

reflected in the moderate root-mean-square displacement for Cl(1) along [010] and a large component for Cl(2).

The structure factor and Fourier calculations were performed with the X-RAY 67 programs of Stewart (1967). The least-squares calculations were computed with a modified version of the ORFLS program of Busing, Martin & Levy (1962). All of the remaining computations were performed with locally written programs.

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The Crystal Structure of R_5Co_{19}

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Formation of the intermetallic compounds in the composition range 66–83 at. % Co of the R–Co intermetallic systems (R=rare earths) is described by the general formula RT_x where $x=(5n+4)/(n+2)$, $n=0, 1, 2, 3, 4, \dots$, T=transition metals Fe, Co and Ni. Using the structural data of the already known RT_x compounds for $n=0, 1$ and 2, simple mathematical relations are developed, with the help of which the lattice parameters and the atomic positions for any RT_x compound can be computed easily. Structural data for R_5Co_{19} are presented. It is shown that the structures of the RT_x compounds are the one-dimensional long-period superstructures of the $CaCu_5$ -type structure.

Introduction

Recently, a new compound having the formula R_5Co_{19} has been reported in the R–Co intermetallic systems for R=Ce, Pr, Nd and CeMM (Khan & Feldmann, 1973; Ray, Biermann, Harmer & Davison, 1973). The existence of this compound was first postulated by Cromer & Larson in 1959 on the basis of simple theoretical considerations. The arrangement of atoms in the structure of this compound is as yet unknown. Investigations were therefore carried out to determine the crystal structure of the R_5Co_{19} compound.

Experimental

Alloys (weighing 1–3 g) were prepared in the composition range RCO_3 – RCO_4 by arc-melting the constituents

on a water-cooled copper hearth under an atmosphere of purified argon. The purity of the elements was 99.9 wt. % for R and 99.99 wt. % for Co respectively.

Since the compounds in the above-mentioned composition range form peritectically (Khan, 1974; Ray *et al.*, 1973), the alloys were homogenized at 900°C for 7–14 days before further investigations. The structural changes were studied by annealing the homogenized alloy specimens at temperatures between 500–1150°C (depending upon the composition and the R element) for one day to three weeks (depending upon the annealing temperature) and subsequent quenching. In order to avoid oxidation of the specimens during heat treatment, they were wrapped in Ta foil and encapsulated in quartz ampoules filled with purified argon. The R–Co alloys for R=Ce were found to react with Ta foil above 950°C. In that case, alumina crucibles in-

stead of Ta foil were used as container materials (Khan, 1974).

For chemical analysis, a Philips X-ray fluorescence spectrometer was used. X-ray diffraction analysis was carried out with an Enraf-Nonius Guinier camera provided with a Philips Co-target fine-focus X-ray tube operating at 1 kW. For metallography, a Leitz polarization microscope was used. The structural calculations were carried out with a Telefunken TR-440 computer.

Results and discussion

In the composition range 75–80 at. % Co of the R–Co systems (for R = Ce, Pr, Nd and CeMM), three intermetallic compounds having the formulae RCO_3 , R_2Co_7 and R_5Co_{19} were identified. The RCO_3 compound was found to exist, throughout its temperature range, in the rhombohedral $PuNi_3$ -type structure. The R_2Co_7 compound was found to crystallize in two polymorphic forms: a high-temperature phase modification of the hexagonal Ce_2Ni_7 -type structure and a low-temperature phase modification of the rhombohedral Gd_2Co_7 -type structure. These results are in agreement with those reported by Bertaut, Lemaire & Schweizer (1965) and Buschow (1970), except that whereas Buschow (1970) reported the high- and low-temperature phase modifications of this compound to be isostructural with the rhombohedral Gd_2Co_7 -type and hexagonal Ce_2Ni_7 -type respectively, we have observed just the opposite.

The alloys having composition close to the formula R_5Co_{19} were found to be single phase by X-ray diffraction analysis. However, by metallographic methods, the presence of 4–5% of the RCO_5 phase on the Co-rich side and of the R_2Co_7 phase on the R-rich side was detected. The Guinier X-ray diffraction photographs of the R_5Co_{19} alloys were easily indexed on the basis of a rhombohedral Bravais lattice with $a_R \approx 16.5 \text{ \AA}$ and $\alpha \approx 17.25^\circ$. The equivalent non-primitive hexagonal cell has then the dimensions $a \approx 5$, $c \approx 48.7 \text{ \AA}$.

