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Rare Earth Cobalt Compounds with the A_2B_{17} Structure

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A series of new compounds corresponding to the formula R_2Co_{17} has been prepared, where R represents the rare earth elements Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm and Lu. The compounds Pr_2Co_{17}, Nd_2Co_{17}, Sm_2Co_{17}, Gd_2Co_{17} and Tb_2Co_{17} are isomorphous with Th_2Zn_{17} (space group $R\bar{3}m$), while Ho_2Co_{17}, Er_2Co_{17}, Tm_2Co_{17} and Lu_2Co_{17} were found to have the Th_2Ni_{17}-type structure (space group $P6_3/mmc$). The patterns of Ce_2Co_{17} and Dy_2Co_{17} were explained on the basis of a coexistence of the hexagonal high temperature modification and the rhombohedral low temperature modification. The volume of the formula unit R_2Co_{17} decreases with increasing atomic number of the rare earth element, except for Ce_2Co_{17} and Pr_2Co_{17}. In Ce_2Co_{17}, cerium appears to occur tetravalent, and in Pr_2Co_{17}, praseodymium seems to have the effective valency 3·3.

Introduction

In the course of studies of the magnetic and structural properties of intermetallic compounds between rare earths and cobalt, a series of new compounds of the approximate formula R_2Co_{17} has been prepared. The results of the magnetic investigation have previously been presented (Strnat, Hoffer, Ostertag & Olson, 1966). It is the purpose of this paper to report on the crystallographic data of this new group of compounds.

The structures of two rare earth cobalt compounds of the composition R_2Co_{17} have already been reported. Savitskii, Terekhova, Burov, Markova & Naumkin (1962) found Ce_2Co_{17} to have the Th_2Ni_{17} structure ($a=8·36$, $c=8·10$ Å) and Zarechnyuk & Kripyakevich (1963) confirmed these observations. The crystallographic data on Gd_2Co_{17} show discrepancies; Savitskii, Terekhova & Burov (1962) observed the phase Gd_2Co_{17} in the course of phase diagram studies and reported it to be isostructural with Th_2Zn_{17} ($a=8·55$, $c=12·45$ Å); Kripyakevich, Terekhova, Zarechnyuk & Burov (1963) found Gd_2Co_{17} to have the Th_2Ni_{17}-type structure ($a=8·37$, $c=8·14$ Å).

Experimental

A first series of samples was prepared by levitation melting of stoichiometric amounts of the rare earth element* and cobalt*. The samples were heated for 400 hours at 800°C and cooled to room temperature within 4 hours. To study the homogeneity range of the R_2Co_{17} structures, a second series of samples was synthesized. Six specimens, containing 87·00, 87·50, 88·24, 88·89, 89·47 and 90·00 at.% Co, were prepared for each rare earth-cobalt system. The specimens underwent a homogenization anneal for 200 hours at 1000°C and were subsequently quenched from various temperatures. The composition of the samples was studied after the heat treatment by chemical analysis. All specimens were examined metallographically. At approximately 900°C, the R_2Co_{17} structures appear to have their homogeneity region between 87·5 and 89·4 at.% Co. Above 900°C, the homogeneity range becomes broader and may even give rise to a continuous solid solubility region between RCo_5 and R_2Co_{17}. The crystallographic data presented in this paper were obtained from samples having a composition close to the cobalt-rich end of the R_2Co_{17} homogeneity range. Most of the samples contained a very slight excess of cobalt which could not be detected by X-ray diffraction. Its presence was indicated, however, by magnetic measurements (Curie point of Co) and by metallographic examination. The X-ray investigation was carried out on powders which were obtained by grinding the intermetallic compounds in an agate mortar under carbon tetrachloride. X-ray diffraction photographs were taken using a 114·6 mm diameter Debye–Scherrer camera along with the standard Norelco equipment. Iron-filtered cobalt radiation ($\lambda=1·7889$ Å) was employed.

The densities of Nd_2Co_{17} and Er_2Co_{17} powder specimens were determined as 8·53 and 9·15 g.cm^{-3} respectively, by the pycnometric method with n-octane as immersion fluid.

