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On the Crystal Structures of $FeOHSO_4$ and $InOHSO_4$

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The basic iron sulfate, $FeOHSO_4$, forms orthorhombic crystals with lattice parameters $a = 7.33$, $b = 6.42$, and $c = 7.14$ Å. The space group is D_{2h}^{16}—*Pnma* and the unit cell contains four formula weights. Each iron atom is octahedrally coordinated with two hydroxogroups and four sulfate oxygens. Each hydroxogroup is bonded to two iron atoms. The structure of the basic indium sulfate, $InOHSO_4$, has been shown to be similar.

Crystal structure determinations of a number of basic salts of group 3b metals have shown that the metal atoms in these salts are linked together by means of single or double bridges of hydroxogroups. In crystals of $AlOHSO_4(H_2O)_5$ the aluminum atoms are joined by double OH bridges, which results in the formation of discrete aluminum oxygen complexes[1]. In the corresponding basic sulfates of indium and thallium, $InOHSO_4(H_2O)_2$[2] and $TlOHSO_4(H_2O)_{2.5}$[3] the metal atoms are joined by single OH bridges leading to infinite metal-oxygen chains. These basic salts can all be obtained from solutions at room temperature. To see if the same type of bridging occurs in basic salts prepared under different conditions, the structure of an indium sulfate formed by hydrothermal hydrolysis at high temperature has been investigated. It has the composition $In_2O_3 \cdot 2SO_3 \cdot H_2O$. An iron sulfate with the same composition, $Fe_2O_3 \cdot 2SO_3 \cdot H_2O$, can be obtained by the same method of preparation[4]. Structurally the two compounds are closely related.

EXPERIMENTAL

Preparation of crystals. $In_2O_3 \cdot 2SO_3 \cdot H_2O$: Solutions of indium sulfate with concentrations ranging from 0.004 to 1.0 M were prepared by dissolving $In_2(SO_4)_3$ in distilled water or in weak sulfuric acid (< 15 % H_2SO_4). Small samples of the solutions were then heated in sealed pyrex tubes at 100°, 160°, or 190°C for about a week. No precipitates were formed in the tubes heated to 100°C. At the higher temperatures two phases were obtained. One formed only in the most dilute solutions and did not contain sulfate. It was shown by powder photographs to be $In(OH)_3$. The other was the basic sulfate $In_2O_3 \cdot 2SO_3 \cdot H_2O$. It crystallized as thin needles which were bound together into larger aggregates of rather irregular shapes with the needle axes parallel.

$Fe_2O_3 \cdot 2SO_3 \cdot H_2O$: The range of stability has been given by Posjnak and Merwin[4]. Crystals sufficiently large for X-ray work, were obtained by heating a solution containing 4.7 % Fe_2O_3, 12.9 % SO_3, and 82.4 % H_2O at 200°C for about a month.

Analysis. The results of the analysis are compared in Table 1 with calculated values for $In_2O_3 \cdot 2SO_3 \cdot H_2O$ and $Fe_2O_3 \cdot 2SO_3 \cdot H_2O$.

Table 1.

	$In_2O_3 \cdot 2SO_3 \cdot H_2O$			$Fe_2O_3 \cdot 2SO_3 \cdot H_2O$	
	Found	Calc.		Found	Calc.
% In_2O_3	60.7	60.91	% Fe_2O_3	47.2	47.27
% SO_3	35.1	35.13	% SO_3	47.0	47.40
% H_2O	4.5	3.95	% H_2O	5.9	5.33
Density	3.9_4	4.05	Density	3.2_9	3.34

The amount of water was determined according to the method of Brush and Penfield[5], and sulfate was determined as $BaSO_4$. In^{3+} and Fe^{3+} were precipitated as hydroxides. After ignition the residue was weighed as In_2O_3 or Fe_2O_3. The density was obtained by comparison of the weight of a sample in benzene and in air.

