	
		$CuSO_4 \cdot 7H_2O$	

The present work is the derivation of the orthorhombic structure.

Previous results concerned with the orthorhombic series are those of Cardoso[1]), Westenbrink[2]), and Barnes and Hunter[3]). The unit cell determinations are shown in Table I.

Table I.

$MgSO_4 \cdot 7H_2O$			$NiSO_4 \cdot 7H_2O$	
Cardoso	Westenbrink	Barnes and Hunter	Westenbrink	Beevers and Lipson[4])
11.94 Å	11.91 Å	11.89 Å	11.86	11.8 Å
12.03	12.02	12.01	12.08	12.0
6.865	6.87	6.86	6.81	6.80

The crystal class is orthorhombic bisphenoidal, and the space-group $P2_12_12_1$ (V_4). There are four molecules to the unit cell, and all atoms must lie in general positions. No previous attempt to find the 39 parameters involved has been published.

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1) Cardoso, Z. Kristallogr. **63** (1926) 19.

2) Westenbrink, Proc. Acad. Sci. Amsterdam **29** (1926) 1223.

3) Barnes and Hunter, Nature **130** (1932) 96.

4) Unpublished.

For the purposes of this paper we shall choose an origin of coordinates which is shifted by $\frac{1}{4}$ in the x direction from the origins of Wyckoff and Astbury and Yardley, so that the equivalent points of the space-group become:

$$(xyz) \quad (\bar{x}\bar{y}\tfrac{1}{2}+z) \quad (\tfrac{1}{2}+x\ \tfrac{1}{2}-y\ \bar{z}) \quad (\tfrac{1}{2}-x\ \tfrac{1}{2}+y\ \tfrac{1}{2}-z).$$

This brings the origin to a position on one of the screw-axes parallel to c_0, which means that a projection of the structure on to the (001) plane has a centre of symmetry.

2. Determination of x and y parameters of Ni and S.

The first work done was an attempt to find the Ni and S positions in the x, y plane by the method of A. L. Patterson[1]). This method involves a double Fourier series using the values of F^2 as the coefficients, and is thus independent of the signs of the F's. It gives peaks whose positions with respect to the origin correspond to vectors between atoms in the crystal. There are, of course, a very large number of such vectors in a crystal containing many atoms in general positions. However the analysis of the resulting projection is not as difficult as would at first appear, for the Ni-Ni vectors should be most prominent (Ni being the heaviest atom present) and should be related to each other. Thus if the Ni coordinates are (x_1, y_1) in the structure we have to expect three Ni-Ni peaks at $(\frac{1}{2}-2x_1, \frac{1}{2})$ $(2x_1, 2y_1)$ $(\frac{1}{2}, \frac{1}{2}-2y_1)$ in the projection.

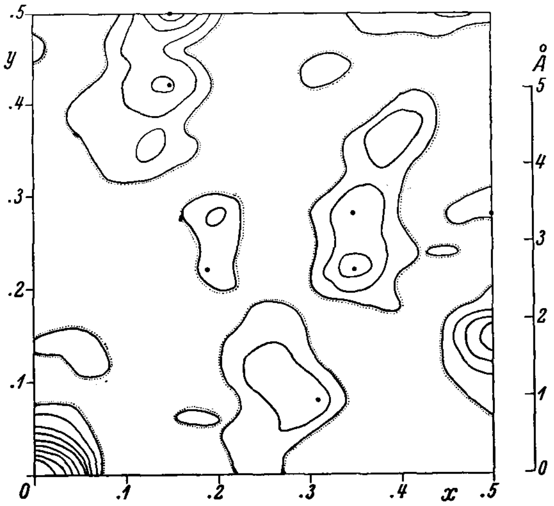

Fig. 1. Patterson synthesis of the $(hk0)$ intensities. Contours are drawn at levels of 110 and every 10 up to 150, and then every 20. The origin peak goes up to 247.

The values of F^2 used were estimated from the $(hk0)$ spot intensities. To place these estimates on an absolute scale a number of intensities were measured on the ionization spectrometer, using the slip method described

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1) Physic. Rev. **46** (1934) 372.

by Bragg and West[1]). The calculation of the Fourier series was carried out by the method described by Beevers and Lipson[2]).

The resulting summation is shown in Figure 1. It is only necessary to consider one quarter of the full cell, and to imagine vertical reflection planes at the edges. It will be seen that along the line $y = \frac{1}{2}$ there is indeed a large peak, with x coordinate .15, suggesting that $x_1 = .175$. We next look out for a peak at $x = 2x_1 = .35$, and find two peaks, with $x = .22$ and $y = .28$, respectively, suggesting that $y_1 = .11$ or .14. The third peak should therefore be at ($\frac{1}{2}$, .28) or ($\frac{1}{2}$, .22). No such large peak is to be found, however, although the background of the summation is everywhere high, (of the order of 100).