The structures of all compounds were indexed as hexagonal. Table 1 presents the parameters of the R_2Co_{17} structures. In order to facilitate comparison, the unit-cell dimensions of Pr_2Co_{17}, Nd_2Co_{17}, Sm_2Co_{17}, Gd_2Co_{17} and Tb_2Co_{17} are listed for the triply primitive hexagonal cells although the systematic extinctions of reflections other than $h-k+l=3n$ or $-h+k+l=3n$ indicate rhombohedral symmetry for these compounds. The lattice parameters a_0 were obtained from graphical extrapolations of $hk0$ powder data after Nelson & Riley (1945) while the c_0 parameters were obtained from least-squares plots using the so determined a_0 parameters and hkl powder data with large l. Table 2 presents the observed and calculated interplanar spacings of Pr_2Co_{17},

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* The rare earth elements and cobalt were of 99·9 % nominal purity.

Table 1. *Crystallographic data for* R_2Co_{17} *compounds*

	a_0	c_0	c/a	Calculated density	Space group	Formula units per unit cell
Ce_2Co_{17}	8·335±0·002 Å	12·153±0·004 Å	1·458	8·73 g.cm^{-3}	$R\bar{3}m$	3
Ce_2Co_{17}	8·335±0·002	8·102±0·004	0·972	8·73	$P6_3/mmc$	2
Pr_2Co_{17}	8·415±0·002	12·170±0·004	1·446	8·56	$R\bar{3}m$	3
Nd_2Co_{17}	8·441±0·002	12·181±0·004	1·443	8·55	$R\bar{3}m$	3
Sm_2Co_{17}	8·402±0·002	12·172±0·004	1·449	8·72	$R\bar{3}m$	3
Gd_2Co_{17}	8·361±0·002	12·159±0·004	1·453	8·91	$R\bar{3}m$	3
Tb_2Co_{17}	8·341±0·002	12·152±0·004	1·457	8·98	$R\bar{3}m$	3
Dy_2Co_{17}	8·335±0·002	12·153±0·004	1·458	9·04	$R\bar{3}m$	3
Dy_2Co_{17}	8·335±0·002	8·102±0·003	0·972	9·04	$P6_3/mmc$	2
Ho_2Co_{17}	8·335±0·002	8·101±0·003	0·973	9·07	$P6_3/mmc$	2
Er_2Co_{17}	8·301±0·002	8·100±0·003	0·976	9·18	$P6_3/mmc$	2
Tm_2Co_{17}	8·285±0·002	8·095±0·003	0·977	9·24	$P6_3/mmc$	2
Lu_2Co_{17}	8·247±0·002	8·093±0·003	0·981	9·41	$P6_3/mmc$	2

Table 2. *Powder diffraction data for* Pr_2Co_{17}, Nd_2Co_{17}, Sm_2Co_{17}, Gd_2Co_{17} *and* Tb_2Co_{17}

