Ag^+ [$O\cdots Ag^+ = 2\cdot 75$ (2) Å], is much farther from $OW(1)$ [$O\cdots O = 3\cdot 11$ (2) Å]. The alternate, 'disordered' site provides a stronger hydrogen bond [$2\cdot 78$ (2) Å] at the expense of lost Ag^+ coordination [$O(1)$NitD is $3\cdot 18$ (2) Å from the silver on the opposite side of NNit]. At the same time, because each nitrite ion lies between two silver ions on the twofold axis, there is presumably no great change in coulombic stabilization of the crystal. The distance from the second silver ion to $O(2)$NIT of the nitrate group in crystal II is $2\cdot 70$ (2) Å.

Other than the contacts discussed above, there are no unusually short distances in the structure. Table 9 lists the shortest remaining van der Waals contacts.

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The Crystal Structures of R_2Co_{17} Intermetallic Compounds

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The R_2Co_{17} intermetallic compounds are known to crystallize in two polymorphic forms, a hexagonal of the Th_2Ni_{17}-type structure and a rhombohedral of the Th_2Zn_{17}-type structure. The crystal structure of a new high-temperature disordered phase of R_2Co_{17} is given. The two above-mentioned crystal modifications of R_2Co_{17} are shown to be the superstructures of this disordered phase. The stability of the new phase and the conditions for its transformation into its super-structures are given. The degree of order of R_2Co_{17} of the Th_2Ni_{17}-type structure is discussed.

Introduction

The R_2Co_{17} intermetallic compounds (R = rare earths including Y) exhibit polymorphism (Ostertag & Strnat, 1965; Buschow, 1966; Lemaire, 1966). Most of them have been reported to crystallize in two modifications, a high-temperature phase of the Th_2Ni_{17}-type structure and a low-temperature phase of the Th_2Zn_{17}-type structure (Bouchet, Laforest, Lemaire & Schweizer, 1966). However, it has been recently reported that the

high-temperature modification of Sm_2Co_{17} is a defect-type phase (of the $CaCu_5$-type structure) which, on annealing, transforms into the Th_2Zn_{17}-type structure and that Sm_2Co_{17} of the Th_2Ni_{17}-type structure does not exist (Khan & Mueller, 1973).

In view of these anomalous results, the R_2Co_{17} compounds with R = Y, Ce, Pr, Nd, Sm, Gd, Dy, Ho and Er were investigated.

Experimental

Alloys, having a composition close to R_2Co_{17} and weighing about 1–3 g, were arc-melted on a water-cooled copper-hearth in a highly purified argon atmosphere. The alloy buttons were broken into pieces and remelted to obtain adequate homogeneity. The purity of the starting elements was 99·9 wt.% for the rare-earths and 99·999 wt.% for Co.

The alloys were investigated in the as-cast state as well as after homogenization at 1000 °C for a week. To study the structural changes with temperature, the homogenized alloy-specimens were annealed at temperatures between 500 and 1150 °C for 24–72 and above 1150 °C for 1–2 h and subsequently quenched in liquid N_2. In order to avoid oxidation, the alloys were heat-treated in quartz capsules lined with Ta foil and filled with highly purified argon. Because of the high chemical reactivity of rare earths with water, liquid N_2 was used as a quenching medium.

The chemical analysis was carried out with a Philips X-ray fluorescence spectrometer. The weight losses during sample preparation were found to be negligible. Metallography was carried out with a Leitz polarization microscope. For X-ray diffraction analyses an Enraf–Nonius–Guinier camera and a Philips horizontal goniometer both provided with a cobalt-anode fine-focus X-ray tube working at 1 kW were used.

Results and discussion

For the structural study of R_2Co_{17}, only those alloys were selected which were free from the neighbouring phases RCo_5 and α-Co. As a result of this selection, it was found that a small homogeneity region of R_2Co_{17} exists only on the R-rich side of the nominal composition.

