Acta Cryst. (1967). **22**, 766

The Preparation, Crystal Structure and Magnetic Properties of $Na_3Fe_5O_9$

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(*Received* 2 *November* 1966)

$Na_3Fe_5O_9$ was prepared by firing Na_2CO_3 and Fe_2O_3 at 1100°C. The crystals are monoclinic with space group $C2/c$. The lattice dimensions are $a = 13{\cdot}39$, $b = 12{\cdot}07$, $c = 5{\cdot}29$ Å, $\beta = 89^{\circ}\,10'$ and $Z = 4$. The structure was solved by Patterson methods and heavy-atom technique. Some of the Fe ions are found in general positions $8(f)$ and surrounded tetrahedrally by oxygen ions; others are in the special positions $4(e)$, surrounded octahedrally by oxygen atoms. The Na ions are in an irregular fivefold coordination of oxygen ions. The crystals are antiferromagnetic and a possible arrangement of magnetic spins is discussed.

Introduction

In the system Na_2O–Fe_2O_3 the 1:1 compound $NaFeO_2$ has been known for a considerable time. It exists in two modifications. The low-temperature modification (α), first described by van Bemmelen & Klobbie (1892), has a cubic close-packed array of oxygen ions with sodium and iron ions in octahedral interstices. The layer stacking order present in this rocksalt type of structure leads to a hexagonal cell, determined by Goldsztaub (1935). At a temperature of about 800°C (Collongues & Théry, 1959) this structure transforms into an ordered structure of the wurtzite type (β), as determined by Bertaut & Blum (1954). Here the sodium and iron ions are both four-coordinated. The transformation is accompanied by a large volume expansion of almost 30%, from 42·3 to 54·4 Å^3 per mole; the specific gravities of the α and β modifications are 4·34 and 3·36 respectively.

Recently a new compound has been observed in this system. Its existence was first mentioned by Collongues & Théry (1959), and its composition was said to be near $2Na_2O.3Fe_2O_3$ or $Na_4Fe_6O_{11}$. According to these authors, the X-ray diagram could be indexed with a tetragonal unit cell. Independently this compound was investigated by one of us (Rooymans, 1959). Although the composition was first stated to be $Na_{10}Fe_{16}O_{29}$, careful observation, made possible by the availability of single crystals, demonstrated that the real formula is $Na_3Fe_5O_9$ (Rooymans, 1962). The unit cell, derived from polycrystalline and single-crystal data, is monoclinic. Its specific gravity is $3{\cdot}82_6$ ($d_{\text{rö}} = 3{\cdot}82_0$). The conformity of some of the lattice constants of $Na_3Fe_5O_9$ with those of β-$NaFeO_2$ and the fact that its specific weight is just between the specific weights of the two $NaFeO_2$ modifications, made it interesting to know which coordination for the iron and sodium ions was present here.

Experimental

The compound $Na_3Fe_5O_9$ can be prepared by firing mixtures of Na_2CO_3 and Fe_2O_3 at temperatures of about 1100°C for two hours. It is advisable to start with a slight excess of sodium carbonate over the stoichiometric quantity, because at the firing temperature there is evidently some loss of sodium oxide by vaporization. This explains why the first assumptions of the composition are on the sodium-rich side. In mixtures fired at temperatures below 1050°C, the presence of β-$NaFeO_2$ and α-Fe_2O_3 is shown by the X-ray diagrams.

A mixture of about the composition $5Na_2CO_3$ to $8Fe_2O_3$ was melted, at a temperature of about 1250°C. From the frozen melt some single crystals of irregular shape were obtained. One of these crystals was mounted with [001] parallel to the rotation axis of a Weissenberg goniometer. The first five reciprocal layers with $l =$ 0, 1, 2, 3, and 4 were recorded with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å) using multiple films (interleaved with copper foil) and equi-inclination technique. The reflexion intensities were estimated visually and reduced to structure factor moduli after multiplication by Lorentz, polarization and spotshape factors. The linear absorption coefficient of $Na_3Fe_5O_9$, amounting to 87 cm^{-1} for Mo $K\alpha$ radiation, is sufficiently small to allow the omission of absorption correction. The cross section of the crystal used was less than 0·6 mm.