	Pr_2Co_{17}		Nd_2Co_{17}		Sm_2Co_{17}		Gd_2Co_{17}		Tb_2Co_{17}		
hkl	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	I_{obs}
101	6·257	6·262	6·257	6·2685	6·238	6·244	6·219	6·221	6·200	6·209	*vvw*
102	4·670	4·671	4·680	4·6794	4·670	4·667	4·660	4·656	4·649	4·649	*vvw*
110	4·210	4·208	4·219	4·2210	n.o.	4·201	n.o.	4·180	n.o.	4·170	*vvw*
201	n.o.	3·491	n.o.	3·5012	3·475	3·485	n.o.	3·470	3·453	3·462	*vvw*
202	n.o.	3·126	3·128	3·1342	3·110	3·122	3·106	3·110	3·101	4·104	*vvw*
113	2·916	2·920	2·924	2·9262	2·916	2·918	2·904	2·910	2·900	2·905	*m*
104	2·806	2·808	2·810	2·8110	2·803	2·807	2·795	2·803	2·799	2·800	*w*
121	2·681	2·687	2·695	2·6948	2·681	2·682	2·665	2·670	2·659	2·664	*vvw*
122	2·506	2·509	2·515	2·5164	2·503	2·506	2·492	2·495	2·486	2·490	*vw*
300	2·426	2·429	2·437	2·4369	2·425	2·425	2·413	2·413	2·408	2·408	*m-s*
204	2·322	2·335	2·327	2·3397	2·317	2·334	2·310	2·328	2·319	2·325	*m*
105		2·309		2·3112		2·308		2·305		2·303	
220	2·102	2·104	2·110	2·1105	2·098	2·100	2·088	2·090	2·085	2·085	*vs*
303	2·083	2·084	2·089	2·0895	2·081	2·082	2·072	2·074	2·068	2·070	*vs*
124	2·041	2·042	2·044	2·0463	2·041	2·040	2·030	2·034	2·028	2·030	*w-m*
006	2·026	2·028	2·029	2·0301	2·025	2·028		2·027		2·025	*m-s*
205		2·024		2·0272		2·023	2·017	2·019	2·015	2·016	*w*
132	1·919	1·918	1·924	1·9238	1·916	1·915	1·907	1·907	1·901	1·902	*vvw*
223	1·867	1·868	1·871	1·8726	1·866	1·865	1·855	1·858	1·855	1·854	*m-s*
116	1·826	1·827	1·829	1·8295	1·825	1·827	1·820	1·824	1·818	1·822	*m*
125		1·824		1·8274		1·823		1·818		1·815	
401	1·799	1·802	1·810	1·8075	1·796	1·799	1·790	1·790	1·789	1·786	*vvw*
402	1·745	1·745	1·751	1·7506	1·742	1·743	1·734	1·735	1·733	1·731	*vw*
107	1·692	1·691	1·694	1·6928	1·691	1·691	1·689	1·689	1·689	1·688	*vw*
134	1·684	1·684	1·687	1·6877	1·680	1·682	1·675	1·676	1·673	1·672	*w*
232	1·613	1·612	1·619	1·6170	1·611	1·610	1·601	1·602	1·598	1·599	*vw*
207	1·565	1·569	1·569	1·5712	1·565	1·569	1·564	1·564	1·563	1·564	*vvw*
404		1·563		1·5671		1·561	1·552	1·555	1·550	1·552	*vw*
306	1·555	1·557	1·558	1·5598	1·555	1·556		1·552		1·550	*w-m*
135		1·555		1·5584		1·553		1·548		1·546	*w-m*
143	1·482	1·481	1·486	1·4848	1·477	1·478	1·470	1·472	1·468	1·469	*w-m*
127	1·468	1·470	1·471	1·4724	1·466	1·470	1·461	1·467	1·468	1·465	*w-m*
234		1·465		1·4691		1·463		1·458	1·455	1·455	
226	1·460	1·460	1·463	1·4631	1·457	1·459	1·454	1·455	1·451	1·453	*m-s*
405		1·459		1·4620		1·457		1·452		1·449	
330	1·403	1·403	1·406	1·4070	1·401	1·400	1·394	1·393	1·392	1·390	*w-m*
235	1·379	1·378	1·383	1·3815	1·376	1·376	1·372	1·372	1·370	1·369	*w*
242	1·344	1·343	1·348	1·3474	1·341	1·341	1·336	1·335	1·333	1·332	*vvw*
333	1·327	1·326	1·329	1·3294	1·322	1·323	1·318	1·318	1·317	1·315	*vs*
137	1·316	1·318	1·319	1·3205	1·313	1·317	1·309	1·314	1·308	1·312	*w-m*
504		1·315		1·3181		1·313		1·307		1·305	
119	1·288	1·287	1·288	1·2888	1·290	1·288	1·286	1·286	1·285	1·285	*w-m*
152	1·278	1·279	1·282	1·2835	1·278	1·278	1·271	1·272	1·268	1·269	*vvw*
407	1·256	1·258	1·257	1·2602	1·255	1·257	1·250	1·253	1·248	1·251	*w-m*
244		1·255		1·2582		1·253		1·248		1·245	
146	1·251	1·251	1·254	1·2544	1·249	1·250	1·245	1·256	1·242	1·244	*vw*
505		1·250		1·2537		1·249		1·244		1·242	
600	1·215	1·215	1·218	1·2184	1·212	1·212	1·207	1·207	1·204	1·204	*vs*

Table 3. *Powder diffraction data for* Ho_2Co_{17}, Er_2Co_{17}, Tm_2Co_{17} *and* Lu_2Co_{17}

