The results of this investigation, taken alone, are insufficient to explain unambiguously the mechanism of the hydrolysis of bismuth(III) nitrate, the possible ways of condensation of the $[Bi_6(OH)_{12}]^{6+}$ species and the existence of various bismuth basic nitrates. More structural and chemical information is needed for the solution of this problem. It is hoped that the structural analysis of the first hydrolysis product $BiONO_3.H_2O$, which is in progress, as well as that of $2BiONO_3.H_2O$, will give more decisive answers concerning the hydrolysis of bismuth salts.

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Sc₃Co, a New Structure Type Related to Fe₃C and Re₃B by Periodic Unit-Cell Twinning

BY BERNARD CHABOT AND ERWIN PARTHÉ

Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 Quai Ernest Ansermet, CH-1211 Genève 4, Switzerland

Sc₃Co, orthorhombic, *Pnma*, $a = 13 \cdot 102$ (9), $b = 8 \cdot 624$ (6), $c = 5 \cdot 829$ (3) Å, $Z = 8$, $D_x = 3 \cdot 91_3$ g cm⁻³, μ(Mo $K\alpha$) = 107 cm⁻¹. Least-squares refinement gave $R = 0 \cdot 048$ for 535 independent diffractometer data which were corrected for absorption. The structure is characterized by trigonal prisms of Sc atoms which are centred by Co atoms. Centred trigonal prisms are also found in the Fe₃C and Re₃B structure types. Using the concept of periodic unit-cell twinning, the point positions of all three structure types can be derived. Fe₃C is based on a hexagonal, and Re₃B on a cubic close-packed base structure, while Sc₃Co derives from a close-packed base structure with mixed stackings corresponding to the atom arrangement in the Nd structure type.

Introduction

The compound Sc₃Co was prepared by the arc-melting technique from elements of high purity (Sc 99·95%, Co 99·99%). A single trigonal prismatic crystal (base: 0·14 × 0·12 × 0·12 mm, height: 0·14 mm) was isolated from the crushed melt. Systematic absences in precession photographs showed the space group to be either $Pn2_1a$ or $Pnma$ (0*kl* with $k + l = 2n + 1$ and *hk*0 with $h = 2n + 1$). Intensities of 588 independent reflexions out to a limit of $\sin \theta/\lambda = 0 \cdot 702$ Å⁻¹ were measured with graphite-monochromated Mo $K\alpha$

radiation on a Philips PW 1100 automatic four-circle diffractometer in the θ–2θ scan mode. Cell parameters were determined from least-squares refinement of the 2θ values of 30 reflexions using the program *PARAM* (XRAY system, 1976). An empirical absorption correction, based on the comparison of several sets of equivalent reflexions, was applied with the program *CAMEL JOCKEY* (Flack, 1977). The structure was solved by direct methods in the space group *Pnma*. The phases of the 230 reflexions with $|E| > 1.2$ were determined with *SINGEN* and *TANGEN* (XRAY system, 1976). Positional and isotropic thermal parameters refined satisfactorily with the least-squares program *CRYLSQ* (XRAY system, 1976). Relativistic Hartree–Fock scattering factors were taken from Cromer & Mann (1968) and anomalous dispersion corrections from *International Tables for X-ray Crystallography* (1974). The R value ($R = \sum |\Delta F|/\sum |F_o|$) with isotropic thermal parameters was 0.048 for 535 nonequivalent reflexions with $|F_o| > 3\sigma(F_o)$. The final positional and isotropic thermal parameters are listed in Table 1 and bond lengths in Table 2.*

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* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33714 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2 shows that certain Sc—Co distances are very short. For this reason a refinement in $Pn2_1a$ was performed but neither the R value nor the contact distances changed significantly. These short distances are not unusual however: similar phenomena can be found, *e.g.* Zr₃Co (Kripyakevich, Marvik & Burnasova, 1970), Y₃Rh₂ (Moreau, Paccard & Parthé, 1975), Y₈Co₅ (Moreau, Paccard & Parthé, 1976) and Y₃Ni₂ (Le Roy, Moreau, Paccard & Parthé, 1977).

