The Crystal Structure of a New Hexagonal Phase of AgFeO₂

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A new silver ferrite, δ-AgFeO₂, which is hexagonal with the space group $P6_3/mmc$ and the lattice dimensions, $a = 3\cdot039$ and $c = 12\cdot395$ Å, $Z = 2$, was synthesized hydrothermally. The structure has been determined by the heavy-atom method and refined by the block-diagonal least-squares approximation to a final R value of $0\cdot063$. The hexagonal cell consists of two double layers of oxygen atoms with two layers of silver atoms interleaved with the double layers. The basal plane containing the silver atom is a mirror plane of the structure. Silver atoms are linearly coordinated by oxygen atoms with Ag–O distance $2\cdot07$ Å, and ferric ions are surrounded octahedrally by oxygen atoms with Fe–O distance $2\cdot04$ Å.

Introduction

Two modifications have been known in silver ferrite; α- and β-AgFeO₂. α-AgFeO₂ was prepared from Ag₂O and ferric oxide or hydroxide in NaOH solution under hydrothermal conditions (Krause, Ernst, Gawrych & Kockay, 1936; Feitknecht & Moser, 1960). It is rhombohedral with the cell dimensions $a_{rh} = 6\cdot427$ Å and $\alpha = 27°22'$ (in the hexagonal description, $a = 3\cdot041$ and $c = 18\cdot55$ Å) (Croft, Tombs & England, 1964). According to Gessner (1968), β-AgFeO₂ was prepared by fusing β-NaFeO₂ in AgNO₃ melt. Although the crystal structures of these two modifications have not been determined by the single-crystal method, some speculations on the structures were given on the basis of the powder patterns. According to Feitknecht & Moser (1960), the structure of α-AgFeO₂ is similar to that of α-NaFeO₂ (the space group $R\bar{3}m$). Each ferric ion in the structure is octahedrally coordinated by oxygen atoms, and the octahedra form hexagonal layers which are interleaved with silver atoms. On the other hand, the ferric ion in β-AgFeO₂ is tetrahedrally coordinated by oxygen atoms (Gessner, 1968).

We have prepared a new hexagonal phase of AgFeO₂ hydrothermally. The present paper deals with the structure determination of the new AgFeO₂.

Experimental

Sample preparation and chemical analyses

The preparation involved the reaction of Ag₂O and α-Fe₂O₃ in Ba(OH)₂ solution under hydrothermal conditions. A silver crucible containing 1g of fine grained α-Fe₂O₃ powder dispersed in 20 ml of 1N Ba(OH)₂ solution was placed in a stainless steel pressure vessel which contained another 50 ml of 1N Ba(OH)₂ solution. The vessel was filled with 75 kg.cm⁻² of oxygen at room temperature by connecting it to a high pressure oxygen container, and then heated to 270 ± 5°C under 180–200 kg.cm⁻² for 40 hr, followed by quenching.

After the treatment, the silver crucible was found to

be coated with black Ag₂O. Shiny hexagonal platelets up to about 0·1 mm in diameter and about several microns thick were found in the solution. Many of the thinner platelets were ruby red in transmission. The crystalline product gave the single phase X-ray diffraction pattern of a hexagonal cell. Standard wet chemical analyses showed that the product is composed of 58·3 wt.% of Ag₂O and 41·3 wt.% of Fe₂O₃, and all iron ions in the structure are trivalent. This composition is very close to the calculated value for AgFeO₂ (59·1 wt.% of Ag₂O and 40·9 wt.% of Fe₂O₃).

The X-ray powder diffraction was made with Mn-filtered Fe $K\alpha$ ($\lambda = 1\cdot9373$ Å) radiation. The d-spacings, hkl indices and relative intensities for the observed lines are shown in Table 1. These diffraction data differ distinctly from those of α-AgFeO₂ (Croft *et al.*, 1963) and β-AgFeO₂ (Gessner, 1968). Thus, the product must be a new phase with the composition AgFeO₂, which we designate here δ-AgFeO₂.*

Crystal data

Silver ferrite, AgFeO₂
Hexagonal, space group $P6_3/mmc$
$a = 3\cdot039 \pm 0\cdot002$, $c = 12\cdot395 \pm 0\cdot005$ Å, $Z = 2$
$V = 99\cdot14 \pm 0\cdot05$ Å³
$D_m = 6\cdot37$, $D_x = 6\cdot55$ g.cm⁻³

The lattice constants were determined by the single-crystal method using eight high-angle reflexions recorded by Straumanis's method around the a axis with Cu $K\alpha_1$ radiation (1·54051 Å). The density was measured with a pycnometer. The measured value agreed with the calculated value with $Z = 2$.