	Ho_2Co_{17}		Er_2Co_{17}		Tm_2Co_{17}		Lu_2Co_{17}		
hkl	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	I_{obs}
101	5·381	5·389	5·367	5·3766	5·367	5·369	5·354	5·355	*vw*
110	4·152	4·168	4·144	4·1505	n.o.	4·143	4·111	4·124	*vvw*
102	n.o.	3·532	3·522	3·5285	n.o.	3·525	n.o.	3·521	*vvw*
201	3·292	3·297	2·382	3·2854	3·272	3·280	3·262	3·267	*w*
112	2·897	2·904	2·888	2·8986	2·885	2·895	2·885	2·888	*m*
202	n.o.	2·694	2·685	2·6883	2·681	2·685	n.o.	2·678	*vvw*
121	2·583	2·571	2·574	2·5760	2·568	2·571	2·559	2·561	*w*
103	2·526	2·529	2·525	2·5276	2·525	2·526	2·524	2·524	*w*
300	2·400	2·406	2·395	2·3962	2·392	2·392	2·379	2·381	*s*
122	n.o.	2·263	2·256	2·2563	2·252	2·253	2·245	2·246	*vw*
203	2·163	2·162	2·156	2·1587	2·156	2·156	2·152	2·153	*m*
220	2·083	2·084	2·074	2·0752	2·070	2·071	2·060	2·062	*vs*
302	2·066	2·069	2·060	2·0623	2·057	2·059	2·052	2·052	*vs*
004	2·024	2·025	2·026	2·0250	2·022	2·024	2·023	2·023	*ms*
131	1·943	1·944	1·936	1·9360	1·932	1·932	1·920	1·924	*vw*
123	1·918	1·919	1·914	1·9152	1·913	1·913	1·909	1·908	*m*
222	1·852	1·853	1·846	1·8469	1·844	1·844	1·835	1·837	*m*
114	1·821	1·821	1·820	1·8199	1·817	1·818	n.o.	1·816	*vvw*
132	1·796	1·795	1·789	1·7888	1·785	1·786	1·775	1·779	*vvw*
204	n.o.	1·766	1·764	1·7642	n.o.	1·763	1·761	1·760	*vvw*
401	1·760	1·761	1·755	1·7545	1·752	1·751	n.o.	1·744	*vw*
124	1·623	1·626	1·624	1·6236	1·621	1·622	n.o.	1·619	*vvw*
231		1·622	1·615	1·6160	1·613	1·613	1·605	1·606	*vvw*
105	n.o.	1·581	1·580	1·5803	n.o.	1·579	n.o.	1·579	*vvw*
140	n.o.	1·575	1·569	1·5686	1·565	1·566	1·559	1·559	*vvw*
304	1·549	1·549	1·547	1·5466	1·545	1·545	1·543	1·542	*w-m*
232	n.o.	1·533	1·527	1·5274	1·525	1·525	n.o.	1·519	*vvw*
403	1·499	1·500	1·495	1·4960	1·495	1·494	1·489	1·489	*vvw*
205	1·477	1·478	1·477	1·4769	n.o.	1·476	n.o.	1·474	*vvw*
142	1·469	1·468	1·463	1·4628	1·461	1·460	1·455	1·454	*w-m*
224	1·453	1·452	1·450	1·4493	1·448	1·447	1·445	1·444	*m-s*
134	1·423	1·424	1·421	1·4207	1·418	1·419	1·414	1·415	*vvw*
501	1·421	1·421	1·416	1·4156	1·413	1·413	n.o.	1·407	*vw*
233	1·412	1·412	1·408	1·4074	1·404	1·405	1·400	1·400	*w-m*
125	1·392	1·393	1·392	1·3914	1·391	1·390	1·389	1·388	*vw*
330	1·389	1·389	1·385	1·3835	1·381	1·381	1·375	1·375	*w-m*
006	n.o.	1·350	1·351	1·3500	n.o.	1·349	n.o.	1·348	*vvw*
404	n.o.	1·347	1·343	1·3441	n.o.	1·342	n.o.	1·339	*vvw*
241	1·345	1·345	1·340	1·3398	1·336	1·337	1·331	1·331	*vvw*
332	1·314	1·314	1·310	1·3092	1·308	1·307	1·303	1·302	*s*
242	n.o.	1·293	1·288	1·2880	1·286	1·286	1·282	1·280	*vvw*
116	1·285	1·284	1·284	1·2837	1·283	1·283		1·282	*w-m*
234	1·281	1·282	1·276	1·2787	n.o.	1·277	n.o.	1·273	*vvw*
151		1·280		1·2750	1·274	1·273	n.o.	1·267	*vvw*
503	1·272	1·273	1·266	1·2690	1·265	1·267	1·261	1·262	*vvw*
135	1·259	1·259	1·258	1·2573	1·257	1·256	1·252	1·253	*vvw*
152	n.o.	1·235	1·230	1·2301	n.o.	1·228	n.o.	1·223	*vvw*
243	1·217	1·218	1·214	1·2135	1·216	1·216	1·207	1·207	*w-m*
405	1·206	1·206	1·203	1·2033	1·202	1·202	n.o.	1·199	*vvw*
600	1·203	1·203	1·198	1·1980	1·197	1·196	1·190	1·190	*vs*