Discussion

Information on the Sc-rich part of the Sc—Co phase diagram is limited. The existence of the following phases has been reported: ScCo with CsCl structure type (Aldred, 1962), Sc₂Co with CuAl₂ type (Aldred, 1962) and Sc₃Co supposedly isostructural with Zr₃Co (Markiv, Pet'kov, Gavrilenko & Beryavina, 1974). According to Kripyakevich. Markiv & Burnasova (1970) Zr₃Co crystallizes with the Re₃B type structure. To verify that Sc₃Co is isostructural with Re₃B a simulated powder pattern was calculated for Sc₃Co with the *LAZY PULVERIX* program (Yvon, Jeitschko & Parthé, 1977) assuming the Re₃B structure type. As the comparison of a powder diagram with the calculated one did not show good agreement with respect to

Table 1. *Idealized and experimental positional parameters for* Fe₃C, Sc₃Co, *and* Re₃B

For Sc₃Co the isotropic temperature factors are expressed as $T = \exp[-2\pi^2 \times 10^{-2} U(2 \sin \theta/\lambda)^2]$. E.s.d.'s are given in parentheses.

Stacking notation of the untwinned segment of the base structure		Idealized point positions			Experimental point positions			Isotropic temperature factors U (Å²)	Reference
		x	y	z	x	y	z		
			Structure type Fe₃C (*Pnma*)						(a)
$(h)_2$	4Fe(1) in 4(c)	1/22 = 0.045	1/4	1/6 = 0.166	0.036	1/4	0.148		
	8Fe(2) in 8(d)	4/22 = 0.182	1/12 = 0.083	2/3 = 0.666	0.186	0.063	0.672		
	4C in 4(c)	0.384	1/4		0.93	0.390	1/4	0.950	
			Structure type Sc₃Co (*Pnma*)						(b)
$(hc)_2$	4Sc(1) in 4(c)	31/88 = 0.352	1/4	5/12 = 0.416	0.3540 (1)	1/4	0.4564 (4)	1.10 (4)	
	4Sc(2) in 4(c)	9/88 = 0.102	1/4	1/4	0.1108 (2)	1/4	0.2062 (4)	1.20 (4)	
	8Sc(3) in 8(d)	69/88 = 0.784	1/12 = 0.083	7/12 = 0.583	0.7874 (1)	0.0649 (2)	0.5905 (2)	1.17 (3)	
	8Sc(4) in 8(d)	47/88 = 0.534	1/12 = 0.083	3/4	0.5342 (1)	0.0607 (2)	0.7539 (3)	1.22 (3)	
	4Co(1) in 4(c)	0.435	1/4	0.01	0.4417 (1)	1/4	0.0570 (3)	1.37 (3)	
	4Co(2) in 4(c)	0.185	1/4	0.66	0.1782 (1)	1/4	0.6279 (3)	1.58 (3)	
			Structure type Re₃B (*Cmcm*)						(c)
$(c)_3$	4Re(1) in 4(c)	0	9/22 = 0.409	1/4	0	0.4262	1/4		
	8Re(2) in 8(f)	0	3/22 = 0.136	1/12 = 0.083	0	0.1345	0.0620		
	4B in 4(c)	0	0.73	1/4	0	0.744	1/4		

References: (a) Herbstein & Smuts (1964). (b) This work. (c) Aronsson, Backman & Rundqvist (1960).

Table 2. *Interatomic distances in* Sc_3Co *up to* 3·80 Å

The Sc atoms forming the surrounding trigonal prisms are marked with asterisks.

