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The Orthorhombic Structure of Y_3Co_2, a Shift Structure Variation of the Monoclinic Dy_3Ni_2 Type

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Y_3Co_2 crystallizes with a new orthorhombic structure type. Space group *Pnnm* (No. 58); $a=12{\cdot}248$, $b=9{\cdot}389$, $c=3{\cdot}975$ Å; $Z=4$, $D_x=5{\cdot}58$ g cm^{-3}, F.W. 384·58, $F(000)=684$, μ(Mo $K\alpha$)$=426$ cm^{-1}, $R=0{\cdot}10$. The structures of Y_3Co_2 and the earlier determined Dy_3Ni_2 are shift structure variants. Both structures are characterized by infinite bands formed by joining four infinite trigonal prism columns. The arrangement of these bands is, however, different in the two structure types. Slicing one of the structure types in blocks of equal size and shifting them with respect to one another leads to an atom arrangement characteristic of the other structure type.

Introduction

The published data for the binary phase diagram of Y and Co near 37 at.% Co is contradictory.

Buschow (1971) reported the existence of a phase Ln_xCo with 37 at.% Co for Ln = Gd, Dy, Ho, Er and Y. Schweizer (1972) determined the structure of $Ho_{12}Co_7$ (monoclinic, $P2_1/b$, $a=9{\cdot}30$, $b=13{\cdot}85$, $c=11{\cdot}16$ Å, $\beta=144°$) which composition corresponds to 37 at.% Co. Ray (1974) published a phase diagram of of the Y–Co system due to Strnat, Ostertag, Adams & Olson (1965) in which the Y_xCo phase mentioned by Buschow does not appear. Thermoanalytical and metallographic examinations do not give a stoichiometry as precise as do single-crystal X-ray structure determinations.

The purpose of this paper is to present the results of our single-crystal structure determination for this phase of which the composition is Y_3Co_2 or 40 at.% Co.

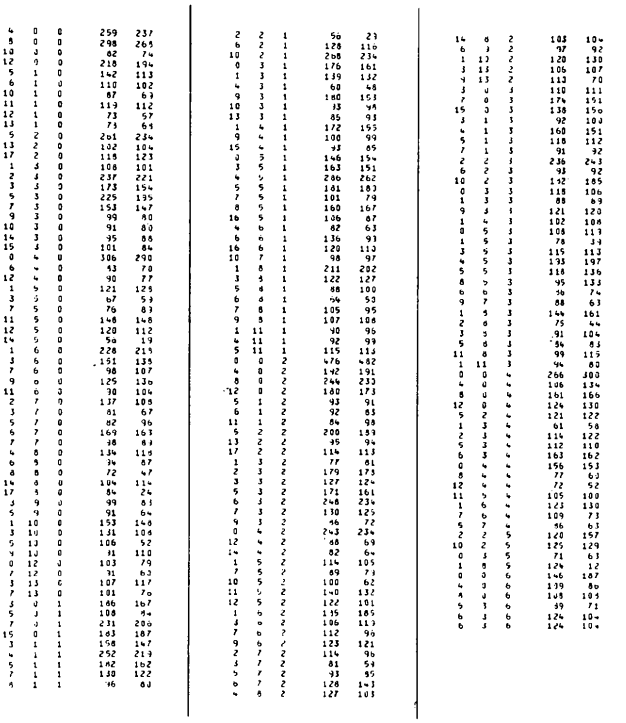
Experimental

Yttrium of 99·9% and cobalt of 99·99% purity were used to prepare the samples studied in this investigation. The constituents in proportions ranging from 35 to 40 at.% Co were induction-melted in an alumina crucible under argon atmosphere. Needle-shaped single crystals were directly isolated from the crushed melt. Preliminary Weissenberg and precession photographs showed the crystals to be orthorhombic with space group *Pnnm* or *Pnn*2. Lattice constants and intensities were measured with graphite-monochromated Mo $K\alpha$ radiation and a Philips PW 1100 computer-controlled four-circle goniometer. The cell parameters are: $a=12{\cdot}248$ (8), $b=9{\cdot}389$ (6) and $c=3{\cdot}975$ (3) Å.

The intensities of 190 non-equivalent observed reflexions ($I>2\sigma$) were recorded out to a limit of 0·7 Å^{-1} and all were used in the structure determination (see Table 1).