X-Ray data. Rotation and Weissenberg photographs taken around the three crystallographic axes showed that the crystals are orthorhombic. The following values for the unit cell dimensions were calculated from powder photographs taken with Cu*Ka* radiation (λ = 1.54050 Å) in a Guinier focusing camera with KCl (a_0 = 6.2929 Å) as internal standard:

$a = 7.67_1$ Å $b = 6.64_9$ Å $c = 7.32_3$ Å for $In_2O_3 \cdot 2SO_3 \cdot H_2O$
$a = 7.33_1$ Å $b = 6.41_9$ Å $c = 7.14_2$ Å for $Fe_2O_3 \cdot 2SO_3 \cdot H_2O$

(Estimated accuracy ± 0.005 Å). The first lines on the powder photographs are given in Table 2.

A comparison between observed and calculated densities shows that there are two formula weights, thus 4 Fe(In) atoms, in the unit cell (Table 1).

For $Fe_2O_3 \cdot 2SO_3 \cdot H_2O$ the systematically absent reflections are $0kl$ with $k + l$ odd and $hk0$ with h odd. This is characteristic for the space groups No. 62: *Pnma* and No. 33: $Pn2_1a$. The non-centrosymmetric $Pn2_1a$ was not considered as it was possible to find a satisfactory structure with the higher symmetry.

The crystals are extended along the *a* axis. The odd layer lines of rotation photographs taken around this axis are very weak. On the even layer lines all reflections with $\frac{1}{2}h + k + l$ odd are absent, which indicates that for every atom at x, y, z there must also be an atom at $1/4 + x$, $\frac{1}{2} + y$, $\frac{1}{2} + z$ or $\frac{3}{4} + x$, $\frac{1}{2} + y$, $\frac{1}{2} + z$.

Difficulties were encountered in finding good single crystals of the corresponding indium compound. The spots on the Weissenberg films were often rather extended and diffuse. This was especially true for crystals prepared at 190°C. Weissenberg photographs showed that the systematic absences are the same as for $Fe_2O_3 \cdot 2SO_3 \cdot H_2O$ except for the presence of very weak reflections $hk0$ for h odd. The odd layer lines around the *a* axis are extremely weak in comparison with the even layer lines which have the same systematic absences for $\frac{1}{2}h + k + l$ odd as was noted for the Fe salt.

For the collection of intensity data Weissenberg photographs were taken around all three axes using the multiple film technique with Mo*K* radiation for the Fe salt and Cu*K* radiation for the In salt. The maximum dimension of the crystals used were 0.2 mm for the Fe and 0.1 mm for the In salts. The intensities were estimated visually by comparison with a calibrated intensity strip and were corrected for Lorentz and polarization factors.

Because $Fe_2O_3 \cdot 2SO_3 \cdot H_2O$ has a higher symmetry and gave more reliable intensity data, a complete structure determination was carried out only for this compound.

STRUCTURE DETERMINATION

The very weak odd layer lines around the *a* axis for both the iron and the indium compound indicate that there is no or at least only a very small contribution to these reflections from the metal atoms. Thus, if one Fe atom has the position xyz, there must be a corresponding atom at $\frac{1}{2} + x,y,z$. The extinction on the even layer lines of reflections with $\frac{1}{2}h + k + l$ odd further shows that there must also be Fe atoms at $1/4 + x, \frac{1}{2} + y, \frac{1}{2} + z$ and $3/4 + x, \frac{1}{2} + y, \frac{1}{2} + z$. The only position in space group *Pnma* that can accomodate four Fe atoms related in this way, is 4(c): $\pm(x, 1/4, z)$, $\pm(\frac{1}{2} + x, 1/4, \frac{1}{2} - z)$. The parameter values must then be $x = \pm 1/8$ or $\pm 3/8$ and $z = \pm 1/4$. All these positions are equivalent and any set of parameters can be chosen, for example: $x = 1/8$, $z = 1/4$, ($y = 1/4$).

The Fe atoms make a maximum contribution to all $0kl$ reflections and therefore probably determine their signs. On this assumption the electron density projected on the yz plane was calculated. As no signs were later changed because of the contributions from the light atoms, the resulting Fourier map was the same as the final electron density map shown in Fig. 1a. It reveals clearly the positions of the four sulfate groups of the unit cell, and it also indicates the positions of the four oxygen atoms (O_4) not associated with the sulfate groups.