The phases found in the R_2Co_{17} intermetallic compounds at different temperatures are shown in Table 1 and Fig. 1. The lattice parameters of the different crystal structures of R_2Co_{17} are given in Table 2. In these tables and figures the R elements have been arranged according to the different types of structures found in the R_2Co_{17} series. The listing of R_2Co_{17} in this way leads to the sequence of rare earths with Y and Ce inserted. It is seen from Fig. 1 and Table 1 that the crystal structures of Sm_2Co_{17} and Gd_2Co_{17} present exceptions at higher temperatures. The crystal structure of the high-temperature phase of Sm_2Co_{17} is that of the $TbCu_7$-type instead of that of the Th_2Ni_{17}-type (Bouchet et al., 1966) or $CaCu_5$-type (Khan & Mueller, 1973). The same is true for Gd_2Co_{17} except that traces of Th_2Ni_{17}-type structure are present. The low-temperature phases of these two R_2Co_{17} compounds are of the Th_2Zn_{17}-type structures. For the other R_2Co_{17} compounds the phases are either of the Th_2Ni_{17}-type or of the Th_2Zn_{17}-type structures or composites of both.

The crystal structure of R_2Co_{17} of the Th_2M_{17}-type

Table 1. Polymorphic forms of R_2Co_{17}

R_2Co_{17}	As cast	Alloy 1d 1100°C/LN$_2$	Alloy 3d 700°C/LN$_2$
Pr_2Co_{17}	Th_2Zn_{17}	Th_2Zn_{17}	Th_2Zn_{17}
Nd_2Co_{17}	Th_2Zn_{17}	Th_2Zn_{17}	$ThZn_{17}$
Sm_2Co_{17}	$TbCu_7$ (disordered)	Th_2Zn_{17}	Th_2Zn_{17}
Gd_2Co_{17}	$TbCu_7$ (disordered) + traces of Th_2Ni_{17}	Th_2Zn_{17}	Th_2Zn_{17}
Y_2Co_{17}	Th_2Ni_{17} (defect-type)	Th_2Zn_{17}	Th_2Zn_{17}
Dy_2Co_{17}	Th_2Ni_{17} (defect-type)	$Th_2Zn_{17} + Th_2Ni_{17}$	Th_2Zn_{17}
Ce_2Co_{17}	Th_2Ni_{17} (defect-type)	Th_2Ni_{17} (defect-type)	Th_2Ni_{17} + traces of Th_2Zn_{17}
Ho_2Co_{17}	Th_2Ni_{17} (degree of order close to 'ideal' structure)	Th_2Ni_{17} (degree of order close to 'ideal' structure)	Th_2Ni_{17} + traces of Th_2Zn_{17}
Er_2Co_{17}	Th_2Ni_{17} (ordered)	Th_2Ni_{17} (ordered)	Th_2Ni_{17} (ordered)

Table 2. Lattice parameters of the polymorphic forms of R_2Co_{17}

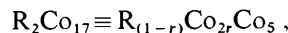| Compound	Th_2Zn_{17}-type			$TbCu_7$-type			Th_2Ni_{17}-type		
	a (Å)	c (Å)	c/a	a (Å)	c (Å)	c/a	a (Å)	c (Å)	c/a
Pr_2Co_{17}	8·441$_9$	12·260$_5$	1·4523						
Nd_2Co_{17}	8·427$_9$	12·243$_3$	1·4527						
Sm_2Co_{17}	8·401$_9$	12·230$_8$	1·4557	4·856$_2$	4·081$_3$	0·8404			
Gd_2Co_{17}	8·378$_7$	12·209$_1$	1·4572	4·837	4·066	0·8406	8·378	8·139	0·9714
Y_2Co_{17}	8·355	12·192	1·4593				8·355	8·128	0·9728
Dy_2Co_{17}	8·365	12·169	1·4548				8·361$_4$	8·117	0·9707
Ce_2Co_{17}	8·378	12·206	1·4569				8·377$_9$	8·137$_3$	0·9713
Ho_2Co_{17}	8·332	12·201	1·4644				8·331$_5$	8·133$_9$	0·9763
Er_2Co_{17}							8·312$_6$	8·130$_6$	0·9781