We shall see later that the ($\frac{1}{2}$, $\frac{1}{2} - 2y_1$) *Ni-Ni* peak is actually at ($\frac{1}{2}$, .28) but does not stand out well from the background.

The x and y parameters of *Ni* may be found with certainty by a determination of the difference of the $(h00)$ and $(0k0)$ F's observed from crystals of $MgSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 7H_2O$. For these sets of planes the structure-factors are cos $2\pi hx$ and cos $2\pi ky$, respectively. The intensities were measured with the X-ray spectrometer using the crystal-slip method.

Table II shows the results for the $(h00)$ planes. Columns 1 and 2 give the F values of the various planes for the two crystals, column 3 the difference in the atomic scattering factors of *Ni* and *Mg* (this is the greatest possible change in the F's) and column 4 is the change of F (i. e. column 1 minus column 2) divided in each case by column 3. Column 4 should therefore be equal to the structure factor (cos $2\pi hx$)

Table II.

Plane	F values		Change of f value Ni-Mg	Ratio	cos $2\pi hx$		
	$MgSO_4$	$NiSO_4$			x .06	.08	.10
2 0 0	$5\frac{1}{2}$	0	16	.34	.73	.54	.31
4 0 0	6	0	13	.46	.06	$\overline{.43}$	$\overline{.81}$
6 0 0	< 1	12	11	1.00	$\overline{.64}$	$\overline{.99}$	$\overline{.81}$
8 0 0	$< 1\frac{1}{2}$	6	9	.50—.78	$\overline{.99}$	$\overline{.64}$	.31
10 0 0	$< 1\frac{1}{2}$	0	8	$< .19$	$\overline{.81}$	.31	1.00
12 0 0	< 2	$7\frac{1}{2}$	8	.69—1.10	$\overline{.19}$	.97	.31
14 0 0	< 2	7	7	.71—1.28	.54	.73	$\overline{.81}$
	(1)	(2)	(3)	(4)	(5)		

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[1] Bragg and West, Z. Kristallogr. **69** (1928) 120.

[2] Philos. Mag. **17** (1934) 855.

and the remaining colums show the value of cos $2\pi hx$ for $x = .06$, .08, .10. Comparison of columns 4 and 5 shows that the *Ni* x parameter is .08 or the associated value .17, which gives the same value of cos $2\pi hx$. This confirms very well the value .17 deduced from the Patterson synthesis. This value of x was therefore adopted.

An identical procedure may be carried out for the $(0k0)$ planes with the results of Table III. The best agreement here is obtained with $y = .10$ (or the associated value .15).

Table III.

Plane	*F* values		Change of *f* value *Ni-Mg*	Ratio	cos $2\pi ky$ y		
	$MgSO_4$	$NiSO_4$			.08	.10	.12
0 2 0	$8\frac{1}{2}$	8	16	.03	.54	.31	.06
0 4 0	$9\frac{1}{2}$	< 3	13	.50—.96	$\overline{.43}$	$\overline{.81}$	$\overline{.99}$
0 6 0	< 1	7	11	.54—.73	$\overline{.99}$	$\overline{.81}$	$\overline{.19}$
0 8 0	13	10	9	.33	$\overline{.64}$	.31	.97
0 10 0	$< 3\frac{1}{2}$	8	8	.56—1.44	.31	1.00	.31
0 12 0	< 2	< 2	8	0—.50	.97	.31	$\overline{.93}$
0 14 0	8	$13\frac{1}{2}$	7	.79	.73	$\overline{.81}$	$\overline{.43}$
	(1)	(2)	(3)	(4)	(5)		

The Patterson synthesis had given roughly the same two alternative values of y and choice between them was made from a consideration of the change in intensity (when *Mg* is replaced by *Ni*) for the more general $(hk0)$ reflections. Spot intensities from rotation photographs were sufficient for this purpose, and there was good agreement between change of intensity and the value of the *Ni* structure factor calculated for the position (.17, .10). The other possibility (.17, .15) gave bad agreement here. Three examples are given in Table IV. The *Ni* position was therefore taken to be close to (.17, .10).

Table IV.

