narrow than the older ones and, therefore, of broader applicability. In fact it is concerned with the analysis of a kind of structure which lies beneath the crystal structure. The electronic structure is at present less exactly known than the set of atomic radii; however it is a natural and necessary extension of that set and it may be analysed by legitimate methods similar to those which have led to the less hidden atomic radii.

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The Monoclinic Crystal Structure of R_5Co_2 (R=Pr, Nd, Sm) with the Mn_5C_2 Structure Type

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Sm_5Co_2 crystallizes in the monoclinic Mn_5C_2 structure type, space group $C2/c$, $a=16{\cdot}282$ (8), $b=6{\cdot}392$ (5), $c=7{\cdot}061$ (5) Å, $\beta=96{\cdot}6$ (1)°, $Z=4$. Patterson method, counter technique, absorption correction, least-squares refinement. $R=0{\cdot}07$ for 664 independent reflexions. Pr_5Co_2 and Nd_5Co_2 are isostructural with Sm_5Co_2. This series is related to Sm_3Co with the Fe_3C structure type. All rare-earth atoms are at the corners of regular trigonal prisms centred by Co atoms. The trigonal prisms are arranged in zigzag chains as in FeB and Fe_3C, but in Sm_5Co_2 the chains are joined by the edges of the prisms to form pairs.

Introduction

The binary phase diagrams of Pr–Co and Nd–Co have been reported by Ray (1974). He showed the existence of phases at about 29% Co and labelled them $Pr_{\sim7}$ $Co_{\sim3}$ and $Nd_{\sim7}$ $Co_{\sim3}$. These phases are not isotypic with the hexagonal Th_7Fe_3 type which occurs with Ni alloys such as Pr_7Ni_3 and Nd_7Ni_3 (Kissel, Tsuchida & Wallace, 1966). Reported in the binary phase diagram of Sm–Co, Buschow & Van der Goot (1968), is the existence of a phase at 31% Co, which has been labelled Sm_9Co_4. A powder pattern was indexed in terms of an orthorhombic cell, but the structure was not identified. The present investigation was undertaken on a single crystal to determine the stoichiometry of these phases and to verify if some predictions about the atomic model could be postulated from the prism linkage coefficient calculation (Moreau, Paccard & Parthé, 1976).

Experimental

The alloys were made from commercially available elements of high purity: rare earth and Co 99·9%. The constituents were melted under an argon atmosphere. X-ray diffraction patterns of the powders in the as-cast conditions were taken on a Guinier–de Wolff focusing camera with Cu $K\alpha$ radiation. Single crystals of Sm_5Co_2 were isolated by mechanical fragmentation from the crushed melt.

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Lattice constants and intensities of Sm_5Co_2 were measured with graphite-monochromated Mo $K\alpha$ radiation on a Philips PW 1100 computer-controlled four-circle goniometer in the θ–2θ scan mode. Lattice parameters (Table 1) were refined by least squares to fit 2θ values for 20 reflexions. The intensities of 664 non-equivalent reflexions ($|F_o| < 2\sigma_F$) were recorded out to a limit of $(\sin\theta)/\lambda = 0{\cdot}5$ Å^{-1} and all were used in the structure determination. The crystal had a very irregular shape and thus absorption corrections were made with the experimental method of Flack (1974, 1975). Intensities of the four symmetry-equivalent reflexions were automatically collected at intervals of 20° in ψ for the range 0 to 180° for each reflexion. In this way measurements were made for a set of eight independent reflexions in the θ range 7–20°. Examination of systematic absences showed the space group to be $C2/c$ or Cc. The ambiguity was resolved from a Patterson map which showed the true space group to be $C2/c$.