(M = Ni or Zn) is derived from that of RCo_5 of the $CaCu_5$-type by an ordered substitution of two small Co-atoms in place of one large R atom (Makarov & Vinogradov, 1956; Pearson, 1972). A basal plane projection of R_2Co_{17} of the Th_2M_{17}-type structure is given in Fig. 2(a). From Fig. 2(b) it is seen that the structure of R_2Co_{17} of the Th_2M_{17}-type is built up of blocks such as block 1, block 2, etc. These blocks differ only in the positions of the pair of substituted Co atoms [A and A' in block 1, B and B' in block 2 in Fig. 2(b)]. However, if this substitution is not ordered, these blocks are statistically similar and the structure of R_2Co_{17} reduces to that of the $TbCu_7$-type (Buschow & van der Goot, 1971) [as shown in Fig. 2(c)] in the following way:

$$R_2Co_{17} \equiv R_{(1-r)}Co_{2r}Co_5 ,$$

where $r = \frac{1}{3}$. On this basis the crystal structure of the high-temperature phase of Sm_2Co_{17} has been calculated and is given in Table 3 and Fig. 3(a) as representative for R_2Co_{17}.

At lower temperatures, ordering sets in and the high-temperature disordered phase of the $TbCu_7$-type structure transforms into R_2Co_{17} of the Th_2Ni_{17}-type or Th_2Zn_{17}-type structures depending upon which structure is favourable for a particular element R.

Fig. 3 shows the Guinier X-ray diffraction patterns of Sm_2Co_{17} ($TbCu_7$-type), Sm_2Co_{17} (Th_2Zn_{17}-type) and Ce_2Co_{17} (Th_2Ni_{17}-type). A comparison of Fig. 3(a) and (b) reveals that

(1) there are additional diffraction lines present in the latter;
(2) the intensities and positions of the main X-ray diffraction lines (marked at the bottom) in both are exactly the same, which is typical for a substructure.

Table 3. Crystal structure of the high-temperature phase of Sm_2Co_{17}

Experiment: Sm_2Co_{17} alloy 2h 1320°C/LN$_2$; Guinier-photograph 2h Co K (30 kV/30 mA) calibrated with Si.
Strcuture: $TbCu_7$-type (Buschow & Van der Goot, 1971), D_{6h}^1, $P6/mmm$; $a = 4\cdot856_2$, $c = 4\cdot081_3$ Å; $Sm_2Co_{17} \equiv$ $Sm_{(1-r)}Co_{2r}Co_5$ where $r = \frac{1}{3}$.
(1 − r) Sm (a) 0,0,0;
2r Co (e) ± (0,0,Z), Z = 0,296;
2 Co (c) ± ($\frac{1}{3}$,$\frac{2}{3}$,0);
3 Co (g) $\frac{1}{2}$,0,$\frac{1}{2}$; 0,$\frac{1}{2}$,$\frac{1}{2}$; $\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$.
Remark: I_c = HPLG$|F_c|^2$.

h	k	l	$\sin^2\theta_c$	$\sin^2\theta_o$	$10^{-3}I_c$	I_o
1	0	0	0·0453	0·0453	2	3
0	0	1	0·0481	0·0481	1	1
1	0	1	0·0934	0·0934	43	50
1	1	0	0·1359	0·1359	72	56
2	0	0	0·1812	0·1812	85	77
1	1	1	0·1840	0·1840	179	179
0	0	2	0·1924	0·1924	52	50
2	0	1	0·2293	0·2293	42	39
1	0	2	0·2377	0·2377	5	5
2	1	0	0·3171	C·3171	1	0
1	1	2	0·3283	0·3283	20	15
2	1	1	0·3652	0·3652	18	22
2	0	2	0·3736	0·3736	38	35
3	0	0	0·4077	0·4080	20	14