Plane	Observed Intensities		Structure Factor of *Ni*	
	$MgSO_4 \cdot 7H_2O$	$NiSO_4 \cdot 7H_2O$	x y (.17 .15)	x y (.17 .10)
2 3 0	o	m, w—m	.26	.80
3 5 0	o	w—m	.00	1.00
9 7 0	o	o	.93	.30

The Patterson synthesis can now be used to derive the *S* position. After the *Ni-Ni* peaks the next largest peaks to be expected in Figure 1 are those corresponding to *Ni-S* vectors. If the *Ni* is at $(x_1\ y_1)$, and equivalent points, and the *S* at $(x_2\ y_2)$ then there will be four such peaks at positions $(x_1 - x_2\ \ y_1 - y_2)$ $(x_1 + x_2\ \ y_1 + y_2)$ $(\frac{1}{2} + x_1 - x_2\ \ \frac{1}{2} - y_1 - y_2)$ $(\frac{1}{2} - x_1 - x_2\ \ \frac{1}{2} + y_1 - y_2)$. If we write $x = x_1 + x_2$, $x' = x_1 - x_2$, $y = y_1 + y_2$, $y' = y_1 - y_2$ the expected peaks are at $(x'\ y')$ $(x\ y)$ $(\frac{1}{2} + x'\ \ \frac{1}{2} - y)$ $(\frac{1}{2} - x\ \ \frac{1}{2} + y')$. Now three of the remaining large peaks in the F^2 synthesis together with a smaller peak at (.19 .22) do satisfy these conditions. The four sets of parameters are $(.19\ \ .\overline{22}$ (.15 .42) (.31 .08) (.35 .28), from which we may derive

$$x_1 = .17,\ y_1 = .10,\ x_2 = .\overline{02},\ y_2 = .32.$$

These values of x_1 and y_1 confirm those found previously. It is interesting to note, therefore, that both *Ni* and *S* parameters were found independently from the Patterson synthesis, but the *Ni* *y* value derived from a consideration of the *Ni-S* peaks was not wholly supported by the *Ni-Ni* peaks, a fact which did not give us enough confidence to use the *Ni* and *S* parameters derived from the Patterson synthesis alone for further work. However the *Ni* parameter values being confirmed by the $(h00)$ and $(0k0)$ intensity changes described above showed that the discrepancy was in the F^2 synthesis, and these parameters were accepted as good approximations.

3. Determination of remaining parameters.

The oxygen and water x and y parameters were found from a double Fourier synthesis using the $(hk0)$ planes. The signs of the F's were obtained from two considerations, a) the signs of the *Ni* and *S* contributions to the structure factors, b) the change of intensity when *Ni* is replaced by *Mg*. The signs obtained by the two methods agreed in general. The first synthesis was carried out using only those planes whose signs were beyond doubt. The projection obtained indicated roughly the positions of the oxygens and waters, but the peaks were badly shaped. However the approximate structure thus obtained permitted about twenty more planes to be brought into the series and a second synthesis gave the result of Figure 2 (upper portion). The F's used are shown in Table VI.

The $(hk0)$ projection suggested that six of the waters are around *Ni* in an approximate octahedron and that the SO_4 group is of the usual shape and size. Making assumptions as to interatomic distances, it should therefore have been possible to deduce the whole structure. However it was not found easy to obtain in this way values of the z's which gave very good agreement of the $(h0l)$ intensities. A double Fourier synthesis on the (010) face was therefore carried out. The F's were again obtained from rotation photographs, and the signs were calculated from the approximate structure. The resulting projection is shown in Figure 2, (lower portion).