Nd_2Co_{17}, Sm_2Co_{17}, Gd_2Co_{17} and Tb_2Co_{17}, Table 3 those of Ho_2Co_{17}, Er_2Co_{17}, Tm_2Co_{17} and Lu_2Co_{17}.

The intensities of reflections of two representative structures, Nd_2Co_{17} and Er_2Co_{17}, were calculated. It was assumed that Nd_2Co_{17}, representing also the similar structures Pr_2Co_{17}, Sm_2Co_{17}, Gd_2Co_{17} and Tb_2Co_{17}, has the Th_2Zn_{17}-type structure, space group $R\bar{3}m$ (D^5_{3d}) (Makarov & Vinogradov, 1956). Er_2Co_{17}, being isostructural with Ho_2Co_{17}, Tm_2Co_{17} and Lu_2Co_{17}, was assumed to have the Th_2Ni_{17}-type structure, space group $P6_3/mmc$ (D^4_{6h}) (Florio, Baenzinger & Rundle, 1956).

The computation of the relative intensities of reflections was carried out according to the equation

$$I_{hkl}=g\ .\ \mathrm{Lp}\ .\ |F^2|\ .\ A(\theta)$$

where I_{hkl} is the relative intensity of a reflection, g the multiplicity factor, F the structure factor and $A(\theta)$ the absorption factor, Lp is the combined Lorentz-polarization factor. The wavelength used to compute the Lp factor was 1·7889 Å. A μr value of 4·2 was used to calculate the absorption factors for Nd_2Co_{17} as well as for Er_2Co_{17}. In the calculation of the structure factors, the atomic scattering factors of Nd and Er as listed in *International Tables for X-ray Crystallography* (1962) and of Co as given by Thomas & Umeda (1957) were used.

The atomic positions of Nd_2Co_{17}, in terms of $R\bar{3}m$ and hexagonal axes, are:

$\mathrm{Nd_{I}}$ in 6(*c*) ($z=\frac{1}{3}$), $\mathrm{Co_{I}}$ in 6(*c*) ($z=0{\cdot}1$), $\mathrm{Co_{II}}$ in 9(*d*), $\mathrm{Co_{III}}$ in 18(*f*) ($x=\frac{1}{3}$), $\mathrm{Co_{IV}}$ in 18(*h*) ($x=\frac{1}{6}$, $z=\frac{1}{6}$).

The structure of Er_2Co_{17} has atoms in the following positions of space group $P6_3/mmc$:

Er_{I} in 2(*b*), Er_{II} in 2(*c*), Co_{I} in 4(*f*) ($z=0{\cdot}89$),
Co_{II} in 6(*g*), Co_{III} in 12(*j*) ($x=\frac{1}{3}$, $y=0$),
Co_{IV} in 12(*k*) ($x=\frac{1}{6}$, $z=0$).

The results of the computations are shown in Tables 5 and 6. The observed intensities* are, in general, in