Weissenberg photographs showed a systematic absence of hhl reflexions with l odd. Therefore, possible space groups were $P\bar{6}2c$, $P6_3mc$ and $P6_3/mmc$. A

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* Close relations exist between α-NaFeO₂ and α-AgFeO₂, and between β-NaFeO₂ and β-AgFeO₂, as described above. However, γ-NaFeO₂ is orthorhombic (Therry & Collongues, 1962) and has no relation to the new hexagonal AgFeO₂. It is, therefore, convenient to designate the new hexagonal silver ferrite as δ-AgFeO₂ instead of γ-AgFeO₂.

Table 1. *Powder diffraction data of* δ-$AgFeO_2$

d (Å)	I/I_o	h	k	l
6·20	30	0	0	2
3·10	100	0	0	4
2·574	45	1	0	1
2·423	25	1	0	2
2·219	14	1	0	3
2·066	14	0	0	6
1·805	20	1	0	5
1·625	16	1	0	6
1·549	16	0	0	8
1·520	14	1	1	0
1·475	4	1	1	2
1·469	12	1	0	7
1·364	12	1	1	4
1·309	4	2	0	1
1·224	2	1	1	6
1·220	2	1	0	9
1·162	2	2	0	5
1·121	6	1	0	10
1·116	2	2	0	6
1·085	12	1	1	8
1·056	2	2	0	7
1·036	10	1	0	11
1·033	16	0	0	12

centrosymmetric space group $P6_3/mmc$ was assumed, which was subsequently confirmed to be correct by the determination of the structure.

Intensity measurements

Three-dimensional intensities were measured with the equi-inclination type diffractometer, READ-1 (Sakurai, Ito & Iimura, 1970), up to the 5th layer around the a axis. The crystal was rotated in the ω-scan mode at a scanning speed of $0.5°.min^{-1}$. Mo $K\alpha$ radiation was used with a graphite monochromator. The crystal used for the measurements was a plate of approximately 70μ in diameter and 5μ in thickness. Altogether 141 crystallographically independent reflexions were collected. No absorption or extinction corrections were applied. After Lorentz and polarization corrections were applied, the intensities were put on a common scale using the equivalent reflexions on different layers. The relative scales of the six layers determined in this way were found at the later stage to be correct within 2%.

Determination of the structure

The unit-cell content is $Ag_2Fe_2O_4$; therefore, all the atoms must be on special positions. On the basis of the approximate systematic absences of $h,h+3n,l$ reflexions with l odd, silver atoms were considered to be on the special positions $2(c)$ or $2(d)$ in terms of the Wyckoff notation (*International Tables for X-ray Crystallography*, 1965). We put them on $2(c)$, since the two special positions are equivalent at a first choice. Approximate coordinates of the other atoms were obtained from a three-dimensional Fourier map using the phases based on the parameters of the silver atoms. The ferric ions and oxygen atoms were found to be on $2(a)$ and $4(f)$ respectively.

The structure was then refined by the block-diagonal least-squares approximation. Employing isotropic temperature factors for each atom, the R value was 0·088 after five cycles of the least squares. Subsequent anisotropic refinement gave an R of 0·064. Further refinement, taking into account the anomalous dispersion of silver and iron atoms, gave a final R of 0·063; however, no significant difference in atomic parameters was observed. The final positional and thermal parameters, and the comparison of the observed and calculated structure factors are listed in Tables 2 and 3.