The precisely determined lattice parameters for R_5Co_{19} are given in Table 1. The lattice parameters for the corresponding RCO_3 , R_2Co_7 , and RCO_5 compounds have also been included in this table for comparison.

The crystal structures of the RT_x compounds for $x = 3$, $\frac{7}{2}$ and $\frac{19}{2}$ are usually derived from the $CaCu_5$ -type structure by replacing one Cu-representative atom by one Ca-representative atom every second, third and fourth cell respectively (Cromer & Larson, 1959). This derivation procedure for the structure of RT_x appears to be very simple. However, the determination of the atomic positions for a particular RT_x compound is quite laborious. In the following, we shall describe a procedure with the help of which the lattice parameters and the atomic positions for any RT_x compound can be easily calculated.

The RT_2 compound crystallizes in the Laves face-centred cubic $MgCu_2$ -type structure (Schubert, 1964). The true primitive unit cell of this structure-type would

Table 1. Lattice parameters for the RCO_x compounds

RCO_x		Ce	Pr	Nd	CeMM
RCO_3	a (Å)	4.96 ₄	5.08	5.06 ₇	5.04 ₄
	c (Å)	24.81 ₄	24.63 ₆	24.82 ₂	24.77 ₃
	c/a^*	0.833 ₁	0.808 ₃	0.812 ₆	0.818 ₆
	D	1.026	1.027	1.037	1.031
R_2Co_7	a (Å)	4.95 ₆	5.07	5.06 ₅	5.02 ₃
	c (Å)	36.52 ₅	36.87 ₆	36.74 ₈	36.74 ₇
	c/a^*	0.818 ₉	0.808 ₂	0.806 ₁	0.812 ₉
	D	1.007	1.024	1.024	1.020
R_5Co_{19}	a (Å)	4.947 ₅	5.06 ₅	5.05 ₂	5.01 ₂
	c (Å)	48.743 ₄	49.14 ₄	48.66 ₆	48.71 ₆
	c/a^*	0.821	0.808 ₆	0.802 ₈	0.801
	D	1.007	1.024	1.017	1.014
RCO_5	a (Å)	4.92 ₂	5.01 ₃	5.00 ₂	4.99 ₁
	c (Å)	4.03	4.00	3.98 ₈	4.00 ₄
	c/a	0.818 ₆	0.798	0.797 ₃	0.802 ₂
	D	1.000	1.000	1.000	1.000

* c/a has been calculated for the sub-structure from relation (4). $D = c/\rho c_{RCO_5}$, where $\rho = 6, 9$ and 12 for RCO_3 , R_2Co_7 and R_5Co_{19} respectively.

then be rhombohedral, with the lattice parameters $a_R = (1/\sqrt{2})a$ ($MgCu_2$ -type), $\alpha = 60^\circ$.

The equivalent non-primitive hexagonal unit cell has the dimensions $a = (1/\sqrt{2})a$ ($MgCu_2$ -type), $c = \sqrt{3}a$ ($MgCu_2$ -type).

This f.c.c.-to-rhombohedral structural transformation leads to the following atomic positions for the new rhombohedral structure of RT_2 (space group $R\bar{3}m$ (D_{3d}^5) relative to hexagonal axes):

$$(0, 0, 0), \left(\frac{1}{3}, \frac{2}{3}, \frac{2}{3}\right) \text{ and } \left(\frac{2}{3}, \frac{1}{3}, \frac{1}{3}\right) + \\ 6R(c) \ 0, 0, 0.125; \\ 3T(b) \ 0, 0, 0.5; \\ 9T(e) \ 0.5, 0, 0.$$

One-half of the thus transformed non-primitive hexagonal unit cell of the $MgCu_2$ -type structure is shown in Fig. 1(a). One-half non-primitive hexagonal unit cells of the rhombohedral $PuNi_3$ -type and Gd_2Co_7 -type structures, in which RT_3 and R_2T_7 crystallize respectively, are shown in Fig. 1(b) and (c). The atomic positions for the former were taken from Cromer & Olsen (1959) and those for the latter were taken from Bertaut, Lemaire & Schweizer (1965).