Sc(1)–Co(2)	2·510 (3)	Sc(2)–Co(1)	2·610 (3)
–Co(1)	2·596 (3)	–Co(2)	2·612 (3)
–Co(1)	3·685 (3)	–Co(2)	3·485 (3)
–2Sc(2)	3·206 (2)	–2Sc(3)	3·249 (2)
–2Sc(4)	3·291 (2)	–2Sc(4)	3·296 (3)
–2Sc(3)	3·299 (2)	–2Sc(4)	3·297 (2)
–2Sc(4)	3·354 (2)	–2Sc(3)	3·300 (2)
–Sc(2)	3·496 (3)	–Sc(1)	3·496 (3)
–Sc(2)	3·504 (3)	–Sc(1)	3·504 (3)
–2Sc(3)	3·671 (2)	–2Sc(4)	3·684 (3)
Sc(3)–Co(2)	2·700 (2)	Sc(4)–Co(2)	2·589 (2)
–Co(1)	2·716 (2)	–Co(1)	2·693 (2)
–Co(2)	3·033 (2)	–Co(1)	2·914 (2)
–Sc(3)	3·193 (2)	–Sc(4)	3·183 (2)
–Sc(1)	3·206 (2)	–Sc(3)	3·238 (2)
–Sc(4)	3·238 (2)	–Sc(4)	3·264 (2)
–Sc(2)	3·249 (2)	–Sc(4)	3·266 (2)
–2Sc(3)	3·272 (2)	–Sc(1)	3·291 (2)
–Sc(1)	3·299 (3)	–Sc(2)	3·296 (3)
–Sc(2)	3·300 (2)	–Sc(2)	3·297 (2)
–Sc(4)	3·359 (2)	–Sc(1)	3·354 (3)
–Sc(4)	3·451 (2)	–Sc(3)	3·359 (2)
–Sc(1)	3·671 (2)	–Sc(3)	3·451 (2)
		–Sc(2)	3·684 (3)
Co(1)–Co(2)	3·281 (3)	Co(2)–Co(1)	3·281 (3)
–Sc(1)*	2·596 (3)	–Sc(1)*	2·510 (3)
–Sc(2)*	2·610 (3)	–2Sc(4)*	2·589 (2)
–2Sc(4)*	2·693 (2)	–Sc(2)*	2·612 (3)
–2Sc(3)*	2·716 (2)	–2Sc(3)*	2·699 (2)
–2Sc(4)	2·914 (2)	–2Sc(3)	3·033 (2)
–Sc(1)	3·685 (3)	–Sc(2)	3·485 (3)

intensities and line positions it was obvious that Re_3B and Sc_3Co were not of the same type. The present study demonstrates that Sc_3Co crystallizes with a new structure type.

A drawing of the Sc_3Co structure is presented in Fig. 1. The structure is characterized by trigonal prisms of Sc atoms which are centred by Co atoms. From the interatomic distances (Table 2) one can conclude that the trigonal prisms are not regular but deformed.

Centred trigonal prisms are also found in two other structure types with the same composition: Fe_3C (DO_{11} type) and Re_3B (Aronsson, Backman & Rundqvist, 1960). Since Sc_3Co, Fe_3C and Re_3B are built up exclusively of trigonal prisms the trigonal-prism linkage coefficient LC (Parthé & Moreau, 1977) must be 2. Table 3 shows the calculation of the trigonal-prism linkage coefficients for these three structure types.

Structures with centred trigonal prisms have only recently been derived from periodic unit-cell twinning of close-packed base structures (Andersson & Hyde, 1974; Hyde, Bagshaw, Andersson & O'Keeffe, 1974). Following the procedure and notation used by Parthé (1976), the twinning of the base structure along every third possible twin plane and occupation of the trigonal-prismatic holes by the alloying partner must lead to a structure of composition R_3T. It is not unreasonable to expect that the difference between Fe_3C, Sc_3Co and Re_3B is to be found in the base structure. It has already been shown by Andersson & Hyde (1974) that Fe_3C

Table 3. *Tables for the calculation of the linkage coefficient in* R_3T *structures built up of centred trigonal prisms*