Structure determination

A comparison of the lattice parameters of Sm_5Co_2 with those of Sm_3Co (Buschow & Van der Goot, 1968)

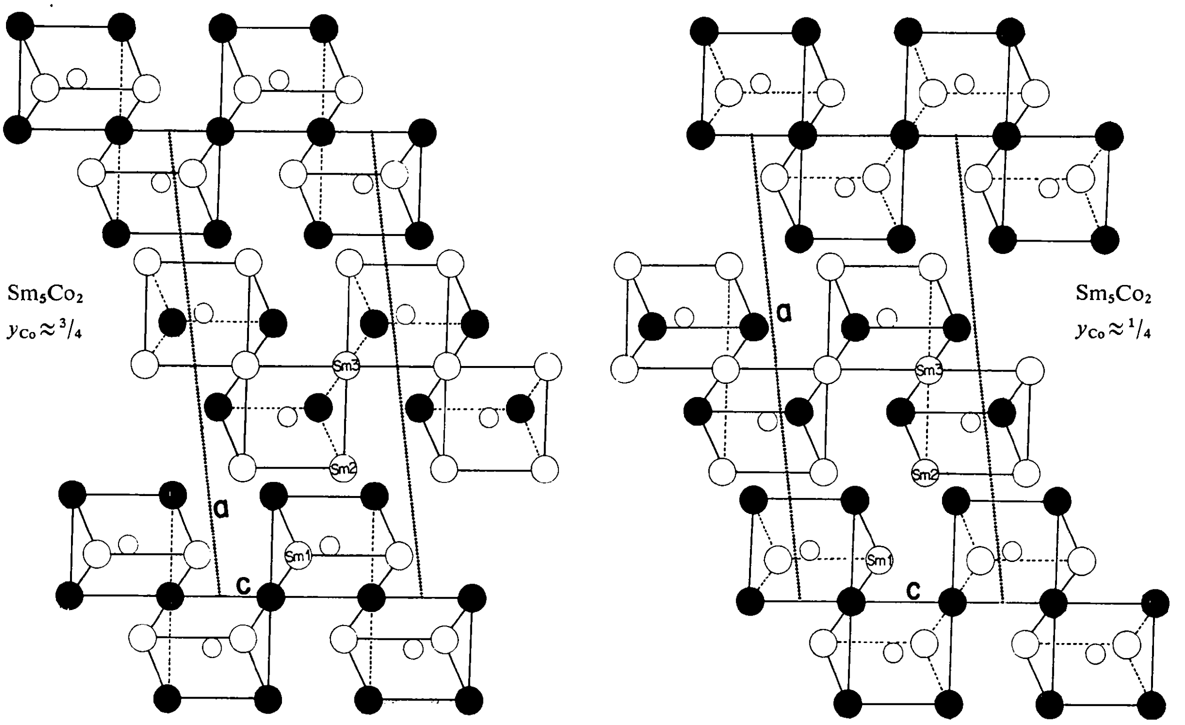
Table 1. *Crystal data of* Sm_5Co_2 *and of* Sm_3Co (*Buschow & Van der Goot*, 1969)

	Sm_5Co_2	Sm_3Co
Space group	$C2/c$ (No. 15)	*Pnma* (No. 62)
a	16·282 (8) Å	7·055 Å
b	6·392 (5)	9·605
c	7·061 (5)	6·342
β	96·6 (1)°	
Z	4	2

Table 2. *Atomic parameters for* Sm_5Co_2 *with e.s.d.'s in parentheses*

The isotropic temperature factor is defined as $\exp[-8\pi^2U(\sin\theta/\lambda)^2]$. Space group $C2/c$.

	Equipoint	x	y	z	U (Å^2) $\times 10^2$
Sm(1)	8*f*	0·0940 (1)	0·1116 (3)	0·4156 (2)	1·61 (4)
Sm(2)	8*f*	0·2162 (1)	0·5701 (3)	0·3156 (2)	1·56 (4)
Sm(3)	4*e*	0·00	0·5750 (4)	0·25	1·58 (8)
Co	8*f*	0·1107 (3)	0·2901 (7)	0·0738 (6)	1·9 (1)



(*a*) (*b*)

Fig. 1. The linkage of the trigonal prisms in Sm_5Co_2 shown in projection down **b**. Large circles represent Sm atoms, small circles at the centres of the prisms, Co atoms. The numbers inscribed correspond to the numbers of the atoms given in Table 2. (*a*) Arrangement of prisms centred by Co atoms with $y_{Co} \approx \frac{3}{4}$. White Sm atoms with $y \approx \frac{1}{2}$ and black Sm atoms with $y \approx 1{\cdot}0$. (*b*) Arrangement of prisms centred by Co atoms with $y_{Co} \approx \frac{1}{4}$. White Sm atoms with $y \approx \frac{1}{2}$ and black Sm atoms with $y \approx 0{\cdot}0$.