The lattice constants, measured on the single crystal, fully confirm the dimensions of the monoclinic unit cell given previously (Rooymans, 1962). The new measurements, which are more accurate, give:

$$\begin{array}{ll} a = 13{\cdot}39^{\circ} \pm 0{\cdot}005 \text{ Å} & d_{\text{exp}} = 3{\cdot}82_6 \pm 0{\cdot}003 \\ b = 12{\cdot}07_5 \pm 0{\cdot}005 & d_{\text{rö}} = 3{\cdot}82_0 \\ c = 5{\cdot}29_4 \pm 0{\cdot}002 & \\ \beta = 89^{\circ}\,10' \pm 2' & Z = 4 \end{array}$$

In addition to the absence of reflexions with $h+k \neq 2n$ (see Rooymans, 1962), the reflexions $h0l$ with $l \neq 2n$ are also absent. Possible space groups are therefore $C2/c$ and Cc. The former was chosen and its validity was ultimately confirmed by the analysis.

Structure determination and refinement

An unsharpened three-dimensional Patterson function was searched for iron–iron vectors. Since the reciprocal layers $hk5$ to $hk9$ were not incorporated in the calculation of this Fourier synthesis its resolution was rather poor in the direction [001]. Nevertheless it proved possible to postulate a model with

ions Fe(1) and Fe(2) in general positions 8(f)
and Fe(3) in fourfold positions 4(e) (on twofold axes).

Structure factor calculations based upon the contribution of these iron(III) ions resulted in an R value of 55%. The remaining ions were found in a subsequently calculated electron density function.

These positions are

Na(1), O(1), O(2), O(3) and O(4) in 8(f)
and Na(2) and O(5) in 4(e).

The structure was refined by the method of least-squares minimizing $\Sigma\, w(|F_c|-|F_o|)^2$ in a block-diagonalized approximation with a program developed by E.W.M. Rutten (Geise, Romers & Rutten, 1966). The refining of separate scaling factors for different reciprocal layers is optional in this program and was used during the refinement. The weighting function used was

$$w=\frac{a+F_{\min}}{a+|F_o|+bF_o^2}\,.$$

The observed minimum value $F_{\min}$ is 5 and the constants a and b are 10 and 0·01 respectively. The atomic scattering curves of Fe^{3+} and Na^{+} were taken from *International Tables for X-ray Crystallography* (1962). As scattering curve of O^{2-} the function calculated by Suzuki (1960) was adopted. The reliability index (defined in the usual way, and calculated for observed reflexions only) dropped in four cycles with individual isotropic temperature factors from 38 to 13%.

Next, anisotropic temperature factors of the form

$$\exp[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+ \\ +2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})]$$

were introduced into the calculation and after two more cycles R dropped to 12·4%. At this stage a three-dimensional difference Fourier synthesis with coefficients F_o-F_c was computed. The highest peaks in the resulting map were lower than 0·4 e.Å^{-3} and were considered to be insignificant. Finally, a number of punching, intensity-estimation, indexing and various other errors were corrected. A complete list of observed and calculated structure factors based upon the final R value of 11·2% is available upon request.

The atomic parameters and their standard deviations are listed in Table 1. The vibrational parameters are found in Table 2. The standard deviations $\sigma(z)$ are about 55% higher than $\sigma(x)$ and $\sigma(y)$, because the structure factors of the reciprocal layers $hk5$ to $hk9$ were not incorporated in the refinement.

The standard errors in bond distances are within the range 0·005 to 0·013 Å with a mean value of 0·01 Å. The mean standard deviation of bond angles is about 40′.

Discussion of the structure

A part of the crystal structure of $Na_3Fe_5O_9$ is projected along [001] in Fig. 1. The iron ions Fe(1) and Fe(2) are surrounded tetrahedrally by four oxygen ions,

Table 1. *Atomic parameters (in fractions of cell edges) and their standard deviations* (Å)

	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Fe(1)	0·1153	0·3196	0·2823	0·0012	0·0013	0·0021
Fe(2)	0·3591	0·3393	0·2181	0·0013	0·0013	0·0021
Fe(3)	0·0000	0·0637	0·2500	—	0·0018	—
Na(1)	0·2384	0·0767	0·2724	0·0057	0·0054	0·0077
Na(2)	0·0000	0·5954	0·2500	—	0·0084	—
O(1)	0·0943	0·1822	0·1181	0·0071	0·0069	0·0114
O(2)	0·3674	0·2019	0·3773	0·0086	0·0080	0·0122
O(3)	0·2295	0·3909	0·1767	0·0068	0·0075	0·0112
O(4)	0·4180	0·4470	0·4248	0·0070	0·0066	0·0105
O(5)	0·0000	0·4048	0·2500	—	0·0088	—