Table 4. *Powder diffraction data of* Ce_2Co_{17} *and* Dy_2Co_{17}

Ce_2Co_{17}	Dy_2Co_{17}		Th_2Zn_{17}-type		Th_2Ni_{17}-type	
d_{obs}	d_{obs}	I_{obs}	*hkl*	d_{calc}	*hkl*	d_{calc}
5·382	5·386	*vvw*			101	5·389
4·168	4·160	*vw*	110	4·168	110	4·168
3·458	3·452	*vvw*	201	3·460		
n.o.	3·282	*vvw*			201	3·297
3·101	2·997	*vvw*	202	3·103		
2·900	2·893	*m*	113	2·904	112	2·904
2·799	2·799	*vw*	104	2·800		
2·662	2·658	*vvw*	121	2·662		
2·583	2·583	*vw*			121	2·586
2·528	2·528	*vvw*			103	2·529
2·489	2·489	*vvw*	122	2·489		
2·405	2·402	*m-s*	300	2·406	300	2·406
2·319	2·317	*w-m*	204 105	2·324 2·303		
2·161	2·160	*w-m*			203	2·162
2·803	2·081	*vs*	220	2·084	220	2·084
2·068	2·067	*vs*	303	2·069	302	2·069
2·027	2·027	*m-s*	124 006	2·030 2·025	004	2·025
2·016	2·016	*vw*	205	2·016		
1·921	1·922	*w*			123	1·921
1·852	1·853	*s*	223	1·852	222	1·852
1·819	1·817	*w-m*	116 125	1·822 1·815	114	1·821
1·785	1·785	*vvw*	401	1·785		
1·761	1·762	*vw*			401	1·761
1·728	n.o.	*vvw*	402	1·729		
1·687	n.o.	*vvw*	107	1·688		
1·672	1·672	*vvw*	134	1·672		
1·640	1·641	*vw*	232	1·641		
1·623	1·624	*vvw*			124 231	1·626 1·622
1·574	1·574	*vw*	140	1·575	140	1·575
1·549	1·549	*m*	404 306 135	1·551 1·549 1·545	304	1·549
1·467	1·467	*m*	143 127	1·468 1·465	142	1·468
1·452	1·451	*s*	243 226 405	1·454 1·452 1·449	224	1·452
1·414	1·415	*w-m*			233	1·414
1·392	1·393	*vvw*			125	1·393
1·388	1·388	*m*	330	1·389	330	1·389
1·367	1·368	*vw*	235	1·369		
1·351	n.o.	*vvw*	009	1·350	006	1·350
1·345	1·346	*vvw*			241	1·345
1·314	1·314	*vs*	333 137	1·314 1·312	332	1·314
1·303	1·304	*vvw*	504	1·304		
1·285	1·286	*m*	119	1·284	116	1·284
1·281	1·280	*vvw*			234 151 503	1·282 1·280 1·275
1·267	1·267	*vvw*	152	1·268		
1·259	1·259	*vvw*			135	1·259
1·250	1·249	*vvw*	407	1·251		
1·242	1·242	*w*	244 505	1·244 1·241		
1·220	1·220	*w*			243	1·220
1·206	1·206	*vvw*			405	1·206
1·203	1·203	*vs*	600	1·203	600	1·203

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* The intensities of the diffraction lines were measured with a Joyce Loebl double beam microdensitometer.

satisfactory agreement with the calculated intensities, although in a few cases discrepancies are obvious. These discrepancies are most likely caused by the fact that practically all Co atoms were assumed to occupy ideal positions. It is thought that a refinement of the Co positions might lead to a considerably closer agreement of I_{obs} and I_{calc}.

The powder data of Ce_2Co_{17} and Dy_2Co_{17} might be interpreted on the basis of a single-phase structure (U_2Zn_{17}-type, Makarov & Vinogradov, 1956) with the unit-cell dimensions: $a=8{\cdot}335$, $c=24{\cdot}306$ Å. A two-phase explanation, as presented in Tables 1 and 5, appeared, however, more reasonable since it was observed that a variation of temperature and stoichiometry results in a change of the intensities of one set of reflections (Th_2Zn_{17}-type) relative to the other (Th_2Ni_{17}-type). Patterns of samples quenched from various temperatures indicated that the Th_2Ni_{17} structure is the high-temperature-stable modification. It might be mentioned that by using quenching techniques, the Th_2Ni_{17}-type structure could also be obtained for Gd_2Co_{17} and Tb_2Co_{17} which have, without any doubt, the Th_2Zn_{17}-type structure as room-temperature-stable form. The patterns of Ce_2Co_{17} and Dy_2Co_{17} showed furthermore that the Th_2Zn_{17}-type structure was associated with the rare earth rich side, the Th_2Ni_{17}-type structure with the cobalt-rich side of the homogeneity range. Similar observations have been reported by Zalkin, Sands, Bedford & Krikorian (1961) for the dimorphous behavior of Ti_2Be_{17} and Hf_2Be_{17}.