Table 4. Crystal structure of R_2Co_{17} of the Th_2Ni_{17}-type structure

Experiment: R_2Co_{17} alloys with R = Er, Ho, Ce, Dy and Y (heat-treatment is given in Fig. 1); Guinier-photograph 2h Co K (30 kV/30 mA).
Structure: Th_2Ni_{17}-type (Bouchet et al., 1966; Florio et al., 1956), D_{6h}^4, $P6_3/mmc$;
2 R (a) 0, 0, $\frac{1}{4}$; 2 R (d) $\frac{1}{3}$, $\frac{2}{3}$, $\frac{3}{4}$
4 Co (f) $\frac{1}{3}$, $\frac{2}{3}$, 0·109; 6 Co (g) $\frac{1}{2}$, 0, 0
12 Co (j) $\frac{1}{3}$, 0·968, $\frac{1}{4}$; 12 Co (k) $\frac{1}{6}$, $\frac{1}{3}$, 0·984.
Remark: $I_c = 10^{-3}$ HPLG$|F_c|^2$.

| h	k	l	Er_2Co_{17} I_c	I_o	Ho_2Co_{17} I_c	I_o	Ce_2Co_{17} I_c	I_o	Dy_2Co_{17} I_c	I_o	Y_2Co_7 I_c	I_o
0	0	1	0	0	0	0	0	0	0	0	0	0
1	0	0	0	0	0	0	3	0	5	0	14	0
1	0	1	17	15	16	7	5	0	14	7	3	4
1	1	0	17	22	16	18	3	19	15	24	9	7
0	0	2	12	13	11	12	4	11	10	18	0	0
1	1	1	0	0	0	0	0	0	0	0	0	0
2	0	0	6	8	6	3	4	0	5	0	0	0
1	0	2	19	18	18	8	13	1	18	0	5	0
2	0	1	34	53	33	30	22	21	32	25	6	4
1	1	2	213	246	207	255	150	215	200	205	59	105
2	1	0	3	5	3	0	1	0	3	0	0	0
0	0	3	0	0	0	0	0	0	0	0	0	0
2	0	2	30	27	29	14	24	2	29	10	15	0
2	1	1	45	47	43	55	30	22	42	25	9	6
1	0	3	46	41	45	19	35	13	43	19	18	3
3	0	0	245	235	242	250	208	198	240	211	138	112
3	0	1	0	0	0	0	0	0	0	0	0	0
1	1	3	0	0	0	0	0	0	0	0	0	0
1	2	2	31	33	30	13	24	2	30	7	14	0
2	0	3	160	173	158	221	143	131	157	179	110	99
2	2	0	341	349	339	350	303	287	337	300	231	215
3	0	2	630	630	624	624	558	558	618	618	418	418
0	0	4	186	155	184	193	169	131	182	200	133	105
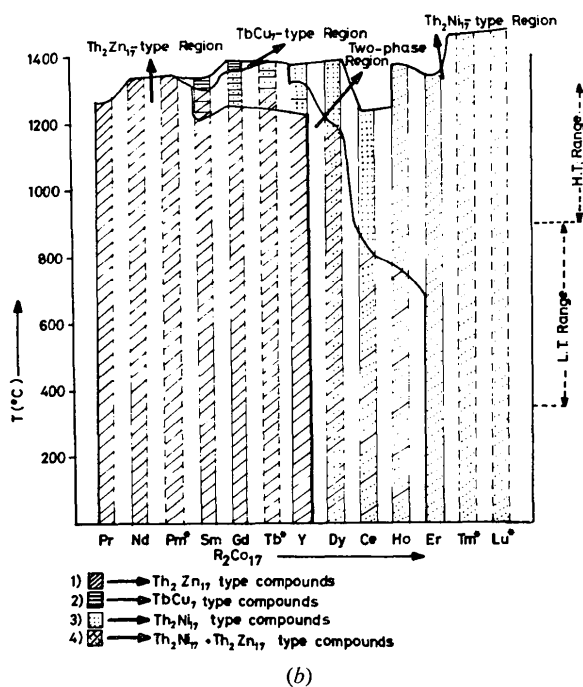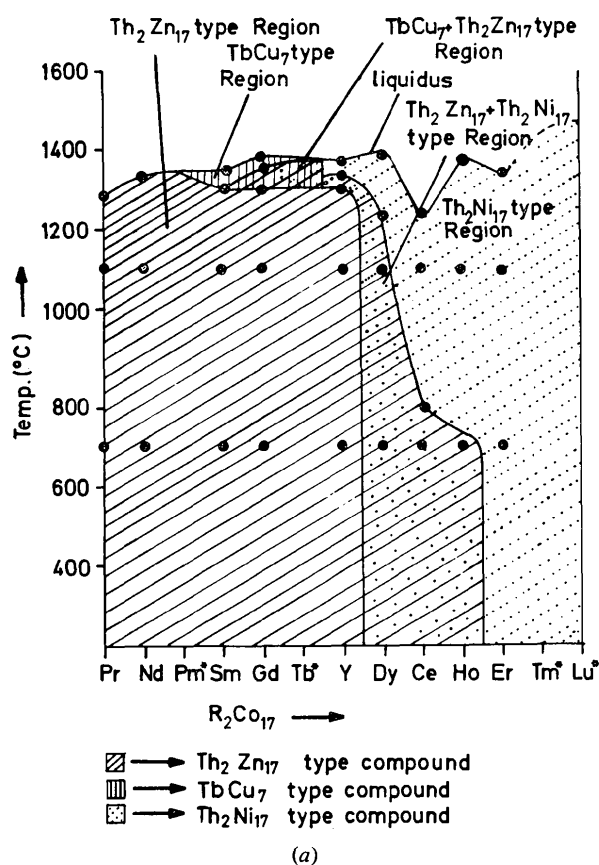
Fig. 1. Polymorphic forms of R_2Co_{17} at different temperatures. The number of points in a line represents the degree of order of the Th_2Ni_{17}-type structure. * Alloys not investigated in this work.