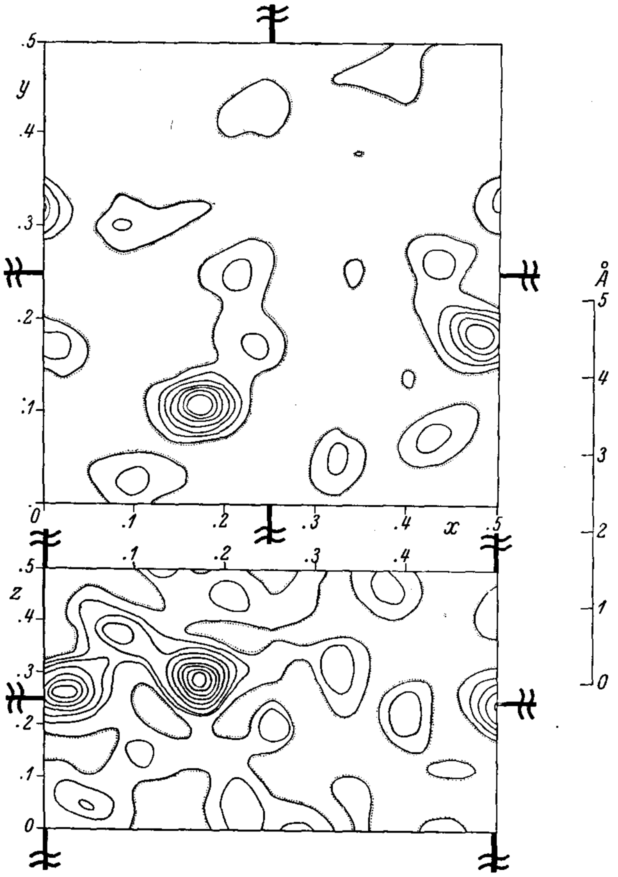

Fig. 2. Double Fourier syntheses projected on to (001) and (010). Contours are drawn at intervals of 50 in $\Sigma\Sigma F\cos 2\pi(hx+ky)$, and at equivalent contours in the $(h0l)$ projection. The zero contour is omitted and the 50 contour is dotted on its lower side to avoid confusion.

The values of the x's obtained from the two projections agreed very well, and the parameters chosen are shown below. The atoms numbered 1, 2, 3, 4, 7, 8, 11 were moved from the positions obtained directly from the projections, viz. (.42 .07 .37), (.60 .19 .48), (.45 .20 .69), (.43 .26 .37), (.225 .18 .$\overline{23}$), (.325 .05 .06), and (.25 .43 .$\overline{04}$) respectively to the positions given below to improve inter-atomic distances. The projections are not considered to be accurate to within about .1 Å, on account of errors in the F's and the finite termination of the series.

	x	y	z		x	y	z
Ni	.170	.110	.04	5 (H_2O)	.01	.17	.01
S	.475	.185	.49	6 (H_2O)	.21	.25	.19
1 (O)	.44	.08	.37	7 (H_2O)	.21	.18	$\overline{.21}$
2 (O)	.61	.19	.48	8 (H_2O)	.32	.04	.05
3 (O)	.44	.19	.69	9 (H_2O)	.11	$\overline{.04}$	$\overline{.09}$
4 (O)	.43	.28	.37	10 (H_2O)	.11	.03	.29
				11 (H_2O)	.23	.44	$\overline{.07}$

The interatomic distances with these parameters are shown in Table V. Every H_2O—O or H_2O—H_2O distance of 3.00Å or less is included in Table V. There are also distances 7 — 11 = 3.27, 5 — 10 = 3.17, and 4 — 10 = 3.23 Å but it does not seem likely that these are bonds.

Table V. Interatomic Distances.

S—O		Ni—H_2O		H_2O—O	
S—1	1.56 Å	Ni—5	2.03	5—3	2.77
2	1.59	6	2.02	5—4	2.82
3	1.43	7	1.96	6—2	2.64
4	1.50	8	1.97	6—4	2.89
		9	2.13	7—2	2.68
O—O		10	2.08	7—3	2.80
1—2	2.52			8—1	2.64
3	2.54	H_2O—H_2O		8—2	2.92
4	2.40	9—10	2.73	9—4	2.67
2—3	2.46	9—11	3.00	11—1	2.94
4	2.50	10—11	2.89		
3—4	2.44	6—11	2.90		

By assuming that the only bonds are the contacts in Table V we shall see that a simple interpretation of the structure is possible. In Table VI the calculated and observed F values are shown. The "observed" values are obtained from spot intensities placed on an absolute scale by means of spectrometer observations. The calculated values are obtained by the use of the F-curves of James and Brindley[1]).

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[1]) Z. Kristallogr. 78 (1931) 470·

Table VI.

Comparison of Observed and Calculated Intensities.

(*hk*0) Planes. Class I.

h	*k*	*F*		*h*	*k*	*F*		*h*	*k*	*F*	
		Calc.	Obs.			Calc.	Obs.			Calc.	Obs.
2	0	½	0	2	10	4½	0	8	2	½	0
4	0	½	0	2	12	5	0	8	4	7½	0
6	0	12½	12	2	14	8	0	8	6	12	12
8	0	$\overline{11}$	$\overline{6}$	4	2	$\overline{18}$	$\overline{17}$	8	8	$\overline{8}$	$\overline{8}$
10	0	2½	0	4	4	1	0	8	10	$\overline{7\frac{1}{2}}$	0
12	0	7	7½	4	6	7½	9	8	12	2½	0
14	0	$\overline{10\frac{1}{2}}$	$\overline{7}$	4	8	$\overline{12}$	$\overline{10}$	10	2	$\overline{2}$	0
0	2	$\overline{7}$	$\overline{8}$	4	10	$\overline{3\frac{1}{2}}$	0	10	4	8	0
0	4	$\overline{3\frac{1}{2}}$	0	4	12	10	7	10	6	6½	8
0	6	0	$\overline{7}$	4	14	2	0	10	8	$\overline{3}$	0
0	8	$\overline{7}$	$\overline{10}$	6	2	2	0	10	10	$\overline{7}$	0
0	10	11½	8	6	4	$\overline{19\frac{1}{2}}$	$\overline{15}$	12	2	5½	0
0	12	$\overline{4\frac{1}{2}}$	0	6	6	0	0	12	4	$\overline{13}$	0
0	14	$\overline{24}$	$\overline{13}$	6	8	9	0	12	6	$\overline{7}$	0
2	2	$\overline{15\frac{1}{2}}$	$\overline{14}$	6	10	10	8	12	8	10	0
2	4	3½	7	6	12	2½	0	14	2	$\overline{6\frac{1}{2}}$	$\overline{5}$
2	6	16½	15	6	14	$\overline{16}$	$\overline{15}$	14	4	6	5
2	8	$\overline{16\frac{1}{2}}$	14								