Discussion

The structure investigation of compounds with the approximate composition R_2Co_{17} showed that with the rare earths Ce, Pr, Nd, Sm, Gd, Tb, and Dy Th_2Zn_{17}-

Table 5. *Calculated and observed intensities of* Nd_2Co_{17}

hkl	I_{obs}	$I_{calc} . 10^{-6}$	*hkl*	I_{obs}	$I_{calc} . 10^{-6}$	*hkl*	I_{obs}	$I_{calc} . 10^{-6}$
101	n.o.	1·1	223	45	43·3	501	n.o.	0·2
102	3	4·6	116	7	5·1	502	n.o.	0·8
110	1	0·5	125	15	13·7	330	15	21·7
003	n.o.	0·4	401	3	0·2	208	n.o.	0·8
201	n.o.	0·5	402	4	1·1	235	9	8·7
202	3	2·6	107	4	2·8	241	n.o.	0·3
113	30	26·1	134	8	9·9	009	n.o.	0·9
104	9	11·6	231	n.o.	0·4	242	1	1·5
121	4	0·8	232	5	1·9	333	70	73·5
122	5	3·7	140	n.o.	0·5	137	14	4·0
300	49	54·4	207	2	2·5	504		3·5
204	31	8·6	404	4	4·4	151	n.o.	0·3
105		10·1	306	16	10·4	119	15	17·7
220	72	73·7	135		10·4	152	2	1·5
303	77	76·7	108	n.o.	0·8	407	11	2·0
124	15	13·8	143	12	9·0	244		6·8
006	41	46·1	127	15	4·5	146	2	2·5
205	8	8·1	234		7·8	505	4	4·0
131	n.o.	0·5	226	45	40·5	600	85	94·9
132	1	2·5	405		4·7			

Table 6. *Calculated and observed intensities of* Er_2Co_{17}

hkl	I_{obs}	$I_{calc} . 10^{-5}$	*hkl*	I_{obs}	$I_{calc} . 10^{-5}$	*hkl*	I_{obs}	$I_{calc} . 10^{-5}$	*hkl*	I_{obs}	$I_{calc} . 10^{-5}$
101	3	2·4	221	n.o.	0·0	304	10	7·9	305	n.o.	0·0
110	2	1·6	130	n.o.	0·1	141	n.o.	0·0	241	1	1·2
002	n.o.	0·7	104	n.o.	1·0	232	2	1·9	106	n.o.	0·0
111	n.o.	0·0	131	2	1·9	115	n.o.	0·0	332	45	46·8
200	n.o.	0·0	123	14	15·3	403	2	2·5	150	n.o.	0·0
102	1	2·1	222	18	21·3	205	n.o.	0·7	242	15	1·6
201	3	1·1	114	1	1.3	142	15	13·6	116		13·7
112	25	21·7	400	n.o.	0·0	224	30	28·4	234	4	2·2
120	n.o.	0·1	303	n.o.	0·0	500	n.o.	0·0	225		0·0
003	n.o.	0·0	132	1	2·5	134	3	2·4	151		1·1
202	1	1·3	204	1	0·9	501	1	0·3	503	3	2·1
121	4	3·1	401	1	0·4	233	10	9·0	206	n.o.	0·0
103	3	6·4	230	n.o.	0·1	125	4	2·5	135	2	2·3
300	39	38·8	223	n.o.	0·0	330	12	14·6	144	n.o.	1·1
301	n.o.	0·0	402	n.o.	0·5	331	n.o.	0·0	333	n.o.	0·0
113	n.o.	0·0	124	1	3·0	240	n.o.	0·1	152	1	1·5
122	5	3·9	005	n.o.	0·0	143	n.o.	0·0	243	11	8·2
203	18	4·8	231	2	1·4	502	n.o.	0·4	126	n.o.	0·1
220	49	48·9	133	7	10·9	006	1	0·9	405	1	0·6
302	51	50·1	105	2	0·7	404	1	0·6	600	55	59·6
004	32	30·7	140	2	0·9						