The Th_2Zn_{17}-type structure of Sm_2Co_{17} is therefore a superstructure of Sm_2Co_{17} of the $TbCu_7$-type structure. Similarly, if we compare Fig. 3(a) and (c), we find that the Th_2Ni_{17}-type structure of Ce_2Co_{17} is also a superstructure of the $TbCu_7$-type structure. It is therefore reasonable to say that the Th_2M_{17}-type structures (M = Ni or Zn) of R_2Co_{17} are superstructures of the $TbCu_7$-type structures of the disordered R_2Co_{17} phases. For Sm_2Co_{17} and Gd_2Co_{17} this disordered phase exists, whereas for other rare earths it is not stable.

By comparing the crystal structures of the different polymorphs of R_2Co_{17}, it is found that both of the following necessary conditions for the order–disorder transformation are fulfilled:

(1) the relative atomic positions in the structure of the disordered phase should remain undisplaced in the ordered structure (Lipson, 1950);

(2) the symmetry of the ordered structure should be lower than, or at least equal to, that of the disordered structure (Lipson, 1950; Stoloff & Davies, 1966; Barrett & Massalski, 1966; Pearson, 1972).

It is seen from Fig. 1 and Tables 1 and 4 that all of the R_2Co_{17} compounds having the Th_2Zn_{17}-type structure are ordered. However, the ordering process for R_2Co_{17} of the Th_2Ni_{17}-type structure depends critically on the element R. The degree of order increases from Y through Dy, Ce, Ho to Er where it is practically 100%. Our X-ray results for R_2Co_{17} (Th_2Ni_{17}-type) are therefore in direct contradiction to those reported by Givord, Lemaire & Moreau (1972) and Givord, Givord & Lemaire (1972), according to whom 'Th_2Ni_{17} is an ideal structure and does not exist at all'. Our investigations show that this structure does exist, at least for Er_2Co_{17} (Table 4).