(*hk*0) Planes. Class II.

1	1	9½	6	3	15	4½	7	9	1	$\overline{1\frac{1}{2}}$	0
1	3	13½	15	5	1	$\overline{4}$	0	9	3	7½	0
1	5	$\overline{10\frac{1}{2}}$	$\overline{13}$	5	3	$\overline{23}$	$\overline{14}$	9	5	14	8
1	7	5	9	5	5	$\overline{11}$	$\overline{11}$	9	7	2	0
1	9	8½	10	5	7	5½	0	9	9	$\overline{13\frac{1}{2}}$	$\overline{10}$
1	11	$\overline{10\frac{1}{2}}$	$\overline{8}$	5	9	9½	8	9	11	$\overline{2\frac{1}{2}}$	0
1	13	4	0	5	11	8½	0	11	1	10	0
1	15	$\overline{10\frac{1}{2}}$	$\overline{12}$	5	13	$\overline{1\frac{1}{2}}$	0	11	3	$\overline{6\frac{1}{2}}$	0
3	1	$\overline{19\frac{1}{2}}$	$\overline{15}$	7	1	11	8	11	5	$\overline{7\frac{1}{2}}$	0
3	3	19	12	7	3	½	0	11	7	0	0
3	5	12½	11	7	5	$\overline{12\frac{1}{2}}$	$\overline{10}$	11	9	6½	5
3	7	$\overline{1}$	0	7	7	3	0	13	1	0	0
3	9	$\overline{15}$	$\overline{12}$	7	9	3½	0	13	3	$\overline{10}$	$\overline{5}$
3	11	$\overline{10}$	$\overline{12}$	7	11	$\overline{\frac{1}{2}}$	0	13	5	3½	0
3	13	17½	11	7	13	$\overline{2\frac{1}{2}}$	0	15	1	$\overline{6}$	0

Table VI (continuation)

(*hk*0) Planes. Class III.

h	*k*	*F*		*h*	*k*	*F*		*h*	*k*	*F*	
		Calc.	Obs.			Calc.	Obs.			Calc.	Obs.
1	2	$\overline{27}$	$\overline{21}$	3	14	½	0	7	12	$\overline{16}$	$\overline{7}$
1	4	$\overline{1\frac{1}{2}}$	0	5	2	7	0	9	2	$\overline{1}$	0
1	6	13½	8	5	4	19	15	9	4	13	12
1	8	3½	0	5	6	$\overline{12}$	$\overline{11}$	9	6	$\overline{4\frac{1}{2}}$	0
1	10	4	0	5	8	$\overline{8}$	$\overline{9}$	9	8	$\overline{\frac{1}{2}}$	0
1	12	$\overline{15\frac{1}{2}}$	$\overline{8}$	5	10	17½	8	9	10	5	6
1	14	½	0	5	12	0	0	11	2	5	0
3	2	$\overline{5}$	$\overline{6}$	5	14	½	0	11	4	12	9
3	4	$\overline{9}$	$\overline{11}$	7	2	$\overline{31\frac{1}{2}}$	$\overline{18}$	11	6	$\overline{11}$	0
3	6	$\overline{\frac{1}{2}}$	0	7	4	3	0	11	8	$\overline{8\frac{1}{2}}$	$\overline{6}$
3	8	$\overline{1\frac{1}{2}}$	0	7	6	$\overline{1}$	0	11	10	7	0
3	10	7½	0	7	8	5½	8	13	2	$\overline{14\frac{1}{2}}$	$\overline{6}$
3	12	$\overline{1\frac{1}{2}}$	0	7	10	1½	0	13	4	$\overline{1\frac{1}{2}}$	0

(*hk*0) Planes. Class IV.