showed that b and c of the monoclinic Sm_5Co_2 cell are almost identical to c and a respectively of the orthorhombic Sm_3Co cell (Table 1). This was an indication that the structure could possibly be built of Co-centred trigonal prisms of Sm with a stacking along the monoclinic b and c identical to that of Sm_3Co along the c and a directions. Moreover, calculations based on the atomic volumes of Sm and Co indicated that the unit cell should contain four Sm_5Co_2 formula units. Thus the prism linkage coefficient calculated from the formula R_6T_{LC} (Moreau, Paccard & Parthé, 1976) was $LC = 12/5$. Considering the multiplicity of each equipoint in the space group $C2/c$ in conjunction with the Patterson map, the 20 Sm atoms contained in the unit cell had to be located on two sites in general positions $8f$ [Sm(1) and Sm(2)] and one special position site with a multiplicity of 4 [Sm(3)]. The eight Co atoms are in general positions. Assuming that all Sm atoms participate in the trigonal prism around one Co atom, and letting integers m, n and p be the number of Sm(1), Sm(2) and Sm(3) atoms respectively at the prism corners, then $m+n+p=6$. Thus $LC = (8 \times m + 8 \times n + 4 \times 2p)/20 = 12/5$ for this condition. There are many possible values of m, n and p which satisfy $LC = 12/5$ so that the model could not be predicted directly from the prism linkage calculation. However, assuming that the structure is based on zigzag chains of trigonal prisms as in Fe_3C, one could see that, if two of these chains were joined by prism edges (Fig. 1), the values of $m=2$, $n=2$ and $p=2$ would satisfy the condition $m+n+p=6$ and $LC = 12/5$. This model was confirmed by examination of Patterson sections. Allowing variation of positional and isotropic thermal parameters the structure refined satisfactorily with the least-squares program *CRYLSQ* (X-RAY system, 1972). Relativistic Hartree–Fock scattering factors were used for Sm and Co (Cromer & Mann, 1968). The value of $R(=\sum|\Delta F|/\sum|F_o|)$ was 0·07 for all 664 reflexions. A difference map did not show any significant electron density.* The final positional and thermal parameters are listed in Table 2. A listing of the low-angle reflexions with corresponding calculated intensities for X-ray powder diagram identification is given in Table 3 (Yvon, Jeitschko & Parthé, 1969). Interatomic distances are listed in Table 4.

Isotypic compounds

The lattice parameters of Pr_5Co_2 and Nd_5Co_2 are shown in Table 5. These parameters were obtained by least-squares refinement of reflexions measured from films taken on a Guinier–de Wolff camera with Cu $K\alpha$ radiation. The variation of the unit-cell parameters with the atomic number of the rare-earth element is a consequence of the normal lanthanide contraction. Furthermore the compounds Eu_5Pd_2 and Yb_5Pd_2 also crystallize with the Mn_5C_2 type structure (Iandelli & Palenzona, 1974).

Discussion

Once the structure was solved and the stoichiometry R_5Co_2 established, it appeared that these alloys were isostructural with Mn_5C_2 (Kuo & Persson, 1954) or Fe_5C_2 (Jack & Wild, 1966), known as χ-carbide or Hägg carbide. This is not surprising as other rare-earth – transition-metal alloys crystallize with carbide structures. The binary compounds R_3Co (Buschow & Van der Goot, 1969) and R_3Ni (Lemaire & Paccard, 1967), where R = the rare-earth elements from La to Lu except Ce (no data for Eu), crystallize with the orthorhombic structure of cementite Fe_3C (Lipson & Petch, 1940). The structural relationship between Fe_5C_2 and Fe_3C has been described by Senateur & Fruchart (1963) and recently by Andersson & Hyde (1974) in

Table 3. *Calculated powder data for* Sm_5Co_2 *for* Cr $K\alpha$ *radiation* ($\lambda = 2{\cdot}29092$ Å)