The R_2Co_{17} compounds of the Th_2Ni_{17}-type structure (R = Y, Ce, Dy and Ho) seem to be defect-type, because the calculated X-ray intensities of a number of reflexions come out to be much higher than those of the observed ones (Table 4). A study of the phase-factors of the Th_2Ni_{17}-type structures has shown that at least 1–2 atoms per cell are statistically missing in these compounds. To verify this X-ray result, we measured the densities of Y_2Co_{17}, Dy_2Co_{17} and Er_2Co_{17} of the Th_2Ni_{17}-type (Table 5). It is seen that the density data support the X-ray results.

Table 5. *Experimental and theoretical values of* 'NM' *for* R_2Co_{17}

NM_{exp} = Density $\times \sqrt{3}/2 \times a^2 \times c/1 \cdot 66$
$NM_{theor} = n(at.wt)_R + m(at.wt.)_{Co}$

R_2Co_{17}	Density (exp)	NM_{exp}	R_2Co_{17}	NM_{theor} R_2Co_{16}	R_2Co_{15}
Y_2Co_{17}	7·55	2234·8	2359·3	2241·5	2123·6
Dy_2Co_{17}	8·292	2454·9	2653·7	2535·9	2417·9
Er_2Co_{17}	9·20	2696·9	2672·8	—	—

From the above discussion it follows that the R_2Co_{17} intermetallic compounds crystallize in one or more of the following three modifications:

(a) TbCu$_7$-type (disordered);
(b) Th$_2$Ni$_{17}$-type (ordered or defect-type);
(c) Th$_2$Zn$_{17}$-type (ordered);

depending upon which R element is participating. The last two modifications are superstructures of the first one. The relation (Florio, Baenziger & Rundle, 1956)

between the c and a axes of these polymorphic forms of R_2Co_{17} is found to be (Table 2):

$$c(\text{Th}_2\text{Zn}_{17}\text{-type}) = \tfrac{3}{2}c(\text{Th}_2\text{Ni}_{17}\text{-type}) = 3c(\text{TbCu}_7\text{-type})$$
$$a(\text{Th}_2\text{Zn}_{17}\text{-type}) = a(\text{Th}_2\text{Ni}_{17}\text{-type}) = \sqrt{3}a(\text{TbCu}_7\text{-type}).$$