h	*k*	Calc.	Obs.	*h*	*k*	Calc.	Obs.	*h*	*k*	Calc.	Obs.
2	1	$\overline{11}$	$\overline{6}$	6	1	4½	0	10	1	4½	0
2	3	$\overline{7\frac{1}{2}}$	$\overline{11}$	6	3	$\overline{1\frac{1}{2}}$	0	10	3	9	0
2	5	11	13	6	5	$\overline{2\frac{1}{2}}$	0	10	5	$\overline{10\frac{1}{2}}$	$\overline{8}$
2	7	15½	11	6	7	10½	8	10	7	$\overline{9\frac{1}{2}}$	0
2	9	$\overline{2}$	0	6	9	$\overline{10}$	$\overline{8}$	10	9	$\overline{3\frac{1}{2}}$	$\overline{6}$
2	11	$\overline{9\frac{1}{2}}$	$\overline{8}$	6	11	5½	0	10	11	12½	6
2	13	$\overline{10}$	$\overline{9}$	6	13	1	0	12	1	$\overline{1\frac{1}{2}}$	0
4	1	38	27	8	1	5	8	12	3	$\overline{\frac{1}{2}}$	0
4	3	7	7	8	3	$\overline{13\frac{1}{2}}$	$\overline{9}$	12	5	1½	0
4	5	$\overline{3\frac{1}{2}}$	0	8	5	3	0	12	7	7½	6
4	7	$\overline{13}$	$\overline{16}$	8	7	20	8	14	1	$\overline{3}$	0
4	9	$\overline{11}$	$\overline{9}$	8	9	$\overline{6}$	0	14	3	$\overline{12}$	$\overline{6}$
4	11	9	0	8	11	$\overline{8\frac{1}{2}}$	0	14	5	$\overline{1}$	0
4	13	7½	7	8	13	2	8				

(*h*0*l*) Planes. Class I.

h	*l*	Calc.	Obs.	*h*	*l*	Calc.	Obs.
2	2	4½	13	8	2	0	0
2	4	$\overline{1}$	0	8	4	0	0
2	6	11½	12	8	6	0	0
2	8	$\overline{16}$	$\overline{13}$	10	2	$\overline{2\frac{1}{2}}$	0
4	2	$\overline{\frac{1}{2}}$	0	10	4	$\overline{4}$	0
4	4	4	8	12	2	$\overline{13\frac{1}{2}}$	$\overline{16}$
4	6	$\overline{6\frac{1}{2}}$	$\overline{8}$	12	4	3	0
4	8	5	5	14	2	$\overline{15\frac{1}{2}}$	$\overline{12}$
6	2	27	17				
6	4	$\overline{19\frac{1}{2}}$	$\overline{16}$				
6	6	5½	6				

Table VI (continuation)

$(h0l)$ Planes. Class II.

h	l	F		h	l	F		h	l	F	
		Calc.	Obs.			Calc.	Obs.			Calc.	Obs.
1	1	7	9	5	1	$\bar{5}$	$\bar{7}$	7	7	13	7
1	3	$\overline{8\frac{1}{2}}$	$\overline{16}$	5	3	$4\frac{1}{2}$	0	9	1	$\bar{3}$	0
1	5	9	8	5	5	$\overline{15}$	$\overline{12}$	9	3	$4\frac{1}{2}$	0
1	7	$\overline{12\frac{1}{2}}$	$\bar{9}$	5	7	12	0	9	5	$\frac{1}{2}$	0
3	1	$\bar{9}$	$\bar{7}$	7	1	$\bar{5}$	0	11	1	2	0
3	3	$\frac{1}{2}$	0	7	3	24	13	11	3	$\overline{11}$	$\bar{7}$
3	5	$2\frac{1}{2}$	0	7	5	$\overline{16\frac{1}{2}}$	$\overline{16}$	11	5	$5\frac{1}{2}$	0
3	7	$\bar{3}$	0								

$(h0l)$ Planes. Class III.

h	l	Calc.	Obs.	h	l	Calc.	Obs.	h	l	Calc.	Obs.
1	2	$6\frac{1}{2}$	6	5	2	4	$7\frac{1}{2}$	9	2	$\overline{13\frac{1}{2}}$	$\bar{8}$
1	4	$\overline{12}$	$\overline{19}$	5	4	$\overline{3\frac{1}{2}}$	0	9	4	$11\frac{1}{2}$	$8\frac{1}{2}$
1	6	3	0	5	6	$10\frac{1}{2}$	$13\frac{1}{2}$	9	6	$\overline{5\frac{1}{2}}$	0
1	8	$\overline{14}$	$\overline{10}$	5	8	$\overline{5\frac{1}{2}}$	$\bar{4}$	11	2	$\bar{6}$	0
3	2	0	$5\frac{1}{2}$	7	2	$\overline{\frac{1}{2}}$	0	11	4	7	0
3	4	$4\frac{1}{2}$	0	7	4	7	0	13	2	$4\frac{1}{2}$	0
3	6	$10\frac{1}{2}$	12	7	6	$\overline{13}$	$\bar{7}$	13	4	$\bar{1}$	0
3	8	$\bar{9}$	$\bar{6}$								