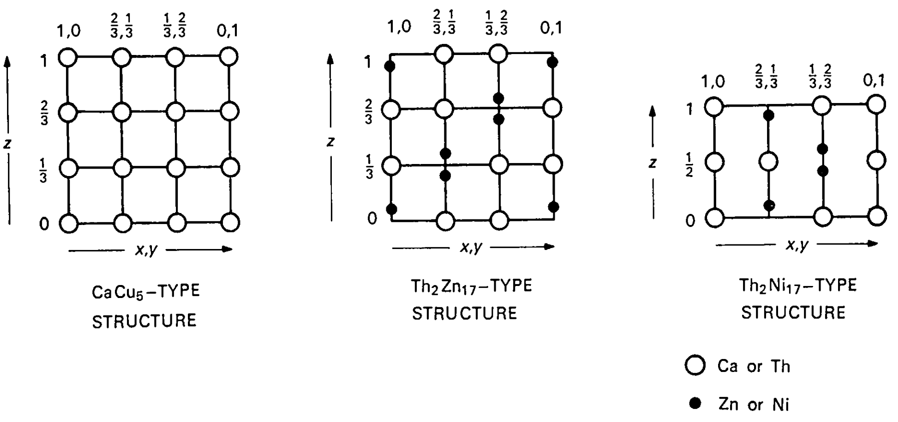

Fig. 1. Relationship between the structure types of $CaCu_5$, Th_2Zn_{17} and Th_2Ni_{17}.

type structures are formed at room-temperature. The corresponding high-temperature-stable modification is isomorphous with Th_2Ni_{17}. The compounds Ho_2Co_{17}, Er_2Co_{17}, Tm_2Co_{17} and Lu_2Co_{17} exhibit the Th_2Ni_{17} structure only. The observed coexistence of the hexagonal and the rhombohedral modification in the specimens of Ce_2Co_{17} and Dy_2Co_{17} is very likely caused by a low transformation temperature which would not allow the crystals to approach complete equilibrium. The transformation temperature may also vary with the stoichiometry which could explain the observed association of the Th_2Zn_{17}-type structure with the rare earth rich side, that of the Th_2Ni_{17}-type structure with the cobalt rich side of the homogeneity range.

Both A_2B_{17}-structures types are closely related. They are derived from an AB_5-structure ($CaCu_5$-type) by a systematic replacement of each third A atom by a pair of B atoms within the basal plane. The stacking of the thus formed basic layers in the sequence *abcabcabc*... leads to the rhombohedral structure type of Th_2Zn_{17}, that of *ababab*... to the hexagonal structure type of Th_2N_{17} (Fig. 1).

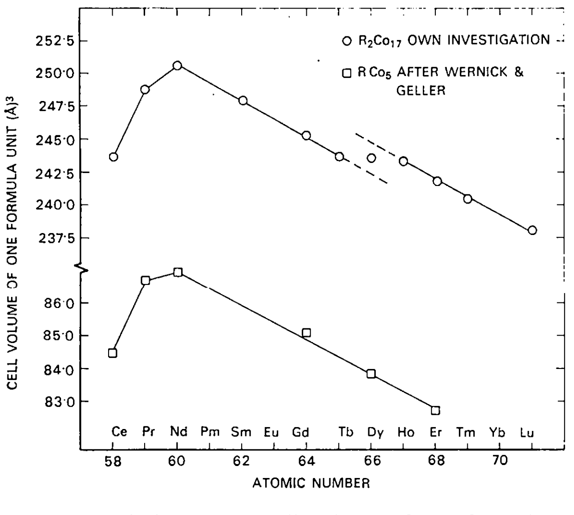

Fig. 2. The variation of the cell volume of one formula unit with the atomic number of the rare earth elements.

Fig. 2 shows the variation of the volume per formula unit R_2Co_{17} with the atomic number of the rare earth elements. The volumes decrease from Nd_2Co_{17} to Lu_2Co_{17} as a result of the lanthanide contraction. The cell dimensions of Ce_2Co_{17} and Pr_2Co_{17} are considerably smaller than expected. Wernick & Geller (1959) observed a similar phenomenon for the RCo_5 compounds (Fig. 2). The unit-cell dimensions of Ce_2Co_{17} and Pr_2Co_{17} suggest that cerium and praseodymium have valencies greater than three. Size considerations and magnetic measurements (Strnat *et al.*, 1966) indicate that Ce has a valency of four in Ce_2Co_{17}, Pr an effective valency of 3·3 in Pr_2Co_{17}.

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