Intensity 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	$10^3 \times \sin^2\theta$	Intensity
2	0	0	20·06	3·7
1	1	0	37·13	12·3
1	1	−1	61·14	0·1
1	1	1	66·46	33·4
3	1	0	77·26	0·0
4	0	0	80·25	1·1
3	1	−1	95·94	26·5
0	0	2	106·68	46·9
3	1	1	111·91	121·4
2	0	−2	116·09	40·6
0	2	0	128·45	101·3
2	0	2	137·39	218·7
1	1	−2	138·48	380·3
2	2	0	148·52	25·1
1	1	2	149·13	113·7
0	2	1	155·12	662·7
5	1	0	157·51	1000·0
4	0	−2	165·63	282·3
3	1	−2	167·96	381·1
2	2	−1	169·86	262·1
5	1	−1	170·86	209·6
2	2	1	180·51	305·0
6	0	0	180·57	97·4
5	1	1	197·49	284·9
3	1	2	199·91	329·2
4	0	2	208·23	229·8
4	2	0	208·71	158·6
4	2	−1	224·72	173·2
0	2	2	235·13	112·7
5	1	−2	237·56	121·9
2	2	−2	244·55	38·0
4	2	1	246·03	4·2
6	0	−2	255·29	154·7
2	2	2	265·85	61·9
1	1	−3	269·17	254·5
7	1	0	277·89	0·1
1	1	3	285·15	63·0
7	1	−1	285·92	1·1

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* A table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31429 (19 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Interatomic distances of* Co *atoms in* Sm_5Co_2 *up to* 4 Å

All e.s.d.'s are less than 0·01 Å. The Sm atoms forming the surrounding trigonal prism are marked with an asterisk.

Sm(1)-Co	2·71 Å	Sm(2)-Co	2·79 Å
Co	2·80	Co	2·90
Sm(3)	3·47	Co	3·16
Co	3·53	Sm(3)	3·50
Sm(3)	3·57	2Sm(2)	3·54
Sm(2)	3·63	Sm(2)	3·55
Sm(1)	3·63	Sm(1)	3·63
Sm(2)	3·65	2Sm(2)	3·64
Sm(2)	3·67	Sm(1)	3·66
Sm(1)	3·70	Sm(1)	3·67
2Sm(1)	3·87	Sm(1)	3·84
Sm(2)	3·84		
Sm(3)	3·88		
Co	3·98		
Sm(3)-2Co	2·83 Å	Co——*Sm(1)	2·71 Å
2Co	2·94	*Sm(2)	2·79
2Sm(1)	3·47	*Sm(1)	2·80
2Sm(2)	3·50	*Sm(3)	2·88
2Sm(1)	3·57	*Sm(2)	2·90
2Sm(3)	3·66	*Sm(3)	2·94
2Sm(1)	3·88	Sm(2)	3·16
		Sm(1)	3·53
		Sm(1)	3·98

Table 5. *Lattice constants for* R_5Co_2 *compounds with space group* $C2/c$

V = Volume of the unit cell.
n = Number of atoms in the unit cell.

	a	b	c	β	$(V/n)^{1/3}$
Sm_5Co_2	16·282 Å	6·392 Å	7·061 Å	96·61°	2·96 Å
Nd_5Co_2	16·37	6·43	7·08	96·7	2·98
Pr_5Co_2	16·54	6·48	7·10	96·8	3·00

terms of unit-cell twinning. Moreover at 30 at. % Ni content the R_7Ni_3 alloys with R = La, Ce, Pr, Nd (Kissel, Tsuchida & Wallace, 1966) crystallize with the hexagonal Th_7Fe_3 type (Roof, Larson & Cromer, 1961) which is also isostructural with the carbide Mn_7C_3 (Fruchart, 1963). As in R_3Co and R_5Co_2, the centred trigonal prism is also the fundamental element of the Th_7Fe_3 structure. A review of all the R_7T_3 phases with T = Ni, Rh, Pd, Ir, Pt has been made by Olcese (1973) but unfortunately the principles of formation for these structures are not really understood. In particular the R_7Co_3 phase does not exist but instead the R_5Co_2 phase occurs with 29 at. % Co content. In addition it should be noted that La forms only La_3Co and not La_7Co_3 or La_5Co_2 compounds (Ray, 1974) and Ce only $Ce_{24}Co_{11}$ (Larson & Cromer, 1962). Finally the common characteristics of all the structures R_3T, R_5T_2 and R_7T_3 can be summarized as follows:

(1) All R atoms participate in the formation of regular trigonal prisms.

(2) All T atoms are at the centres of regular trigonal prisms.

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