$(h0l)$ Planes. Class IV.

h	l	Calc.	Obs.	h	l	Calc.	Obs.	h	l	Calc.	Obs.
2	1	$29\frac{1}{2}$	33	4	5	5	0	8	1	$\overline{16\frac{1}{2}}$	$\overline{10}$
2	3	$1\frac{1}{2}$	0	4	7	$9\frac{1}{2}$	0	8	3	$19\frac{1}{2}$	16
2	5	$\frac{1}{2}$	0	6	1	$20\frac{1}{2}$	14	8	5	$\overline{12}$	$\overline{10}$
2	7	$\overline{\frac{1}{2}}$	0	6	3	$\frac{1}{2}$	0	10	1	$\bar{3}$	0
4	1	$1\frac{1}{2}$	0	6	5	16	22	10	3	$\bar{2}$	0
4	3	$\bar{9}$	$\overline{10}$	6	7	$\overline{3\frac{1}{2}}$	0	10	5	$2\frac{1}{2}$	0

4. Discussion.

The structure of $NiSO_4 \cdot 7H_2O$ consists of SO_4 groups, groups of six waters around Ni, and a seventh water molecule. We have shown already (Table V) that the $Ni\,6(H_2O)$ group is an almost regular octahedron with average distances $Ni - H_2O = 2.03$, $H_2O - H_2O = 2{,}86$ Å. The SO_4 group is tetrahedral with average dimensions $S - O = 1.52$, $O - O = 2.48$ Å.

Each SO_4 group is in contact with six Ni groups, and each Ni group touches six SO_4 groups, but in addition each Ni group touches two neighbouring Ni groups (related to it by the nearest screw axis parallel to c_0).

The details of the contacts are as follows. Four (numbers 5, 7, 8 and 10) of the six coordinated waters make two contacts external to the coordination group. Each of these waters has its three bonds roughly in a plane. The remaining two coordinated waters (viz. 6 and 9) which are at opposite corners of the octahedron) make three external bonds, and in each case these three bonds together with that to the nickel are arranged tetrahedrally. The seventh water also makes four contacts which are arranged tetrahedrally. Two of the oxygens of the SO_4 group make two external bonds and the remaining two make three external bonds.

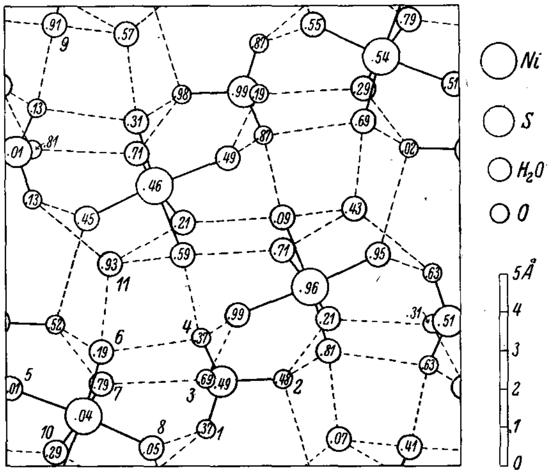

Fig. 3. Diagram of the structure projected on to (001).

Figure 3 is a diagram of the projection of the structure on to the (001) plane. The c parameters are given within the circles representing the various atoms. Bonds within the SO_4 and $Ni\,6(H_2O)$ groups are shown as full lines, and bonds between the groups are shown as dotted lines. The details of the preceding description of the structure may be verified by reference to Figure 3.

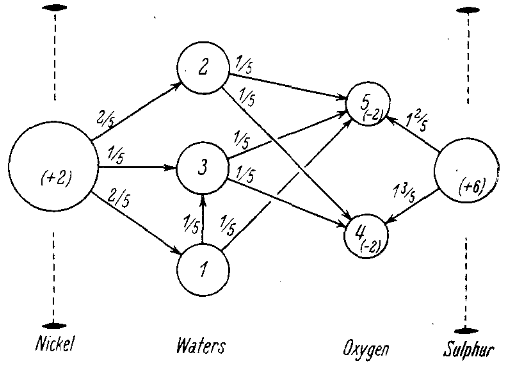

Fig. 4. Diagram of bond-structure. The two types of water molecule present are shown separately as type 1 and type 2.