Table 2. *Vibrational parameters* (Å^2)

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
Fe(1)	0·0057	0·0067	0·0051	−0·0005	0·0003	0·0003
Fe(2)	0·0065	0·0074	0·0040	−0·0010	0·0002	−0·0011
Fe(3)	0·0058	0·0058	0·0058	+0·0000	0·0000	−0·0002
Na(1)	0·0162	0·0149	0·0212	0·0021	−0·0013	−0·0020
Na(2)	0·0238	0·0208	0·0208	0·0000	0·0000	−0·0006
O(1)	0·0102	0·0072	0·0125	−0·0005	−0·0006	−0·0014
O(2)	0·0159	0·0109	0·0161	−0·0024	0·0005	0·0086
O(3)	0·0083	0·0115	0·0119	0·0021	0·0079	0·0031
O(4)	0·0108	0·0080	0·0049	−0·0046	0·0058	−0·0036
O(5)	0·0074	0·0067	0·0067	0·0000	0·0000	−0·0002

namely Fe(1) by O(1), O(2), O(3) and O(5) and Fe(2) by O(1), O(2), O(3) and O(4). The Fe(3) is surrounded octahedrally by six oxygen ions, namely by O(1) (twice) and by O(4) (four times). This is shown in Fig. 2. This Figure and Tables 3, 4 and 5 indicate that the tetrahedra and the octahedron are slightly deformed. The deformations are only minor, although significant in a statistical sense. The tetrahedral Fe–O distances vary between $1{\cdot}83_4$ and $1{\cdot}89_6$ Å. Their mean value (1·867 Å) agrees excellently with the mean Fe–O distance (1·86 Å) found in β-$NaFeO_2$ where the iron(III) ion is also in tetrahedral coordination (Bertaut, Delapalme & Bassi, 1963). The octahedral Fe(3)–O distances are about 6% larger, mean value $2{\cdot}03^0$ Å, in agreement with the Goldschmidt–Pauling rules. These distances are comparable with the Fe–O distance in α-$NaFeO_2$: 1·96 Å (Goldsztaub, 1935) and for example also with α-Fe_2O_3 (Newnham & de Haan, 1962) (1·96 and 2·09 Å) where the iron(III) ions are octahedrally coordinated.

Both sodium ions are irregularly coordinated by five oxygen atoms at a mean distance of 2·44 Å (Table 6). This value compares favourably with the value 2·35–2·49 Å found in $(NaPO_3)_n$ (Wyckoff, 1964), where Na^+ has also a fivefold coordination.

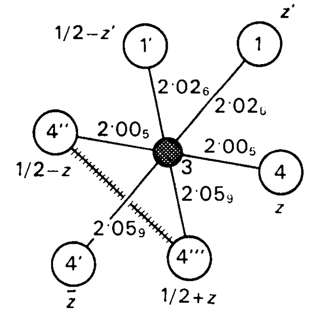

Fig. 2. The octahedral environment of Fe(3), also projected along [001]. The distances of the oxygen atoms to the central iron atom, as well as their relative height, have been indicated. Open circles: O^{2-}; shaded circle: Fe^{3+}. The hatched line represents a shared edge. $z_{Fe(3)}=0{\cdot}2500$; $z_{O(1)}=0{\cdot}1181$; $z_{O(4)}=0{\cdot}4248$.