Fe_3C *Pnma*

	Fe(1) in 4(c)	Fe(2) in 8(d)	N*
C in 4(c)	2	4	6
p†	2	$\frac{4}{8} \times 4 = 2$	

LC = (4 × 2 + 8 × 2)/12 = 2
$R_6T_{LC} = R_6T_2 \equiv R_3T$

Sc_3Co *Pnma:* all Co atoms in 4(c)

	Sc(1) in 4(c)	Sc(2) in 4(c)	Sc(3) in 8(d)	Sc(4) in 8(d)	N
Co(1)	1	1	2	2	6
Co(2)	1	1	2	2	6
p	2	2	$\frac{4}{8} \times 4 = 2$	$\frac{4}{8} \times 4 = 2$	

LC = (4 × 2 + 4 × 2 + 8 × 2 + 8 × 2)/24 = 2
$R_6T_{LC} = R_6T_2 \equiv R_3T$

Re_3B *Cmcm*

	Re(1) in 4(c)	Re(2) in 8(f)	N
B in 4(c)	2	4	6
p	2	$\frac{4}{8} \times 4 = 2$	

LC = (4 × 2 + 8 × 2)/12 = 2
$R_6T_{LC} = R_6T_2 \equiv R_3T$

* N is the number of R atoms around each T atom.
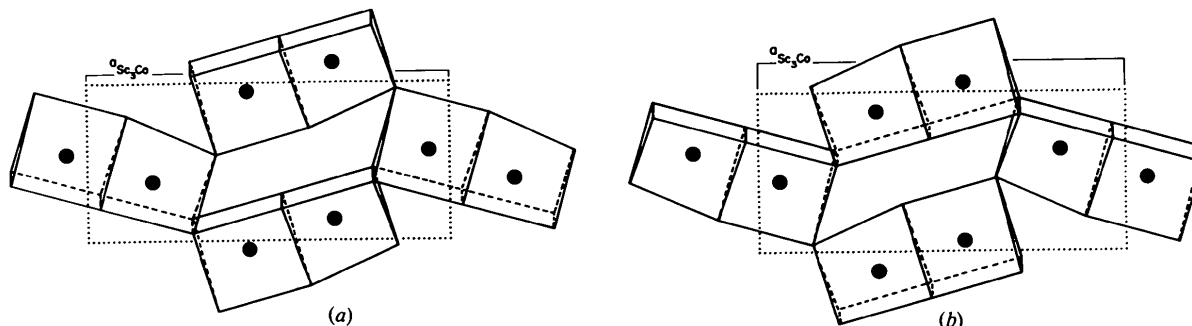† p is the number of prisms in which each R atom participates.