The Pauling diagram of electrostatic valencies may easily be constructed and is shown in Figure 4. The water molecules 5, 7, 8 and 10 have each a bond to the Ni of strength $\frac{2}{5}$, and two outward bonds of strength $\frac{1}{5}$. Such an arrangement is shown separately in Figure 3 as type 1. The remaining "tetrahedral" water molecules, 6, 9 and 11, have two incoming bonds of magnitude $\frac{1}{5}$, and two outgoing bonds of magnitude $\frac{1}{5}$ (type 2).

It is of interest to compare the structure of nickel sulphate heptahydrate with that of nickel sulphate hexahydrate[1]. In the consideration of this latter structure[2], however, the distance between atoms 1 and 4 of 3.27 was called a bond, while the distance 1—3 of 2.89 was neglected. This was done to allow every water to have two outward bonds to oxygens. It was not realised at the time that a water molecule could have an outward bond to another water molecule. If we adopt the now much more reasonable view that 1—3 is a bond and 1—4 is not, we obtain the bond structure shown in Figure 5[3]. This means that two of the waters (at opposite corners of the octahedron) are of the tetrahedral kind. Thus the coordination group is identical with the coordination group in $NiSO_4 \cdot 7H_2O$.

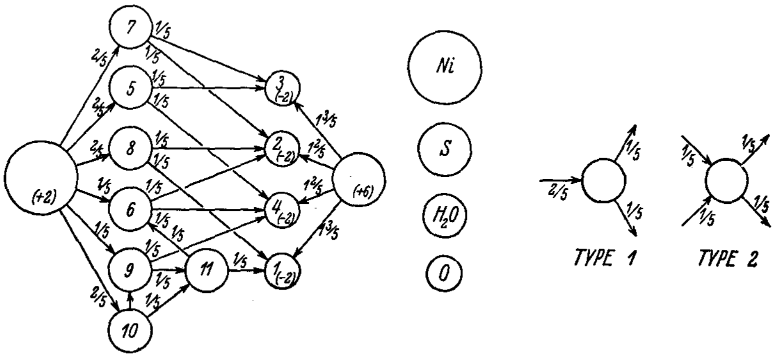

Fig. 5. The bond-structure of $NiSO_4 \cdot 6H_2O$.

It is therefore very reasonable to suppose that a grouping of six waters around an atom like Ni^{+2}, is always different from a grouping of waters around an atom like Al^{+3}, although both arrangements are octahedral. If we regard the water molecule as having two positive bonds (corresponding to regions of positive charge on its surface) and two negative bonds (corresponding to negative areas)[4], then the six waters of an $Al6(H_2O)$ group have all twelve negative bonds directed to Al, leaving only positive bonds to be satisfied externally. Ni, on the other hand, can only satisfy ten of the negative bonds, leaving two

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1) Beevers and Lipson, Z. Kristallogr. 83 (1932) 123.
Wyckoff and Corey, Z. Kristallogr. 84 (1934) 477.

2) Beevers and Lipson, loc. cit. p. 133.

3) This bond structure was first pointed out by Lipson in a private communication.

4) Bernal and Fowler, J. chem. Physics 1 (1933) 515.

negative bonds to be satisfied externally as well as the twelve positive bonds.

In the case of $NiSO_4 \cdot 6H_2O$ the two negative external bonds are satisfied by positive bonds from other $Ni\,6(H_2O)$ groups. Thus each Ni group has two of its twelve positive bonds satisfied in this way and the remaining ten positive bonds go to SO_4 groups.

In the case of $NiSO_4 \cdot 7H_2O$ the two negative bonds from each Ni group are satisfied by one positive bond from another Ni group and by one positive bond from the seventh water. Thus each Ni group has one positive bond going to a second Ni group. Of its remaining eleven positive bonds two go to the seventh water and nine to the SO_4 groups. The seventh water also has one positive bond to an SO_4 group, so that each SO_4 receives ten bonds in all, exactly as in $NiSO_4 \cdot 6H_2O$.

5. Acknowledgements.

We have to thank Mr. Lipson, of Liverpool, for his collaboration in the analysis of the rotation photographs, and Prof. W. L. Bragg for his advice and constant interest.

Summary.

The x and y parameters of Ni and S in the crystal $NiSO_4 \cdot 7H_2O$ are derived by means of a) replacement of Ni by Mg, b) a Patterson synthesis. These are used for two-dimensional Fourier syntheses which give all the parameters to a fair approximation.

The structure has SO_4 groups and octahedral groups of six H_2O around Ni, and an extra water molecule. The water molecules are of two types, and the coordination group contains both types exactly as in the lower hydrate $NiSO_4 \cdot 6H_2O$.

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