Table 2. *Positional and thermal parameters for* δ-$AgFeO_2$

Values in parentheses are standard deviations.
The thermal parameters refer to the expression:

$$T = \exp\{-10^{-4} \cdot 2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^*)\}.$$

From symmetry considerations,

$$U_{22} = U_{11}, \quad U_{12} = \tfrac{1}{2}U_{11}, \quad \text{and} \quad U_{23} = U_{31} = 0.$$

	Position	x	y	z	U_{11}	U_{33}
Ag	(2c)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	84 (7)	54 (8)
Fe	(2a)	0	0	0	25 (14)	78 (16)
O	(4f)	$\frac{1}{3}$	$\frac{2}{3}$	0·0833 (0·0010)	49 (46)	31 (31)

The scattering factors for Ag^+ snd Fe^{3+} were taken from *International Tables for X-ray Crystallography* (1962). The scattering factors for O^{2-} were that of Tokonami (1965). All calculations were made on a FACOM 270 computer, with UNICS programs (Sakurai, Ito, Iwasaki, Watanabe & Fukuhara, 1967).

Results and discussion

The structure of δ-$AgFeO_2$, projected along the a and c axes, is shown in Fig. 1. The interatomic distances and angles are listed in Table 4.

Table 3. *Observed and calculated structure factors*

h	k	l	Fo	Fc		h	k	l	Fo	Fc		h	k	l	Fo	Fc		h	k	l	Fo	Fc
0	0	2	18	-23		0	2	5	46	44		0	4	14	16	18		1	3	2	28	28
		4	86	105				6	52	51				15	10	11				3	19	-13
		6	45	-52				7	41	-40		0	5	1	13	15				5	26	25
		8	74	81				9	26	26				2	16	18				6	31	30
		10	19	-18				10	34	35				5	14	15				7	24	-24
		12	74	73				11	31	-33				6	20	20				9	15	16
		14	15	-15				13	27	30				7	14	-14				10	22	23
		16	47	44				14	26	28		1	1	0	113	101				11	20	-21
		18	25	-22				15	18	-19				2	18	-16				13	18	20
		20	37	33				17	24	24				4	81	74				14	17	20
		22	13	-10				18	26	25				6	33	-32				15	11	-12
		24	36	32				19	22	-21				8	66	62				17	14	16
0	1	0	8	-9				21	15	13				10	14	-14		1	4	0	35	36
		1	77	-74				22	17	17				12	56	59				4	28	29
		2	73	69		0	3	0	64	61				14	10	-13				6	9	-10
		3	44	41				2	10	-10				16	38	38				8	25	27
		4	8	8				4	51	48				18	19	-19		2	2	0	54	52
		5	63	-62				6	21	-20		1	2	1	40	-37				2	7	-6
		6	66	69				8	43	43				2	41	39				4	43	41
		7	50	94				10	9	-9				3	27	25				6	18	-16
		9	29	-32				12	42	45				5	37	-34				8	35	37
		10	39	43				14	7	-8				6	43	41				10	8	-7
		11	37	40				16	27	30				7	35	32				12	38	40
		13	33	-35				18	13	-14				9	23	-21				16	23	27
		14	32	32				20	24	24				10	30	30		2	3	1	19	-20
		15	23	22		0	4	1	22	-22				11	29	28				2	21	22
		17	29	-28				2	25	25				13	24	-25				3	13	13
		18	30	22				3	16	15				13	24	24				5	18	-19
		19	25	24				5	22	-21				14	23	24				6	23	25
		21	16	-15				6	28	27				15	15	16				7	17	18
		22	21	18				7	20	21				17	20	-21				9	13	-13
		23	21	19				9	14	-14				18	22	23				10	18	19
0	2	1	51	48				10	20	21				19	18	19				11	15	16
		2	52	49				11	18	19				21	12	-11				13	14	-15
		3	34	-31				13	16	-17		1	3	1	26	24		3	3	0	28	30
		4	6	5																		

Table 4. *Interatomic distances and angles with standard deviations in parentheses*

Distances

Fe—O	2·04 (1) Å
Ag—O	2·07 (1)
O—O	3·039 (2)
O—O*	2·71 (2)

Angles

O—Ag—O	180·0 (0)°
O—Fe—O	96·6 (3)
O—Fe—O*	83·4 (3)
Ag-O—Fe	120·5 (3)
Fe—O—Fe	96·6 (3)

*Oxygen atoms in the adjacent layer.

The silver atom is linearly coordinated by two oxygen atoms along the c axis with the Ag–O distance of 2·07 (0·01) Å. The ferric ion, on the other hand, is coordinated by six oxygen atoms with a slightly distorted octahedral arrangement. The Fe–O distance is 2·04 (0·01) Å. Each octahedron shares edges with the adjacent six octahedra forming a hexagonal layer of octahedra, as shown in Fig. 2. Each oxygen atom is, in turn, surrounded tetrahedrally by one silver and three iron atoms.