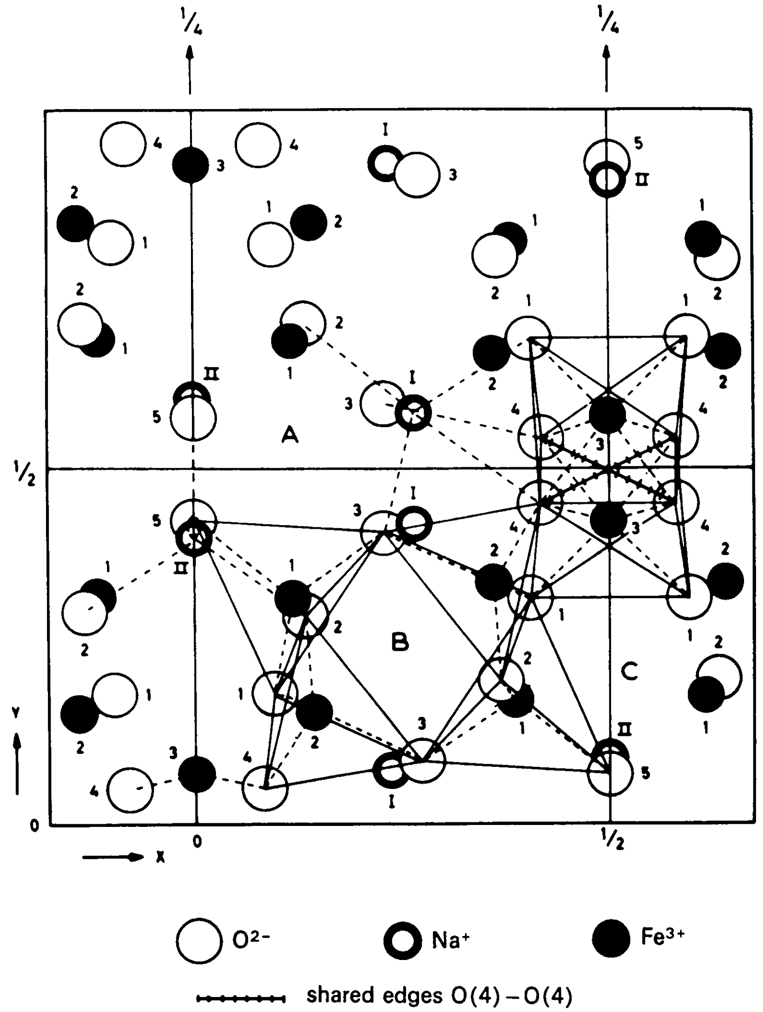

Fig. 1. A projection along [001] of a part of the unit cell of $Na_3Fe_5O_9$. Note the double rows of tetrahedra parallel with *Ox*. The numbers refer to the groups of atoms, as used in the text.

Table 3. *The coordination of* Fe(1)

Ligand	Distance	Bond angle	Value
O(1)	1·89$_6$ ± 0·008 Å	O(1)–Fe–O(2)	110·3°
O(2)	1·83$_9$ ± 0·012	O(1)–Fe–O(3)	113·5
O(3)	1·83$_4$ ± 0·005	O(1)–Fe–O(5)	108·2
O(5)	1·86$_5$ ± 0·007	O(2)–Fe–O(3)	104·4
		O(2)–Fe–O(5)	106·5
Mean value	1·85^9 ± 0·008	O(3)–Fe–O(5)	113·6

Table 4. *The coordination of* Fe(2)

Ligand	Distance	Bond angles	Value
O(1)	1·89$_6$ ± 0·011 Å	O(1)–Fe–O(2)	106·4°
O(2)	1·86$_5$ ± 0·009	O(1)–Fe–O(3)	103·3
O(3)	1·86$_0$ ± 0·007	O(1)–Fe–O(4)	120·4
O(4)	1·88$_0$ ± 0·010	O(2)–Fe–O(3)	114·4
		O(2)–Fe–O(4)	108·9
Mean value	1·87^5 ± 0·009	O(3)–Fe–O(4)	103·7

Table 5. *The coordination of* Fe(3)

Oxygen atoms without superscript refer to the position x,y,z; ′ refers to $\bar{x},\bar{y},\bar{z}$; ″ refers to $\bar{x},y,\frac{1}{2}-z$ and ‴ to $x,\bar{y},\frac{1}{2}+z$.

Ligand	Distance	Bond angle	Value
O(4)	2·00$_5$ ± 0·009 Å	O(4)—Fe–O(4‴)	93°
O(4″)	2·00$_5$ ± 0·009	O(4″)–Fe–O(4‴)	90·5
O(4′)	2·05$_9$ ± 0·008	O(1)—Fe–O(4‴)	90
O(4‴)	2·05$_9$ ± 0·008	O(4)—Fe–O(4″)	82
O(1)	2·02$_6$ ± 0·008	O(4)—Fe–O(1)	90
O(1″)	2·02$_6$ ± 0·008	O(4)—Fe–O(1″)	95·5
Mean value	2·02^9 ± 0·008	O(1)—Fe–O(4‴)	172