According to Fig. 1a the parameters of O_4 are $y = 1/4$ and $z \approx 0.15$, and O_4 therefore occupies the position 4(c). The two nearest Fe atoms are at 1/8, 1/4, 1/4 and 5/8, 1/4, 1/4. The O_4 atom must have a position between these Fe atoms, that is with $x = 3/8$ (or 7/8 which is structurally equivalent), as other values of x would result in Fe—O_4 distances, which are too short. O_4 is therefore in contact with two Fe atoms at distances of approximately 2.0 Å.

The possible x parameters for the sulfur atoms are restricted in the same way as the parameters for the Fe atoms, that is they must be $x = \pm 1/8$ or $\pm 3/8$. With the position of O_4 given ($x = 7/8$, $y = 1/4$, $z \approx 0.35$) and with

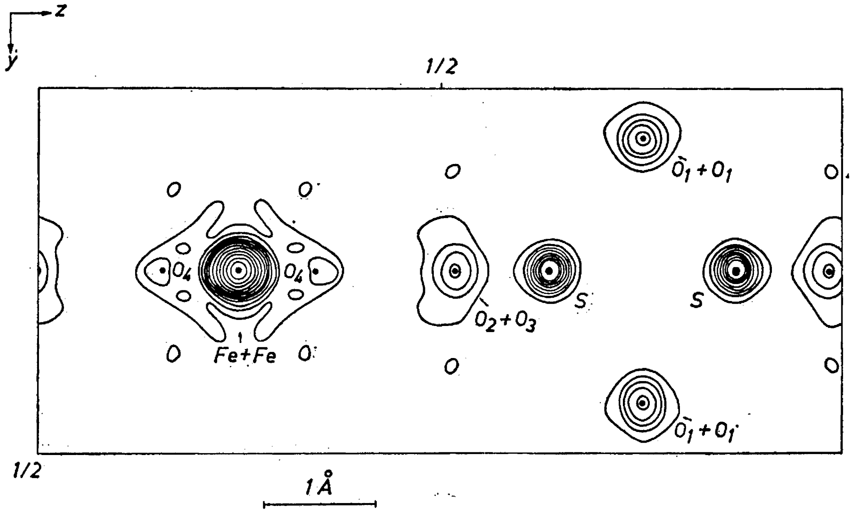

Fig. 1 a. Electron density projection along the *a* axis for $FeOHSO_4$. Contours are drawn at intervals of 10 e·Å^{-2}. The zero contour is omitted. At the Fe peak only every 3rd contour has been drawn above 50 e·Å^{-2}. The final atomic positions are indicated by dots.

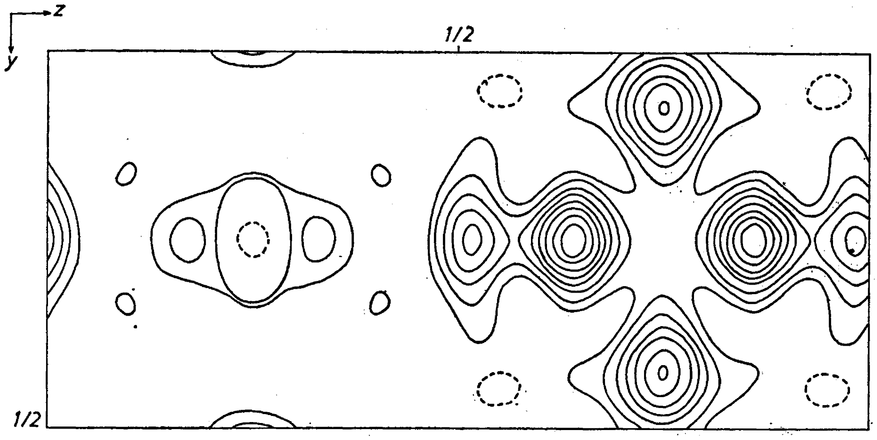

Fig. 1 b. Electron density projection along the *a* axis for InOHSO$_4$ with the contribution from the In atoms subtracted. Contours are drawn at intervals of 4 e·Å^{-2}. The zero contour is omitted. Broken lines indicate negative regions.

the sulfate group oriented as shown by the $0kl$ projection in Fig. 1a, the only possible parameters for the fourfold sulfur position, not leading to O—O distances, which are too short, are $x = 3/8$ and $y = 1/4$, $z \approx 0.63$.