The hexagonal layer of octahedra can be looked upon as an oxygen double layer containing relatively small ferric ions in it. From this point of view, the crystal structure of δ-AgFeO₂ can be described as consisting of silver layers sandwiched with oxygen double layers. The silver layer is a mirror plane of the structure. The spacing between the silver and oxygen layers is equal to the linear Ag–O distance of 2·07 (0·01) Å, and that between the two oxygen layers in a double layer is 2·06 (0·02) Å.

The O–O distance in the same oxygen layer is equal to the length of the a axis, 3·039 (0·002) Å, whereas that between the adjacent layers in a double layer is 2·71 (0·02) Å. The former corresponds to the octahedron edges not shared, and the latter to those shared by the adjacent octahedra. These O–O distances fall within the normal range usually found in similar oxygen frameworks (Pauling, 1960).

The Ag–O distance of 2·07 (0·01) Å found in the structure may be compared with that of 2·05 Å in Ag₂O (*National Bureau of Standards Monograph 25*, 1961) and 2·28 Å in AgCrO₂ (Hahn & de Lorent, 1957). In these crystals the silver atoms are also linearly coordinated by two oxygen atoms. According to Pauling (1960), silver as well as copper atoms may form two covalent bonds of the sp type with oxygen atoms. Hence, the Ag–O distance of 2·07 Å is in good agreement with 2·05 Å, the sum of covalent radii of Ag (1·39 Å) and O (0·66 Å), rather than with 2·66 Å, the sum of ionic radii of Ag^+ (1·26 Å) and O^{2-} (1·40 Å). On the other hand, the Fe–O distance of 2·04 (0·01) Å is in agreement with the sum, 2·04 Å, of the ionic radii of Fe^{3+} (0·64 Å) and O^{2-} (Pauling,

1960). These observations may suggest the existence of complex ions, $(AgO_2)^{3-}$, in the structure.

The unit cell of δ-AgFeO₂ may be considered as consisting of two hexagonal sub-units, which are related to each other by the twofold screw axis parallel to the c axis. Each subunit contains one formula unit of AgFeO₂. The dimensions of the sub-unit are 3·039 Å along the a axis, and 6·197 Å along the c axis. Similar but somewhat different structures are found in a group of rhombohedral oxides, $M^IM^{II}O_2$ (M^I: Ag, Cu, M^{II}: Fe, Cr) with the space group $R\bar{3}m$. The crystal of AgCrO₂, for instance, has the cell dimensions $a=$
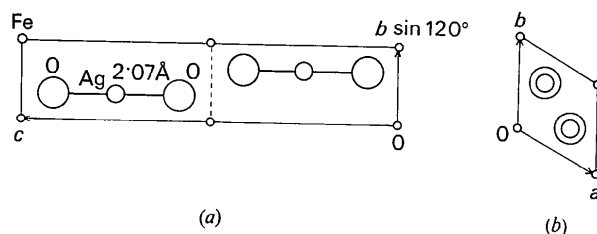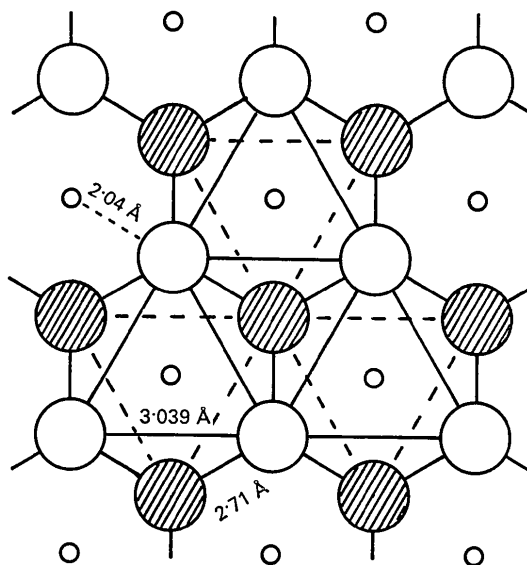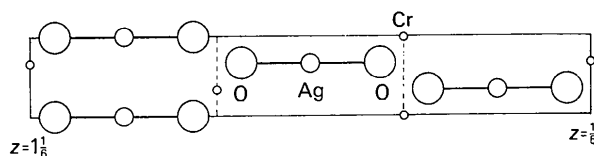

Fig. 1. Crystal structure of δ-AgFeO₂. (*a*) Projection along the a axis. (*b*) Projection along the c axis.