Fig. 1. Arrangement of the Co-centred trigonal Sc prisms in Sc_3Co. (a) Co atoms at $y = \frac{1}{4}$ and (b) Co atoms at $y = \frac{3}{4}$. The drawing represents a |010| projection, which has however been rotated through 10° around the long a axis to give a better perspective to the trigonal prisms.
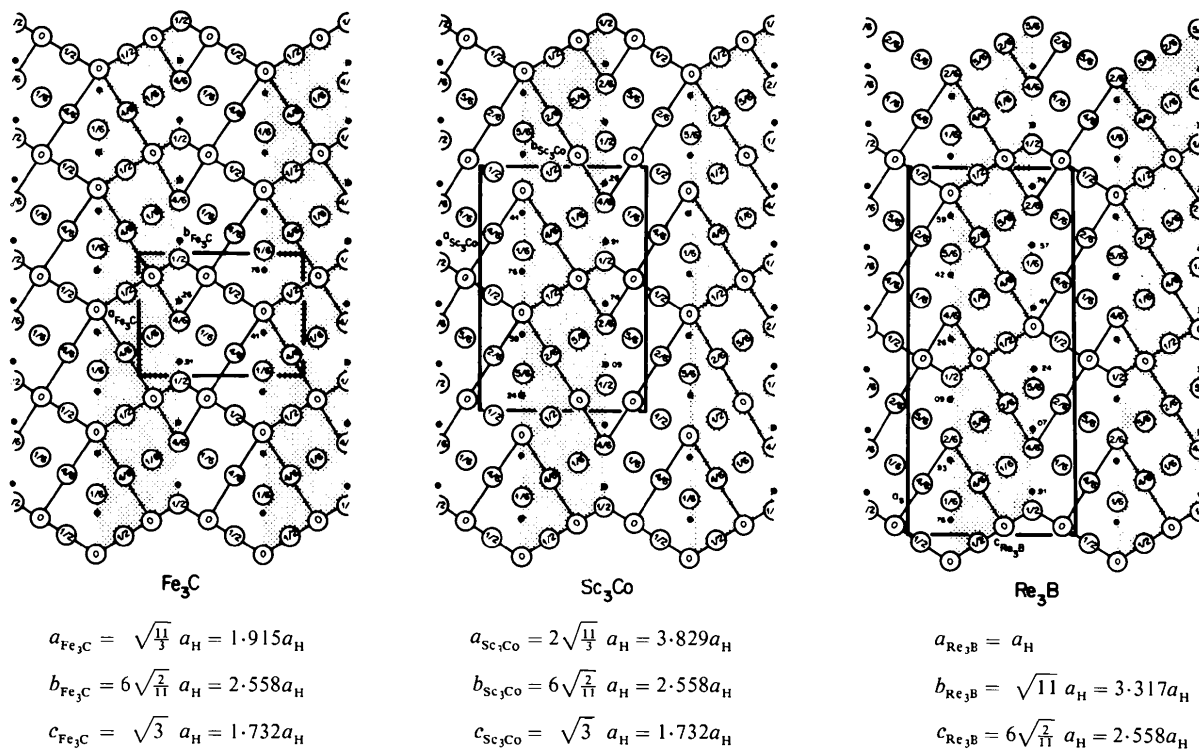
$$a_{Fe_3C} = \sqrt{\tfrac{11}{3}}\, a_H = 1.915a_H$$

$$b_{Fe_3C} = 6\sqrt{\tfrac{2}{11}}\, a_H = 2.558a_H$$

$$c_{Fe_3C} = \sqrt{3}\, a_H = 1.732a_H$$

$$a_{Sc_3Co} = 2\sqrt{\tfrac{11}{3}}\, a_H = 3.829a_H$$

$$b_{Sc_3Co} = 6\sqrt{\tfrac{2}{11}}\, a_H = 2.558a_H$$

$$c_{Sc_3Co} = \sqrt{3}\, a_H = 1.732a_H$$

$$a_{Re_3B} = a_H$$

$$b_{Re_3B} = \sqrt{11}\, a_H = 3.317a_H$$

$$c_{Re_3B} = 6\sqrt{\tfrac{2}{11}}\, a_H = 2.558a_H$$

Fig. 2. The Fe₃C, Sc₃Co and Re₃B structures derived by periodic unit-cell twinning from different close-packed base structures. After adding to the numerical values shown in the drawings ($\tfrac{2}{3}$ for Fe₃C and $\tfrac{1}{4}$ for Sc₃Co) the atom arrangements correspond to the idealized positional parameters listed in Table 1. Except for the z values, the point positions of Re₃B (Table 1) cannot be read directly from the drawing. It will be necessary first to transform the given supercell – as demonstrated for the CrB type (Parthé, 1976) – to the conventional Re₃B cell for which the a_{Re_3B} axis is parallel to the prism columns (inclined by 16·78° with respect to the a_s axis of the supercell). To obtain the point positions as given in Table 1 one has to read the supercell point positions x_s, y_s, z_s from the drawing and then transform them according to $x_{Re_3B} = \tfrac{11}{2}x_s + \tfrac{1}{2}y_s - \tfrac{1}{8}$, $y_{Re_3B} = -\tfrac{1}{2}x_s + \tfrac{1}{2}y_s - \tfrac{1}{8}$ and $z_{Re_3B} = z_s$. The corresponding unit-cell dimensions for the three R_3T structure types are given in the lower part of the figure. The values are normalized to a_H which corresponds to the closest distances between atoms in the close-packed base structures. For an untwinned segment in the drawings, a_H is the shortest distance between two atoms at the zero level or on the zero and one-half levels.