Table 6. Na–O *bond distances in* Å

Na(1)–O(1)	2·46 Å	Na(2)–O(2)	2·29 Å (2×)
Na(1)–O(2)	2·37	Na(2)–O(5)	2·30
Na(1)–O(3)	2·44	Na(2)–O(5)	2·65
Na(1)–O(3)	2·30	Na(2)–O(5)	2·65
Na(1)–O(4)	2·63		
Mean value	2·44	Mean value	2·44

An infinite string of octahedra running parallel to [001] is formed by sharing edges O(4)–O(4′) and O(4″)–O(4‴) as can be seen in Fig. 1. The symmetry of this string is the glide plane *c*. All oxygen ions are shared by two or more cations between different polyhedra:

O(1) between Fe(1) and Fe(2)
O(2) between Fe(1), Fe(2), Na(1) and Na(2)
O(3) between Fe(1), Fe(2) and Na(1)
O(4) between Fe(2), Fe(3) twice, and Na(1)

and finally

O(5) between Fe(1) twice and Na(2) three times.

As a result one would expect an extremely dense packing, but spaces of very dense packing are compensated by empty spaces, the 'holes' indicated by *A*, *B* and *C* in Fig. 1. The holes or channels, running parallel to [001], have diameters of about 4 Å.

Geometrically the structure of $Na_3Fe_5O_9$ is indeed an intermediate between α- and β-$NaFeO_2$, as clearly shown by the coordination of the cations in the three structures. It is worth mentioning in this respect that Ga can be substituted for iron in this compound up to the composition $Na_3Ga_5O_9$. The substitution of aluminum for iron was not possible. Substitution of gallium and aluminum for iron (Toropov & Shishakov, 1939; Théry, Lejus, Briançon & Collongues, 1961; Hoppe, 1965) in $NaFeO_2$ gives in both cases the structure of the β modification. Under high pressure it is possible to transform these into the α modification, although this can be realized for gallium under much more moderate conditions than for aluminum (Rooymans, 1965). In these types of structure gallium and iron ions may thus have either four- or six-coordination, whereas aluminum ions clearly prefer four-coordination.

Stability of the structure

The compound $Na_3Fe_5O_9$ could only be prepared at the rather high temperature of about 1100°C. It is therefore not certain whether this compound is stable at room temperature and atmospheric pressure with respect to α-$NaFeO_2$ and α-Fe_2O_3. Under high pressure conditions (20 Kb and higher), it decomposes into these substances at temperatures of about 500°C; under normal pressure conditions such a decomposition could not be observed in the X-ray powder diagrams of samples after heating at moderate temperatures.

From the magnetic susceptibility measurements, as well as from the Mössbauer experiments, which are much more sensitive in this respect, there are, however, indications that a decomposition indeed takes place. This conclusion agrees with Théry's (1962) results.

Magnetic properties

The compound $Na_3Fe_5O_9$ is antiferromagnetic (Rooymans, 1962). The same is true for compositions between $Na_3Fe_5O_9$ and $Na_3Ga_5O_9$.

With the knowledge of the crystal structure, a possible explanation for this behaviour can be given. As described for example by Goodenough (1963), the magnetic interactions depend on the angle and distance of the Fe–O–Fe bonds. In Table 7 a survey of the bond distances and angles is given.

Table 7. Fe–O–Fe *bond distances*

Bonds	Distances	Angle
Fe(1)–O(2)–Fe(2)	1·836/1·863 Å	125·3°
Fe(1)–O(1)–Fe(2)	1·895/1·904	119·8
Fe(2)–O(3)–Fe(1)	1·857/1·842	125·9
Fe(1)–O(5)–Fe(1)	1·863/1·863	113·0
Fe(2)–O(1)–Fe(3)	1·904/2·032	115·7
Fe(2)–O(4)–Fe(1)	1·874/2·046	116·1

As can be seen from Table 7, neither the distances nor the angles are markedly different. It seems therefore justified to assume that the occurring interactions have about the same strength. The coupling, however, of the octahedra with each other and with the neighbouring tetrahedra takes place *via* two oxygen ions, *i.e.* they share edges. The same is true for the tetrahedra parallel to the *y* axis. This will probably result in a stronger interaction, in contrast with the interaction *via* one oxygen ion of the tetrahedra parallel to the *x* axis. These considerations give rise to a model of the spin configuration as shown in Fig. 3, which is a projection along [001] of a part of the unit cell. The *z* parameter is given for a better steric representation.