Fig. 2. Hexagonal layer of oxygen octahedra containing ferric ions. Oxygen atoms: large circle; ferric ions: small circle.

Fig. 3. Structure of hexagonal sub-units in AgCrO₂; projection along the a axis.

2·95 Å, $c=18·25$ Å and $Z=3$, in the hexagonal description (Hahn & de Lorent, 1957). The hexagonal unit cell consists of three hexagonal sub-units, which are related to each other by the threefold screw axis parallel to the c axis, as shown in Fig. 3. The dimensions of the sub-unit are 2·95 Å along the a axis, and 6·08 Å along the c axis. The structure of this sub-unit is quite similar to that of δ-AgFeO$_2$. The structures of CuFeO$_2$ (Soller & Thompson, 1935; Pabst, 1946) and CuCrO$_2$ (Dannhauser & Vaughan, 1955) are also analogous to that in AgCrO$_2$.

Although the structure of α-AgFeO$_2$ has not been determined, we can build a model structure of it, in which three sub-units of AgFeO$_2$ found in δ-AgFeO$_2$ are stacked along the c axis in a similar fashion as in AgCrO$_2$. The observed cell dimensions of α-AgFeO$_2$, $a=3·041$ and $c=18·55$ Å (Croft et $al.$, 1964), are in good agreement with those of the model structure, $a=3·039$ and $c=18·59$ Å.

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The Structure of Octammine-μ-amido-μ-hydroxodicobalt Disulfate Dihydrate*

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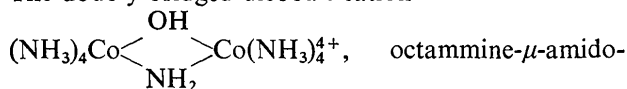Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91109, U.S.A.

The structures of two closely related compounds, octammine-μ-amido-μ-hydroxodicobalt disulfate dihydrate (the 'pure' compound) and the same compound with the hydroxo bridge partially substituted by chlorine (the 'mixed' compound), have been determined by X-ray diffraction techniques. The compounds form isostructural triclinic crystals: for the 'pure' compound, $a=9·066$ (4), $b=8·601$ (4), $c=6·977$ (3) Å, $\alpha=106·92$ (3), $\beta=111·72$ (4), and $\gamma=68·62$ (4)°. The observed density is 1·86 (2) g.cm^{-3} and that calculated for one formula weight in the unit cell is 1·848 (2) g.cm^{-3}. The space group is $P\bar{1}$; 1229 reflections were measured on a GE diffractometer and used to solve the structure. Refinement by full-matrix least-squares methods gave a final R index of 0·027. For the 'mixed' compound, $a=9·151$ (6), $b=8·633$ (6), $c=6·910$ (3) Å, $\alpha=106·66$ (7), $\beta=111·94$ (4), and $\gamma=68·95$ (9)°. The measured density is 1·88 (2) g.cm^{-3} and the calculated density 1·853 (2) g.cm^{-3}. The structure was solved using 1106 reflections and refined to an R index of 0·036. In both compounds, the cation is disordered about a center of symmetry; bond distances and angles in the cation and the sulfate groups are normal.

Introduction

The doubly-bridged dicobalt cation

$$(NH_3)_4Co\underset{NH_2}{\overset{OH}{<>}}Co(NH_3)_4^{4+}, \quad \text{octammine-}\mu\text{-amido-}$$

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μ-hydroxodicobalt^{4+}, is obtained from Vortmann's (1885) sulfate and is a convenient starting material for the preparation of many other di-bridged dicobalt ions. The amide bridge is difficult to break, but the hydroxo bridge can be easily hydrolyzed, or substituted to give other di-bridged ions. The structure of this ion has not yet been reported. We intended to determine the structure several years ago, but instead of preparing the correct material, we made the μ-amido, μ-chloro compound (Barro, Marsh & Schaefer, 1970). We have now