Of the oxygen atoms of the sulfate groups, O_1 occupies an eightfold position since according to Fig. 1a it lies outside the mirror planes at $y = \pm 1/4$. O_2 and O_3 lie on the mirror planes, that is they are in fourfold positions. Their x

Table 2. Powder photographs ($\sin^2\Theta < 0.20$) of FeOHSO$_4$ and InOHSO$_4$, taken with Cu*Ka* radiation in a Guinier camera.

	FeOHSO$_4$				InOHSO$_4$		
h k l	$\sin^2\Theta$ calc.	$\sin^2\Theta$ obs.	*I* obs.	*h k l*	$\sin^2\Theta$ calc.	$\sin^2\Theta$ obs.	*I* obs.
101	0.0227	0.0226	vvw	101	0.0211	0.0211	vvw
011	0.0260	0.0260	m	011	0.0245	0.0245	w+
111	0.0371	0.0370	vvw	002	0.0443	0.0443	w+
002	0.0465	0.0465	w	201	0.0514	0.0514	vs
201	0.0558	0.0558	vs	020	0.0537	0.0537	s
102	0.0575	0.0576	s	210	0.0537		
020	0.0576			102	0.0543	0.0545	vvw
112	0.0719	0.0719	vw	022	0.0979	0.0980	m
212	0.1050	0.1050	vvw	212	0.0980		
221	0.1134	0.1134	w	221	0.1051	0.1052	s
013	0.1190	0.1190	w	013	0.1130	0.1131	w
031	0.1413	0.1413	vw	031	0.1318	0.1318	vw
203	0.1488	0.1488	w	203	0.1399	0.1399	w+
230	0.1738	0.1741	vvw	230	0.1611	0.1612	m
400	0.1766	0.1765	w	400	0.1613		
004	0.1860	0.1859	vvw	004	0.1770	0.1775	vvw
				411	0.1858	0.1857	w
				223	0.1936	0.1935	vw

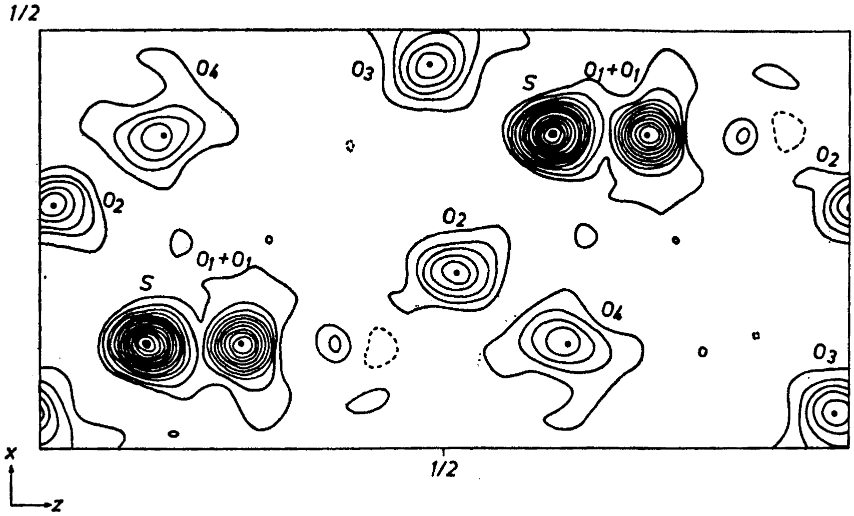

Fig. 2. Electron density projection along the *b* axis for $FeOHSO_4$ with the contribution from the Fe atoms subtracted. Contours are drawn at intervals of 5 $e \cdot Å^{-2}$. The zero contour is omitted. The final atomic positions are indicated by dots.

parameters can be calculated assuming the O—O distance in a sulfate group to be 2.4 Å.

The resulting parameter values were refined from difference syntheses and electron density projections along the *a*, *b*, and *c* axes. The refinement was continued until the difference maps did not indicate any significant shifts in the positional parameters. The final parameters are given in Table 3. The final electron density projection along the *b* axis with the contribution from the Fe atoms subtracted is shown in Fig. 2.