It is interesting to note that the R_2Co_{17} compounds having the Th$_2$Ni$_{17}$-defect type structure transform into R_2Co_{17} of the Th$_2$Zn$_{17}$-type structure on annealing at lower temperatures (Table 1 and Fig. 1). The transformation temperature increases as the degree of order
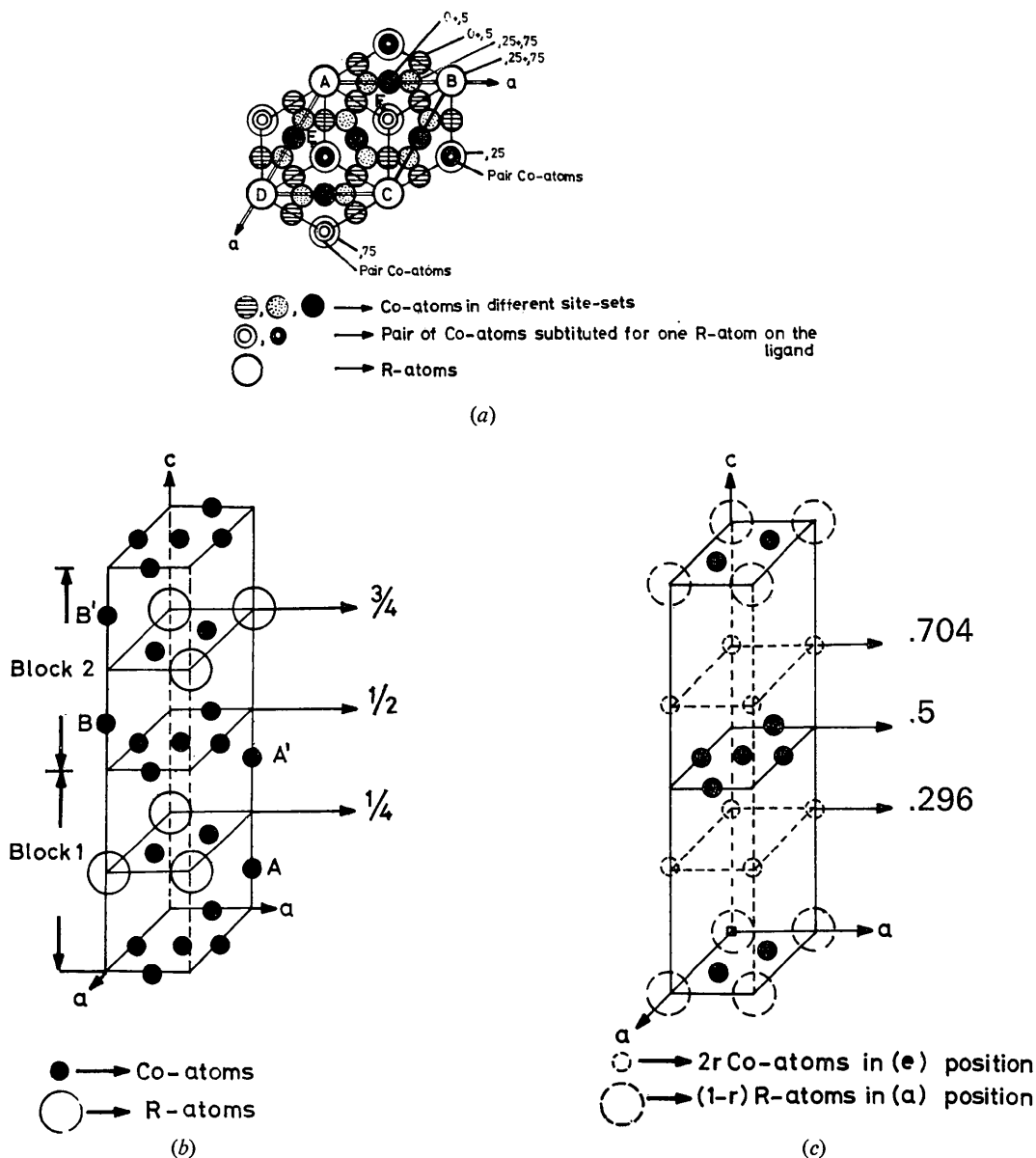

(a)

(b)

(c)

Fig. 2. (a) Basal-plane projection of R_2Co_{17} of the Th$_2$M$_{17}$-type structures (M = Ni or Zn). $ABCD$ is the unit cell. (b) $\frac{1}{3}$ of the unit cell $ABCD$ in (a), i.e. $AFCE$ in (a) showing the Th$_2$Ni$_{17}$-type structure. For the Th$_2$Zn$_{17}$-type structure a third block has to be added. AA', BB' are the pairs of the Co atoms substituted for one R atom. (c) Unit cell of the TbCu$_7$-type structure of the disordered R_2Co_{17} phase. The height of this cell is actually equal to that of block 1 or 2 in (b); for the sake of illustration, it has been extended. If the substitution is not ordered, this cell is similar to block 1 or 2 in (b) with $\frac{1}{2}$ of the block height added.
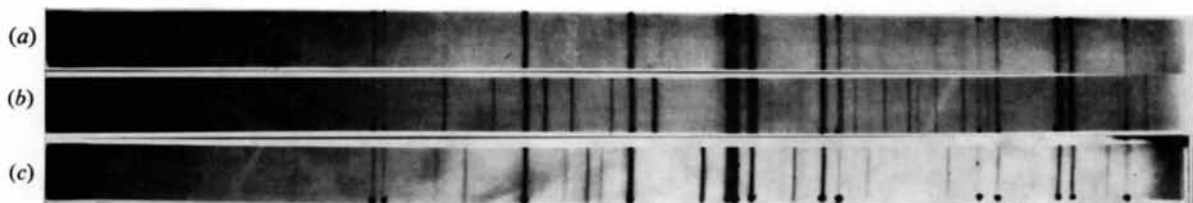
Fig. 3. Guinier X-ray diffraction photographs (a) of the Sm_2Co_{17} alloy annealed at 1320 °C for 2 h and subsequently quenched in liquid N_2. 14 h Co $K\alpha$; (b) of the Sm_2Co_{17} alloy annealed at 1100 °C for 3 days and subsequently quenched in liquid N_2. 14 h Co $K\alpha$; (c) of the Ce_2Co_{17} alloy annealed at 1100 °C for 8 days and subsequently quenched in liquid N_2. 8 h Co $K\alpha$. The diffraction lines marked at the top in (a) and at the bottom in (b) and (c) are the sub-structure lines.