These half unit cells have been divided into blocks B , C , A and D for the sake of illustration. The blocks C and D are similar and have the stoichiometry R_2T ; the former is obtained from the latter by a $(\frac{1}{3}, \frac{2}{3}, 0)$ shift [Fig. 1(a) and (e)]. The block B is built up of the conventional $CaCu_5$ -type motive [Fig. 1(f)] and the block A is obtained from it by a $(\frac{2}{3}, \frac{1}{3}, 0)$ shift.

As seen from Fig. 1(a), (b) and (c), the blocks C and D remain unchanged from RT_2 to R_2T_7 . However, the heights of the blocks B and A increase by multiples of the $CaCu_5$ -type motive. A close study of these changes in these unit cells leads to the following quantitative relation for the structures of RT_x :

$$U_{1/2}(rRT_x) = U_{1/2}(rRT_2) + \frac{n}{2} B + nA \quad (1)$$

$$x = \frac{5n+4}{n+2} \quad (2)$$

$$n=0, 1, 2, 3, 4, \dots$$

$U_{1/2}$ and r stand for $\frac{1}{2}$ unit cell and rhombohedral respectively. The full unit cell is obtained by centrosymmetrical transformation.

It is seen that equation (1) gives not only the structures of RT_2 for $n=0$, RT_3 for $n=1$ and R_2T_7 for $n=2$, but also predicts the existence of a family of rhombohedral, homotypical structures (e.g. R_5T_{19} for $n=3$, RT_4 for $n=4$, etc.), the very first member of which is the rhombohedral $MgCu_2$ -type structure for $n=0$. In other words, we can say that the rhombohedral structures of RT_x are obtained from the rhombohedral $MgCu_2$ -type structure simply by increasing the lengths of the blocks B and A according to equation (1) (see Fig. 1).

The atomic positions for the n th member of this rhombohedral RT_x structure family are given by the following equation:

$$U(rRT_x) = p \cdot [3R(a)] + \alpha \cdot [6R(c)] + [3T(b)] + \beta \cdot [6T(c)] + q \cdot [9T(e)] + \gamma \cdot [18T(h)] \quad (3)$$

If n is even, then: $p=0, q=1, \alpha=(n+2)/2, \beta=n, \gamma=n/2$.
 If n is odd, then: $p=1, q=0, \alpha=(n+1)/2, \beta=n, \gamma=(n+1)/2$. The figures in square brackets stand for the atomic site sets as given for the space group $R\bar{3}m (D_{3d}^5)$ relative to hexagonal axes (*International Tables for X-ray Crystallography*, 1965); i.e.

$$(0, 0, 0), (\frac{1}{3}, \frac{2}{3}, \frac{2}{3}) \text{ and } (\frac{2}{3}, \frac{1}{3}, \frac{1}{3}) +$$

$$3R(a) (0, 0, 0);$$

$$m = 1, 2, 3, \dots, \alpha$$

$$z_{m=\alpha} = \frac{1 \cdot 4 + 2n}{12(n+1)}$$

when n = even:

$$z_{m=1 \text{ to } \alpha-1} = \frac{2m-1}{6(n+1)}$$

when n = odd:

$$z_{m=1 \text{ to } \alpha-1} = \frac{m}{3(n+1)}$$

$$6R_m(c) \pm (0, 0, z_m)$$

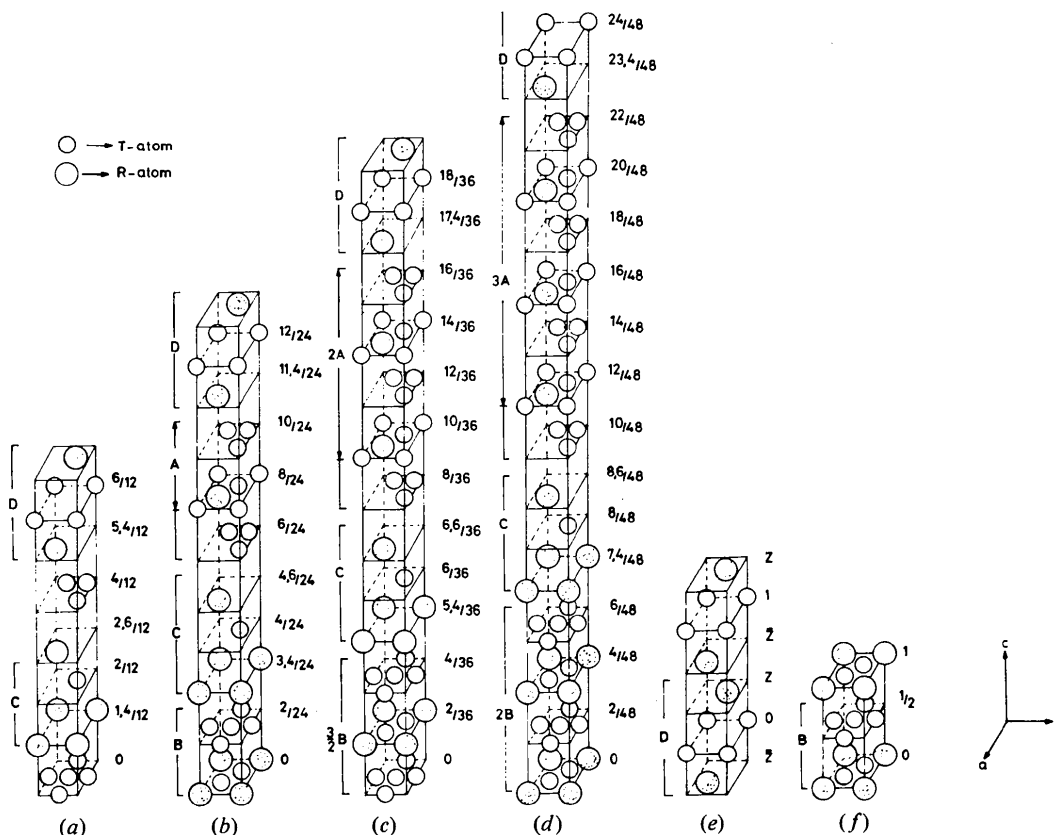


Fig. 1. (a)–(d) Half unit cells (non-primitive hexagonal) of the $MgCu_2$ -type, $PuNi_3$ -type, Gd_2Co_7 -type and Ce_2Co_{19} -type respectively. The other half is obtained through a centre of symmetry. (e)–(f) Unit cells of the I_2Cd (C_6)-type and $CaCu_5$ -type respectively. For the sake of illustration, the height of the unit cell in (e) has been extended in the c direction. Actually, its height and hence that of blocks C and D is nearly half of that of the $CaCu_5$ -type unit cell, $Z \approx 0.4$.

$3T(b)$ $(0, 0, \frac{1}{2})$;
 $9T(e)$ $(\frac{1}{2}, 0, 0)$, $(0, \frac{1}{2}, 0)$, $(\frac{1}{2}, \frac{1}{2}, 0)$;

$6T_m(c)$ $\pm (0, 0, z_m)$
 $18T_m(h)$ $\pm (x, \bar{x}, z_m)$,
 $\pm (x, 2x, z_m)$, $\pm (2\bar{x}, \bar{x}, z_m)$

$$m = 1, 2, 3, \dots, \beta$$

$$z_{m=1 \text{ to } \beta} = \frac{2m+n+1}{6(n+1)}$$

$$x = \frac{1}{2}$$

$$m = 1, 2, 3, \dots, \gamma$$

$$z_{m=1 \text{ to } \gamma} = \frac{1}{3} - \frac{2m+n}{6(n+1)}$$

As an example of the use of equation (3) in the determination of the structures of RT_x , we choose $n=3$. The compound then has the formula R_5T_{19} [equation (2)]. This compound contains three formula units in its non-primitive hexagonal unit cell [equation (1)]. Since n in this case is an odd number, we have from equation (3)

$$p=1, q=0, \alpha=2, \beta=3, \gamma=2$$

and

$$U(rRT_{19/s}) = [3R(a)] + [2\{6R(c)\} + [3T(b)] + 3\{6T(c)\} + 2\{18T(h)\} .$$

The atoms have the positions

$$(0, 0, 0), (\frac{1}{3}, \frac{2}{3}, \frac{2}{3}) \text{ and } (\frac{2}{3}, \frac{1}{3}, \frac{1}{3}) +$$