Of the atoms of the unit cell only O_2 and O_3 give contributions to reflections for which h is even and $\frac{1}{2}h + k + l$ is odd. To maintain the condition that these reflections are systematically absent the parameters of O_2 and O_3 must be related in such a way, that, for example, an O_2 atom at xyz has a corresponding O_3 atom at $1/4 + x$ (or $3/4 + x$), $\frac{1}{2} + y$, $\frac{1}{2} + z$. The final parameters in Table 3 are in accordance with this as there are no indications in the difference maps of any significant deviations from this relation.

Table 3.

Final parameters

	x	y	z
4 Fe in 4(*c*)	0.125	1/4	0.250
4 S in 4(*c*)	0.875	1/4	0.866
8 O_1 in 8(*d*)	0.375	0.067	0.750
4 O_2 in 4(*c*)	0.209	1/4	0.517
4 O_3 in 4(*c*)	0.959	3/4	0.017
4 O_4 in 4(*c*)	0.375	1/4	0.155

For the final calculation of structure factors listed in Table 5, temperature factors of 0.3 Å^2 for Fe and S and 0.5 Å^2 for O atoms were used. The scattering factors were those given by Berghuis *et al.*[6] for O, by Tomiie and Stam [7] for S, and by Thomas and Umeda [8] for Fe. The R factors ($R = \Sigma / |F_o| - |F_c| / / \Sigma |F_o|$) with only observed reflections included are 0.084 for $0kl$, 0.070 for $h0l$, and 0.086 for $hk0$ reflections. For reflections with h odd there are no contributions from the Fe or O_1 atoms. For this class of reflections the R factors are 0.11 for $h0l$ and 0.13 for $1kl$ reflections. Standard deviations in positional parameters estimated according to the formula given by Cruickshank [9] are about 0.005 Å for S, 0.01_5 Å for O_1, O_2, and O_3, and 0.02 Å for O_4. Since most of the atoms are in special positions, the standard deviations in bond lengths will, however, generally be smaller than might be expected from the values given. The structure of $In_2O_3 \cdot 2SO_3 \cdot H_2O$ is essentially the same as that of $Fe_2O_3 \cdot 2SO_3 \cdot H_2O$. The electron density projection calculated from the $0kl$ structure factors with the contributions from the indium atoms subtracted is shown in Fig. 1b. It is in all essentials identical with that of the iron compound (Fig. 1a), but the presence of weak reflections $hk0$ for h odd shows that the symmetry of the indium salt is lower. The differences probably can be explained by rather small deviations of the parameter values of the light atoms in $In_2O_3 \cdot 2SO_3 \cdot H_2O$ from the *Pnma* symmetry. However, attempts to determine these deviations by means of trial and error were not successful and failed to give an R factor below about 0.30 for the weak $1kl$ and $3kl$ reflections, compared with a R factor of about 0.10 for the $0kl$ and $2kl$ reflections.

DISCUSSION OF THE STRUCTURE

Projections of the structure along the a and b axes are shown in Fig. 3. Each metal atom is octahedrally surrounded by six oxygen atoms. Two of

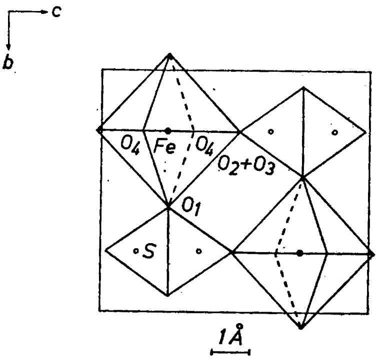

Fig. 3 a. Projection of the structure of $FeOHSO_4$ along the a axis.

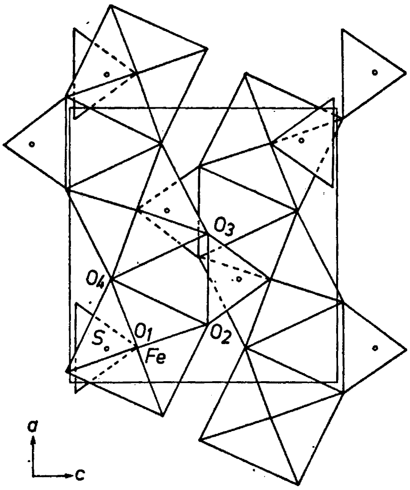

Fig. 3 b. Projection of the structure of $FeOHSO_4$ along the b axis.