of the Th_2Ni_{17}-type structure decreases. This suggests that the degree of order of the Th_2Ni_{17}-type structures of Pr_2Co_{17} and Nd_2Co_{17} is lowest. Therefore, the Th_2Ni_{17}-type compounds for these R elements do not exist. The degree of order of the Th_2Ni_{17}-type structures of Ce_2Co_{17} and Ho_2Co_{17} is nearly ideal. One therefore gets only traces of the Th_2Zn_{17}-type structure even after prolonged annealing at lower temperatures. Dy_2Co_{17} appears to lie in between these two extreme cases. This is the reason that both modifications *i.e.* $Th_2Ni_{17}+Th_2Zn_{17}$-type, are obtained in almost equal proportions below 1200 °C.

Since those R elements, studied in this work are uniformly distributed throughout the whole rare-earth series, the results obtained for their A_2B_{17} compounds can generally be applied to all the R_2Co_{17} compounds (Fig. 1).

Buschow (1966) and Givord, Givord & Lemaire (1972) have explained the polymorphism of R_2Co_{17} in terms of the radii ratios of R and Co atoms. No doubt the atomic radii of R and Co atoms are important factors in the formation of R_2Co_{17}. However, the atomic ratio model alone cannot explain the polymorphism of R_2Co_{17} over the rare-earth series and the degree of order of R_2Co_{17} of the Th_2Ni_{17}-type structure.

In our opinion, the valence-electron concentration and the electron-spatial correlation play a deciding role in the stabilization of one or more of the polymorphic forms of R_2Co_{17} for a particular R element at a particular temperature.

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Crystal and Molecular Structure of 1,2,3,4,5,6,7,8-Octaethylporphinatodichlorotin(IV) Nitromethane Solvate

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The structure of 1,2,3,4,5,6,7,8-octaethylporphinatodichlorotin(IV) has been determined from three-dimensional X-ray counter data. The compound crystallizes in the monoclinic space group $P2_1/a$ with a unit cell of $a = 16\cdot571$ (5), $b = 15\cdot173$ (5), $c = 8\cdot231$ (4) Å, $\beta = 101\cdot12$ (4)°. There are two molecules in the unit cell. The observed and calculated densities are $1\cdot35$ (2) and $1\cdot38$ g cm^{-3}. The structure was solved by Fourier methods and refined by least-squares techniques to a final conventional R index of 0·054 (based on F) for the 2541 reflections having $F^2 > 3\sigma(F^2)$. The metalloporphyrin is a distorted octahedral complex with chlorine atoms at the apices. There are two disordered solvent molecules of nitromethane per formula unit. The Sn–N bond lengths are 2·081 (5) and 2·083 (4) Å. These are quite long for metal–nitrogen distances in porphyrins, but very short compared to normal Sn–N bond distances. The Sn–Cl distance is 2·453 (2) Å. The macrocycle is planar with a macrocyclic angle between adjacent planes of 0·4°. Comparisons with other tin(IV) complexes show many similarities, but some striking differences, especially when *meso*-substituted porphyrins are considered.

Introduction

Recently there has been some interest in the structures of macrocyclic complexes of tin, both in the +2

and +4 oxidation states. These have exhibited a variety of coordination geometries including octahedral (Collins, Scheidt & Hoard, 1972; Cullen & Meyer, 1971a; Rodgers & Osborn, 1971), a four-coordinate phthalo-