$3R(a)$ $(0, 0, 0)$
 $6R_1(c)$ $(0, 0, z_1)$ $z_1 = \frac{1}{12}$
 $6R_2(c)$ $(0, 0, z_2)$ $z_2 = 7 \cdot 4/48 = 0 \cdot 154$
 $3T(b)$ $(0, 0, \frac{1}{2})$
 $6T_1(c)$ $(0, 0, z_1)$ $z_1 = \frac{1}{4}$
 $6T_2(c)$ $(0, 0, z_2)$ $z_2 = \frac{1}{3}$
 $6T_3(c)$ $(0, 0, z_3)$ $z_3 = \frac{5}{12}$
 $18T_1(h)$ (x, \bar{x}, z_1) $x = \frac{1}{2}$
 $18T_2(h)$ (x, \bar{x}, z_2) $x = \frac{1}{2}$
 $z_2 = \frac{1}{24}$

From this structural proposal, the crystal structure of Ce_5Co_{19} has been calculated and is given in Table 2 and Fig. 1(d). It is seen that the agreement between the calculated and observed structural data is quite satisfactory. Small discrepancies at some places between the calculated and observed intensities, e.g. reflexions 003, 0,1,10, 0,1,19 etc. in Table 2 may be due to the following two reasons:

(a) there is some faulting in the structure, which is evidenced by the presence of dark bands between some reflexion pairs, as has been reported by Khan & Feldmann (1973);

(b) some disorder exists in the structure, because of which the super-structure reflexions are not neatly generated.

The refinement of the atomic parameters (with powder X-ray diffraction intensity data) revealed that the parameters, as given above, are quite appropriate.

Table 2. Structural data for the Ce_5Co_{19} intermetallic compound

Experiment:		Structure:		Remark:			
Ce ₅ Co ₁₉ alloy (14 d 900°C, 21 d 500°C/water); Guinier X-ray diffraction photograph, 2h Co K α (30 kV, 30 mA), calibrated with Si.		Rhombohedral, $R\bar{3}m$ (D_{3d}^5); $a=4\cdot9475$, $c=48\cdot743$, Å; c/a (sub-structure of the CaCu ₅ -type)=0.8210.		$I_c=10^{-5}$ HPLG $ F_c ^2$ (see Sagel, 1958).			
h	k	l	$\sin^2 \theta_c$	$\sin^2 \theta_o$	I_c	I_o	
0	0	3	0.0030	—	15	0	
0	0	6	0.0121	—	1	0	
0	0	9	0.0273	—	0	0	
0	1	1	0.0440	0.0440	5	10	5
1	0	2	0.0450	—	0	—	
0	0	12	0.0486	0.0486	13	9	17
0	1	4	0.0490	—	4	9	
1	0	5	0.0521	—	0	0	
0	1	7	0.0602	—	2	0	
1	0	8	0.0652	—	0	0	
0	0	15	0.0759	0.0763	1	6	2
0	1	10	0.0774	—	1	—	
1	0	11	0.0844	0.0843	19	5	
0	1	13	0.1006	0.1010	93	100	
0	0	18	0.1093	0.1095	2	65	50
1	0	14	0.1097	—	48	—	
0	1	16	0.1300	0.1312	13	150	143
1	1	0	0.1309	—	130	—	
1	1	3	0.1340	—	2	0	
1	0	17	0.1411	0.1407	22	10	
1	1	6	0.1431	—	1	0	
0	0	21	0.1487	—	2	0	
1	1	9	0.1582	—	0	0	
0	1	19	0.1654	—	4	0	
2	0	1	0.1749	0.1755	100	115	122
0	2	2	0.1759	—	22	—	
1	0	20	0.1785	0.1797	15	381	354
1	1	12	0.1795	—	354	—	
2	0	4	0.1800	0.1916	12	10	
0	2	5	0.1830	—	7	—	
2	0	7	0.1911	0.1948	9	70	83
0	0	24	0.1942	—	75	—	
0	2	8	0.1962	0.2071	8	5	3
1	1	15	0.2068	—	2	—	
0	1	22	0.2069	0.2079	1	10	
2	0	10	0.2082	0.2079	13	30	
0	2	11	0.2154	0.2160	26	6	
1	0	23	0.2220	0.2223	9	5	
2	0	13	0.2316	0.2313	2	7	
1	1	18	0.2402	0.2405	4	6	4
0	2	14	0.2407	—	0	—	
0	0	27	0.2458	0.2464	3	0	
0	1	25	0.2544	—	1	0	
2	0	16	0.2609	—	0	0	
1	0	26	0.2716	0.2721	11	6	13
0	2	17	0.2720	—	2	—	
1	1	21	0.2796	0.2793	7	3	
2	0	19	0.2963	—	0	0	
0	0	30	0.3035	—	3	0	
1	2	1	0.3058	0.3060	2	6	2
2	1	2	0.3068	—	0	—	
0	1	28	0.3080	—	0	0	
0	2	20	0.3094	—	1	0	
1	2	4	0.3109	—	1	0	
2	1	5	0.3139	—	0	0	
1	2	7	0.3220	—	1	0	
1	1	24	0.3252	0.3252	29	25	
2	1	8	0.3271	0.3270	0	5	7
1	0	29	0.3273	—	7	—	
2	0	22	0.3378	—	5	0	
1	2	10	0.3392	—	0	0	

Table 2 (cont.)