Table 4. *List of different structure types with centred trigonal prisms which can be derived using the concept of periodic unit-cell twinning*

Close-packed base structure						
Trivial name	Stacking notation	R_3T	R_5T_2	R_2T	R_3T_2	RT
Mg	$(h)_2$	Fe₃C	Mn₅C₂			
Sm	$(hhc)_3$					FeB
–	$(hhhhcc)_3$					TbNi(l.t.)*
Nd	$(hc)_2$	Sc₃Co				
–	$(hcc)_2$					TbNi(h.t.)*
Cu	$(c)_3$	Re₃B		(Ni₂Si), Ge₂Os	(Dy₃Ni₂)	CrB

* Low- and high-temperature modifications of TbNi.

can be derived from a hexagonal, and Re₃B from a cubic close-packed base structure. Sc₃Co can also be derived from a close-packed base structure but with mixed stackings corresponding to the atom arrange-

ment in the Nd structure. Fig. 2 presents the three structure types with the twin planes perpendicular to the plane of the paper. For further clarity the untwinned segments of the base structures have been alternately

stippled or left clear. The idealized unit-cell ratios are listed in the lower part of Fig. 2. Table 1 compares idealized point positions with experimental point positions for all three structure types. Table 4 lists all the different structure types built up of centred trigonal prisms which can be derived using the concept of periodic unit-cell twinning of close-packed base structures. The different stackings of the close-packed base structures are denoted using Jagodzinski–Wyckoff symbols (Jagodzinski, 1954a,b). Twelve structure types can at present be derived using this concept; however, for those enclosed in parentheses only a very idealized version can be obtained.

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The Space Group and Structure of α-K₂SO₄

By A. J. van den Berg and F. Tuinstra

Laboratorium voor Technische Natuurkunde, Technische Hogeschool, Lorentzweg 1, Delft, The Netherlands

The structure of the high-temperature form of K_2SO_4 was solved from powder diffraction data at 630°C. The space group appears to be $P6_3/mmc$, with $a = 5·90$ (2), $c = 8·11$ (3) Å and $Z = 2$. The structure was refined with a simplex method from 50 powder diffraction lines. The structure is disordered: For a SO_4^{2-} tetrahedron two orientations are possible, in which a S—O direction is pointing either along the positive c axis or in the opposite direction. The anions are evenly distributed among these two orientations. The structure is closely related to that of the low-temperature form.

Introduction

Two modifications of K_2SO_4 are known: β-K_2SO_4 is stable below 587°C and α-K_2SO_4 above. The structures of both forms have played the roles of structure models for a series of compounds of the type A_2BX_4. The structure of the β form is well established (Robinson, 1958; McGinnety, 1972).

Surprisingly, a complete structure analysis of α-K_2SO_4 has never been reported. Even the choice of

space group for α-K_2SO_4 is controversial. On the basis of X-ray powder data Pannetier (1966) proposed the space group $P\bar{3}m1$. Later, Eysel & Hahn (1970) proposed a hexagonal structure model for α-K_2SO_4 and its isomorphs; in this model the SO_4 tetrahedra are all oriented with a S—O radius in the same sense along the c axis; the corresponding space group is $P6_3mc$. Iwai, Sakai & Watanabe (1973) confirmed this structure using a high-temperature Weissenberg technique. Eysel (1971) showed the space group $P\bar{3}m1$ to be highly