Table 4. Interatomic distances.

Distances within a FeO_6 octahedron:

Fe – 2 O_1	2.03_5 Å	O_1 – O_2	2.86 Å
– O_2	2.00_3	– O_3	2.86
– O_3	2.00_3	– O_4	2.82
– 2 O_4	1.95_4	O_2 – O_4	2.86
		– O_4	2.74
		O_3 – O_4	2.86
		– O_4	2.74

Distances within a SO_4 group:

S – 2 O_1	1.44 Å	O_1 – O_1	2.35 Å
– O_2	1.48	– O_2	2.37
– O_3	1.48	– O_3	2.37
		O_2 – O_3	2.43

Other O—O distances < 4.0 Å

O_1 – O_1	3.67 Å	O_2 – O_3	3.55 Å
– O_2	3.18	– O_3	3.70
– O_3	3.18	– O_4	3.41
– O_4	3.12	O_3 – O_3	3.27
		O_4 – O_4	3.91

these, O_4, are shared between two octahedra. The remaining four belong to sulfate groups. The four hydrogen atoms of the unit cell are probably associated with the bridging oxygens, O_4, as this would increase the sum of electrostatic bond strengths for these atoms from 1 to the expected value of 2. The metal atoms are therefore joined by single hydroxobridges, and the formulae should be written as $FeOHSO_4$ and $InOHSO_4$. The interatomic distances (Table 4) give no evidence for the presence of hydrogen bonds.

The same kind of single hydroxobridges are present in the structure of $InOHSO_4(H_2O)_2$[2]. The two structures are in fact closely related. The two water oxygens of the InO_6 octahedra in $InOHSO_4(H_2O)_2$ are replaced by sulfate oxygens in $InOHSO_4$. The infinite In—OH—In chains, which in the former compound are joined to other similar chains only by means of hydrogen bonds, are in $InOHSO_4$ and $FeOHSO_4$ joined to other chains by means of oxygen atoms belonging to the same sulfate group. The In—In distance, 3.84 Å, within an In—OH—In chain in $InOHSO_4$ is slightly smaller than the corresponding distance in $InOHSO_4(H_2O)_2$, 3.95 Å. Accurate values for the In—O distances can not be calculated, but the approximate structure shows that they do not differ much from the values found for $InOHSO_4(H_2O)_2$[2].

In $FeOHSO_4$, the FeO_6 octahedra are very nearly regular. In view of the standard deviations, however, the difference between the shortest of the Fe—O bond lengths (1.95 Å and involving the bridging oxygens, O_4) and the longest (2.04 Å) is probably significant. The average value of the Fe—O distances, 2.00 Å, is close to the sum of the crystal radii, 2.04 Å[10].

The average S—O distance of 1.46 Å does not differ significantly from S—O distances found for sulfate groups in other structures[1].

Table 5. Observed and calculated structure factors for $FeOHSO_4$.

hkl	F_o	F_c
000	—	328
2	102	−104
4	87	83
6	39	−37
8	83	86
10	52	−53
12	27	27
14	< 17	−17
16	23	23
18	21	−23
011	52	−46
3	85	91
5	57	−50
7	35	35
9	< 11	−3
11	41	41
13	26	−26
15	21	20
020	155	−176
2	21	20
4	28	−26
6	< 8	3
8	63	−60
10	32	35
031	88	90
3	109	−117
5	80	76
7	47	−53
9	17	18
11	49	−51
13	32	34
15	23	−27
040	131	140
2	41	−39
4	32	32
6	16	−13
8	60	62
10	36	−37
12	< 17	17
14	< 17	−9
16	19	16
18	15	−17
051	22	−19
3	54	53
5	41	−36
7	20	22
9	< 15	2
11	33	32
13	22	−19
060	112	−116
2	54	49
4	37	−37
6	28	23
8	60	−63
10	39	41
12	21	−22
14	< 17	14
16	20	−19
18	14	20
071	30	30
3	65	−58
5	50	44
7	31	−30
9	< 16	8
11	34	−35
13	26	23
15	19	−19
080	64	65
2	20	−17
4	< 14	8
6	< 15	−2
8	36	37
10	24	−21
091	29	−27
3	52	50
5	46	−39
7	26	28
9	< 17	−10
11	31	33
13	25	−21
0100	64	−64
2	34	27
4	< 16	−20
6	18	13
8	35	−40
10	30	26
0111	< 16	8
3	24	−26
5	23	19
0120	42	48
2	26	−20
4	< 17	15
6	19	10
8	29	31
10	21	−21