The direction of the spins with respect to the crystallographic axes has been chosen arbitrarily. The given arrangement shows that for the iron ions at each of the crystallographic positions, one half have their spins opposite to the other half. This would give rise to an antiferromagnetic structure for the compositions $Na_3Fe_{5-x}Ga_xO_9$, even in the case of a preferred occupation of any one of the crystallographic positions by iron or gallium ions.

The magnetic structure can be determined unambiguously only by neutron diffraction analysis.

Mössbauer experiments (van Loef & Slegtenhorst, 1966) so far have revealed two magnetic sublattices, one for tetrahedral, one for octahedral sites. The Néel point could be determined at 375 °K. Watanabe & Fukasi (1961) suggest that the peak at about 100 °C in their magnetization measurements on β-$NaFeO_2$ may be identified with the Néel temperature of a compound which they define as $2Na_2O.3Fe_2O_3$. Apart from the composition of the compound this is in good agreement with the results given here.

The susceptibility measurements indicate a somewhat higher Néel point, but these measurements are very sensitive to small traces of α-Fe_2O_3, which is slightly ferromagnetic. It was not possible for us to prepare a sample absolutely free of α ferric oxide, which is not surprising in view of the doubtful stability of the compound at ambiant conditions.

The magnetic behaviour is, in a manner of speaking, also intermediate between the behaviour of α- and β-$NaFeO_2$. β-$NaFeO_2$ is antiferromagnetic (Bertaut, Delapalme & Bassi, 1963), but shows a superimposed weak ferromagnetism (Watanabe & Fukasi, 1961). The Curie temperature is about 720 °K.

The layer compound α-$NaFeO_2$ is paramagnetic, but at temperatures below 100 °K there is a deviation from the linear $1/\chi - T$ curve, indicating some kind of magnetic interaction (Rooymans, 1965). There is a Néel point near 20 °K. The extrapolation of the linear part of the curve goes to 0 °K. This behaviour more or less resembles the metamagnetic behaviour of $FeCl_2$ and related substances, which are in fact also layer structures (Starr, 1940). Evidently there is some exchange at very low temperatures between the layers which are at a distance of 5·3 Å in α-$NaFeO_2$.

The authors are indebted to Prof. Dr E. F. Bertaut and Prof. Dr E. W. Gorter for their stimulating advice, and to Prof. Dr J. van Loef and Ir. Slegtenhorst for their help in performing and discussing the Mössbauer experiments.

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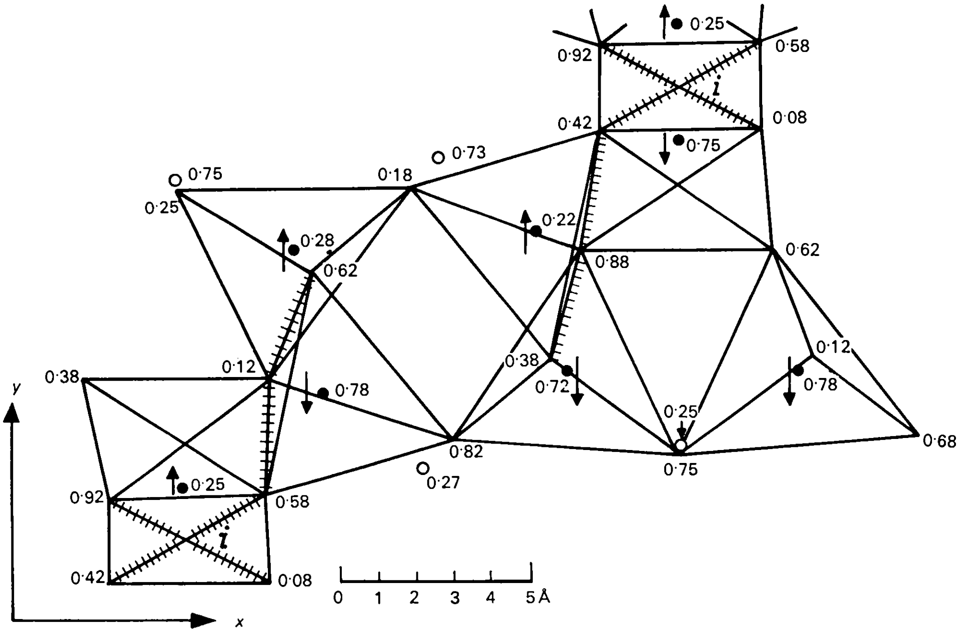

Fig. 3. Schematic projection along [001] of a part of the unit cell, with tentative spin structure. Filled circles: Fe^{3+}; open circles: Na^+; *i*: inversion centre. Oxygen at the corners of the octahedra and tetrahedra. The numbers are the *z* parameters of the atoms. Hatched lines represent shared edges.