<i>h</i>	<i>k</i>	<i>l</i>	$\sin^2 \theta_c$	$\sin^2 \theta_o$	I_c	I_o
2	1	11	0.3463	—	8	0
0	2	23	0.3530	0.3535	12	5
1	2	13	0.3625	0.3626	42	51

Single-crystal experiments may perhaps help further. We have been trying to obtain one useable single-crystal fragment from this material for a year, without success. Oxidation of rare earths during annealing of the fragments of this material has been found to be the main obstacle.

We measured the density of the $\text{Ce}_5\text{Co}_{19}$ alloys and found it to be 8.4 g cm^{-3} . This value gave 2.9 formula units for the non-primitive hexagonal unit cell of $\text{Ce}_5\text{Co}_{19}$. This agrees, within experimental error, with that theoretically obtained from equation (1).

Powder X-ray diffraction intensities were also calculated for the other R_5Co_{19} compounds. The general agreement between the calculated and observed data for these compounds was found to be of the same order as for $\text{Ce}_5\text{Co}_{19}$.

Equation (1) predicts the existence of a number of rhombohedral structures with increasing c parameter as a function of n . Since only the c parameter of these structures varies by integral multiples and the CaCu_5 -type motif (blocks A and B) is repeated with a definite frequency in a particular structure (Fig. 1), these structures may be termed as one dimensional long-period super-structures of the CaCu_5 -type structure, as has been pointed out by Khan & Feldmann (1973). The periodicity M in these structures is given by

$$M = \frac{2n+1}{2} = \frac{3(x-1)}{2(5-x)}$$

If we consider, however, the blocks C and D (Fig. 1) simply as defect layers of the CaCu_5 -type structure, the periodicity M is then given by

$$M = 3(n+1) = \frac{3(x+1)}{5-x}$$

The out-of-step shift in this family of long-period super-structures is $(\frac{2}{3}, \frac{1}{3}, 0)$ in the (001) plane.

The lattice parameters of these super-structures are related to those of the corresponding CaCu_5 -type structure in the following way:

$$a(r\text{RT}_x) = a(\text{CaCu}_5\text{-type}) + \frac{d}{n+1}$$

$$c(r\text{RT}_x) = 3(n+1)c(\text{CaCu}_5\text{-type}) + \frac{d_c}{n+1}, \quad (4)$$

where d is the a -parameter distortion due to the size differences between the R and T atoms, and d_c is the c -parameter distortion partially due to the size differ-

ences, as in case of the a -parameter, and partially due to the super-structure formation. The lattice-parameter distortion due to super-structure formation is about 1% and has its origin in the valence electron to atom ratio (e/a) (Pearson, 1972).

The lattice-parameter distortions have been calculated for a few RT_x compounds and are given in Table 1. In view of the above structural theory of RT_x , the lattice-parameter distortion should be a linear function of n . However, as is seen from Table 1, it is only partially so. This discrepancy may perhaps be due to some experimental error in the lattice parameters.

With a little modification, the above procedure can be used to derive structural relations for the hexagonal phase modifications of the rhombohedral RT_x super-structure family members. The hexagonal RT_x super-structure family is easily obtained from the rhombohedral by removing the block B and giving a $(\frac{2}{3}, \frac{1}{3}, 0)$ shift to the blocks A and C of the unit cells shown in Fig. 1. This leads to a change of space-group symmetry from $R\bar{3}m$ to $P6_3/mmc$.

As is obvious from the above discussion, both hexagonal and rhombohedral phase modifications are possible for R_5Co_{19} . However, during the course of the present investigations we were successful, owing to experimental difficulties (e.g. oxidation of rare earths at elevated temperatures, reaction of rare earths with the container materials at these temperatures), in producing only the rhombohedral phase modification of this R_5Co_{19} compound.

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