Table 1. *Observed and calculated structure factors for* Y_3Co_2

Reading from left to right the columns contain the values *h*, *k*, *l*, $|F_o|$ and $|F_c|$.



The preparation of this phase with 40 at.% Co is not straightforward. In an induction furnace with slow cooling, this phase (I) was obtained with an initial

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stoichiometry of 37 at. % Co. With samples containing an initial 40 at. % Co another phase (II) appears which is neither Y_4Co_3 (Lemaire, Schweizer & Yakinthos, 1969) nor isotypic with $Ho_{12}Co_7$ (Schweizer, 1972). In an arc furnace, only the second phase (II), yet unidentified, was obtained. In the arc-melting technique the sample is quenched, so it may be concluded that Y_3Co_2 is a low-temperature phase and that the unknown phase (II) contains about 40 at. % Co. For verification, a sample of the low-temperature phase, obtained by induction melting and well characterized by a Guinier photograph, was arc melted. It was found that phase I disappears completely and the Guinier film only shows the lines corresponding to phase II.

Structure determination

The volume of the cell together with the space-group restrictions indicates that there are four formula units of Y_3Co_2 per cell. A Patterson map showed peaks only on the $P(x,y,0)$ and $P(x,y,\frac{1}{2})$ sections. This observation is due to the fact that the c parameter is so small that atoms can only be located on planes at $z=0$ or $z=\frac{1}{2}$ assuming the centrosymmetric space group *Pnnm*.

From the location of Patterson peaks various trial structures could be postulated for the 12Y atoms alone. However, only one of these models refined satisfactorily with the program *STEPRF* (X-RAY System, 1972). From an electron-density map it was possible to place eight Co atoms in two different sites. All positional and isotropic thermal parameters refined satisfactorily with the least-squares program *CRYLSQ* (X-RAY system, 1972). Hartree–Fock scattering factors were used. No anomalous dispersion and absorption corrections were considered.

The R ($\sum|\Delta F|/\sum|F_o|$) index calculated with 190 observed reflexions was 0·10. The final positional and thermal parameters are listed in Table 2. Coordination distances are given in Table 3. As this structure is of a new type a listing of the low-angle reflexions with corresponding intensities for X-ray powder diagram identification is given in Table 4.

Table 2. *Least-squares atomic parameters for* Y_3Co_2 *with e.s.d.'s in parentheses*

Isotropic temperature factor is exp $[-2\pi^2 \times 10^{-2} U(2 \sin \theta/\lambda)^2]$. Space group *Pnnm*. All atoms in equipoint 4(*g*).

	x	y	z	U (Å)^2
Y(1)	0·128 (1)	0·193 (1)	0	0·7 (3)
Y(2)	0·387 (1)	0·373 (2)	0	0·6 (3)
Y(3)	0·137 (1)	0·574 (2)	0	0·6 (3)
Co(1)	0·269 (2)	0·860 (2)	0	0·3 (4)
Co(2)	0·462 (2)	0·883 (3)	0	0·8 (4)

Discussion

A projection of the Y_3Co_2 structure along the short c axis is shown on the left-hand side of Fig. 1. Four columns of Co-centered trigonal rare-earth prisms are joined to form a band. The complete structure consists of such four-column bands aligned parallel to **c**. The same structural features are found in the structure of Dy_3Ni_2 (Moreau, Paccard & Parthé, 1974), shown on the right-hand side of Fig. 1.