hkl	F_o	F_c
0131	< 17	− 18
3	31	30
5	28	− 24
7	16	19
9	< 15	− 9
11	18	22
0140	26	− 29
2	< 17	8
4	< 16	− 6
6	< 16	2
8	16	− 18
0151	< 16	11
3	< 16	− 20
5	18	15
7	19	− 13
0160	24	30
2	< 14	− 14
4	< 13	13
6	< 12	− 9
8	16	21
101	34	35
2	53	− 55
3	9	4
4	10	9
5	< 7	− 4
6	19	18
7	17	16
8	16	− 16
9	13	10
10	12	− 14
111	29	33
2	49	52
3	9	3
4	< 6	− 9
5	10	− 5
6	20	− 18
7	20	16
8	17	16
121	30	− 29
2	47	46
3	< 6	− 2
4	13	− 8
5	< 7	5
6	14	− 17
7	11	− 16
8	10	16
9	13	− 10
10	17	14
11	12	10
131	25	− 24
2	38	− 39
3	< 6	0
4	< 7	7
5	< 7	5
6	17	17
7	15	− 15
8	14	− 15
9	< 11	− 9
10	11	− 13
141	21	20
2	33	− 33
3	< 7	− 2
4	< 8	6
5	< 8	− 5
6	13	16
7	10	15
8	< 10	− 14
9	13	9
10	16	− 13
151	17	17
2	25	29
3	< 8	− 3
4	< 8	− 6
5	11	− 5
6	17	− 15
7	17	14
8	15	13
161	14	− 15
2	22	25
3	< 9	4
4	< 9	− 5
5	< 9	5
6	14	− 14
7	12	− 13
171	12	− 14
2	18	− 22
3	< 9	4
4	< 10	5
5	< 10	4
6	13	13
7	14	− 12
181	13	12
2	18	− 20
191	< 11	11
2	15	18
1101	< 12	− 10
2	14	16

hkl	F_o	F_c
201	135	−149
3	97	95
5	55	−59
7	78	79
9	60	−59
11	30	34
301	22	18
2	39	−34
3	36	31
4	21	19
5	24	25
6	29	29
400	125	−140
2	116	119
4	28	−29
6	55	52
8	63	−65
10	53	56
501	19	−19
2	33	32
3	< 9	2
4	< 9	−6
5	< 10	5
6	17	−16
7	18	−14
8	< 15	14
9	< 16	−9
10	17	12
601	83	88
3	47	−47
5	44	50
7	47	−51
9	61	62
701	20	16
2	30	25
800	77	81
2	67	−66
4	18	18
6	37	−36
8	50	50
10	37	−45
901	< 12	−1
2	23	−18
3	20	−16
4	< 16	9
5	16	−14
6	17	18
1001	50	54
3	33	33
1005	24	−25
7	44	45
9	35	−36
1101	< 15	−10
2	19	−16
1200	56	−65
2	27	30
4	24	−23
6	< 19	16
8	41	−41
1401	27	34
3	< 20	−23
5	< 20	18
7	30	−30
1600	26	31
2	23	−27
210	16	−16
3	69	64
5	< 9	−4
7	17	19
9	16	−18
420	79	77
4	87	−79
6	75	78
8	46	−43
10	49	46
12	43	−34
14	< 18	19
16	20	−22
610	18	−18
3	12	−10
5	16	−17
820	58	−55
4	56	57
6	60	−59
8	36	34
10	38	−37
12	31	28
14	19	−16
1010	< 17	−8
3	16	22
1220	48	49
4	45	−50
6	44	51
8	29	−32
10	25	34
12	25	−28

hkl	F_o	F_c	*hkl*	F_o	F_c
1620	23	− 21	1680	19	15
4	23	23	10	16	− 18
6	21	− 25			

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