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Acta Cryst. (1967). **22**, 771

X-ray Studies on the Partially Dehydrated Phases of some Paramagnetic Tutton Salts

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(*Received* 23 *May* 1966 *and in revised form* 18 *October* 1966)

Thermal dehydration study of some paramagnetic Tutton salts, $Co(KSO_4)_2.6H_2O$, $Cu(KSO_4)_2.6H_2O$ and $Cu(NH_4SeO_4)_2.6H_2O$, revealed the formation of lower hydrates, *viz.* $Co(KSO_4)_2.2H_2O$, $Cu(KSO_4)_2.2H_2O$ and $Cu(NH_4SeO_4)_2.2H_2O$. Powder photographs of these phases have been indexed by the methods of Ito and Lipson. $Co(KSO_4)_2.2H_2O$ has been found to be monoclinic with cell dimensions $a=7{\cdot}31$, $b=13{\cdot}25$, $c=5{\cdot}68$ Å, $\beta=97°35'$, and space group $P2_1/a$. The other two dihydrates are orthorhombic with cell-dimensions $a=14{\cdot}58$, $b=11{\cdot}90$, $c=10{\cdot}40$ Å for $Cu(KSO_4)_2.2H_2O$ and $a=14{\cdot}83$, $b=12{\cdot}39$, $c=10{\cdot}31$ Å for $Cu(NH_4SeO_4)_2.2H_2O$. The probable space groups in both cases are $Pmn2_1$ or $Pmnm$. The probable natures of the structures of these dihydrates are discussed.

In a programme of study of thermal dehydration of paramagnetic Tutton salts and X-ray study of the lower hydrates so obtained – some results of which have been reported earlier (Bhowmik, 1961; Ray, 1965) – the dehydration of the following six Tutton salts was studied: $Cu(KSO_4)_2.6H_2O$, $Cu(NH_4SeO_4)_2.6H_2O$, $Co(KSO_4)_2.6H_2O$, $Co(NH_4SO_4)_2.6H_2O$, $Ni(KSO_4)_2.6H_2O$, $Ni(NH_4SO_4)_2.6H_2O$. The dehydration curves for these six salts fall into two distinct categories. Those of the nickel salts and the cobalt ammonium salt show direct transformation to the anhydrous phase, but each of the three other salts shows the formation of a dihydrate at temperatures given in Table 1.

Table 1. *Dehydration data for the six Tutton salts*

Salt	Temperature of transition to Dihydrate phase	 Anhydrous phase
$Cu(KSO_4)_2.6H_2O$	50°C	115°C
$Cu(NH_4SeO_4)_2.6H_2O$	70	102
$Co(KSO_4)_2.6H_2O$	92	130
$Co(NH_4SO_4)_2.6H_2O$	—	78
$Ni(KSO_4)_2.6H_2O$	—	110
$Ni(NH_4SO_4)_2.6H_2O$	—	98

The lower hydrates were highly unstable, having a tendency to reconversion to the hexahydrate forms on exposure to the atmosphere. They could not be obtained as single crystals in spite of many attempts. Thus, information regarding the structure of these phases had to be obtained only from powder photographs. The samples for powder analysis were prepared in the following way: powdered hexahydrate was packed in a glass capillary with both ends open and heated above the transition temperature in an oven for 24 hours; this treatment was found sufficient for complete conversion into the dihydrate. The capillary was then sealed at both ends before removal from the oven so that risk of reconversion into the hexahydrate was avoided. X-ray photographs were taken with a Unicam 19 cm camera. The powder photographs thus obtained were ascertained to be due to the respective dihydrates only.

$Co(KSO_4)_2.2H_2O$

The pattern could not be indexed in terms of a cubic, tetragonal or hexagonal cell, and an attempt to apply Lipson's (1949) method failed, showing that the structure is probably either monoclinic or triclinic. However,

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