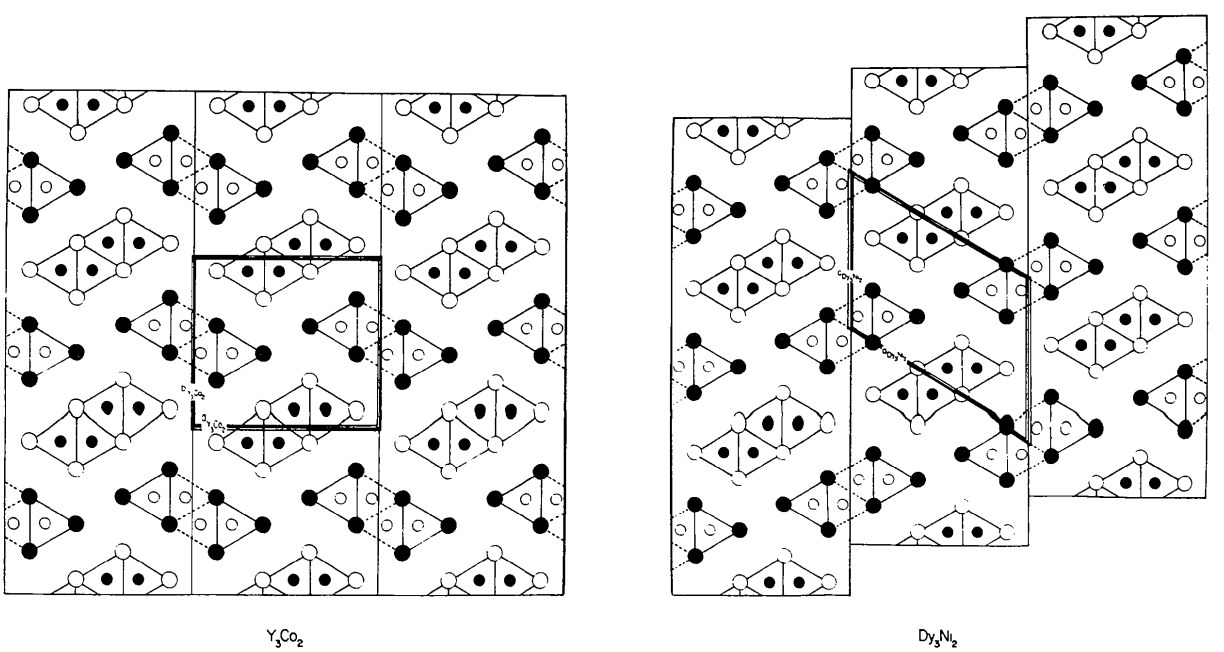

Fig. 1. Projections of orthorhombic Y_3Co_2 along **c** and monoclinic Dy_3Ni_2 along **b**. Full black circles in 0 and white circles in $\frac{1}{2}$. Large circles represent Y or Dy and small circles Co or Ni atoms. Dy_3Ni_2 can be derived from Y_3Co_2 by shifting slabs common to both structures.

Table 3. *Coordination distances in* Y_3Co_2 (Å)

Y(1)–2Co(1)	2·83	Y(3)–2Co(2)	2·94
2Co(2)	2·89	2Co(2)	2·95
Y(3)	3·57	2Co(1)	3·05
Co(1)	3·57	Co(1)	3·14
Y(2)	3·59	2Y(2)	3·45
2Y(2)	3·60	Y(1)	3·57
2Y(2)	3·61	Y(2)	3·59
2Y(3)	3·67	Y(3)	3·63
		2Y(1)	3·67
Y(2)–2Co(1)	2·76	Co(1)–Co(2)	2·37
Co(2)	3·03	2Y(2)	2·76
2Y(3)	3·45	2Y(1)	2·83
Y(1)	3·59	2Y(3)	3·05
Y(3)	3·59	Y(3)	3·14
2Y(1)	3·60	Y(1)	3·57
2Y(1)	3·61		
Y(2)	3·65		
		Co(2)–Co(1)	2·37
		Co(2)	2·39
		2Y(1)	2·89
		2Y(3)	2·94
		2Y(3)	2·95
		Y(2)	3·03

Table 4. *Calculated powder data for* Y_3Co_2 *for* Cr $K\alpha$ *radiation* ($\lambda = 2{\cdot}29092$ Å)

Intensity data calculated with point positions obtained from single-crystal data. $I = mF^2(1+\cos^2 2\theta)/\sin^2\theta \,.\, \cos\theta$ is normalized to the strongest reflexion having intensity 1000.

h k l	$\sin^2\theta$	Intensity	*h k l*	$\sin^2\theta$	Intensity
1 1 0	23·63	68·2	0 3 1	217·08	80·5
2 0 0	34·99	3·7	3 2 1	221·38	2·5
2 1 0	49·87	2·1	1 3 1	225·83	53·8
0 2 0	59·54	0·1	5 1 0	233·54	35·9
1 2 0	68·28	3·9	4 1 1	237·95	187·2
1 0 1	91·87	5·2	0 4 0	238·14	138·9
3 1 0	93·60	2·9	1 4 0	246·89	1·1
2 2 0	94·52	5·1	2 3 1	252·07	41·4
0 1 1	98·01	4·3	2 4 0	273·13	0·3
1 1 1	106·75	10·2	4 3 0	273·90	5·1
2 1 1	132·99	0·2	5 2 0	278·20	151·6
3 2 0	138·25	0·0	4 2 1	282·60	0·0
4 0 0	139·94	140·4	3 3 1	295·80	0·0
1 3 0	142·70	29·9	5 0 1	301·78	7·0
1 2 1	151·41	4·1	6 0 0	314·87	0·7
4 1 0	154·83	2·4	5 1 1	316·67	90·5
3 0 1	161·84	124·5	3 4 0	316·86	0·4
2 3 0	168·94	100·1	6 1 0	329·75	18·4
3 1 1	176·72	125·9	1 4 1	330·01	64·8
2 2 1	177·65	1000·0	0 0 2	332·49	190·8
4 2 0	199·48	0·7	5 3 0	352·62	43·6
3 3 0	212·67	110·2			

The Y_3Co_2 and Dy_3Ni_2 structure types are shift structure variants and are geometrically related in similar fashion to the CrB, FeB and TbNi (Hohnke & Parthé, 1966; Lemaire & Paccard, 1970), or the AlB_2 and $ThSi_2$ (Parthé, 1967) or the CeAl and DyAl structure types (Bècle & Lemaire, 1967).

To demonstrate the geometrical relationship between the two types it is useful to consider idealized structure types where the basis planes of the trigonal prisms are equilateral triangles of length g. The relative cell dimensions and atom positions of the idealized Y_3Co_2 and the idealized Dy_3Ni_2 structure type are given in Table 5. Consider two neighbouring idealized Y_3Co_2 unit cells with a common (100) face. As shown in Fig. 1, a shift of one cell by g in the **b** direction leads to the same atom arrangement as in the idealized monoclinic Dy_3Ni_2 structure type.

Table 5. *Theoretical structure data for the idealized* Y_3Co_2 *and* Dy_3Ni_2 *structure types*

Y_3Co_2	Dy_3Ni_2
Pnnm	*C*2/*m*
$a = 2\sqrt{3}g$	$a = 4g$
$b = 3g$	b = free, same as $c_{Y_3Co_2}$
c = free, same as $b_{Dy_3Ni_2}$	$c = 3g$
	$\beta = 120°$

In the idealized structure types the trigonal prisms have an equilateral triangle as base where g is the length of the triangle side.

	All atoms in 4(*g*)				All atoms in 4(*i*)			
	x	*y*	*z*		*x*	*y*	*z*	
Y(1)	$\frac{\sqrt{3}}{4}\frac{g}{a} = \frac{1}{8}$	$\frac{3}{4}\frac{g}{b} = \frac{1}{4}$	0	Dy(1)	$\frac{1}{2}\frac{g}{a} = \frac{1}{8}$	0	0	
Y(2)	$\frac{3\sqrt{3}}{4}\frac{g}{a} = \frac{3}{8}$	$\frac{5}{4}\frac{g}{b} = \frac{5}{12}$	0	Dy(2)	$\frac{3}{2}\frac{g}{a} = \frac{3}{8}$	0	$1\frac{g}{c} = \frac{1}{3}$	
Y(3)	$\frac{\sqrt{3}}{4}\frac{g}{a} = \frac{1}{8}$	$\frac{7}{4}\frac{g}{b} = \frac{7}{12}$	0	Dy(3)	$\frac{1}{2}\frac{g}{a} = \frac{1}{8}$	0	$1\frac{g}{c} = \frac{1}{3}$	
Co(1)	$\frac{7\sqrt{3}}{12}\frac{g}{a} = \frac{7}{24}$	$\frac{11}{4}\frac{g}{b} = \frac{11}{12}$	0	Ni(1)	$\frac{13}{6}\frac{g}{a} = \frac{13}{24}$	0	$\frac{1}{3}\frac{g}{c} = \frac{1}{9}$	
Co(2)	$\frac{11\sqrt{3}}{12}\frac{g}{a} = \frac{11}{24}$	$\frac{11}{4}\frac{g}{b} = \frac{11}{12}$	0	Ni(2)	$\frac{17}{6}\frac{g}{a} = \frac{17}{24}$	0	$\frac{2}{3}\frac{g}{c} = \frac{2}{9}$	

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