R$_{12}$Co$_7$ Compounds with R=Gd, Tb, Dy, Ho, Er

By Wade Adams

AFML/M.B.P., Wright Patterson Air Force Base, Ohio 45433, U.S.A.

Jean-Michel Moreau

*Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 Quai Ernest-Ansermet,
CH-1211 Genève 4, Switzerland and Centre Universitaire de Savoie,
I.U.T. Annecy et Laboratoire de Magnétisme, CNRS, Grenoble, France*

Erwin Parthé

*Laboratoire de Cristallographie aux Rayons X, Université de Genève,
24 Quai Ernest-Ansermet, CH-1211 Genève 4, Switzerland*

and Jacques Schweizer*

University of Dayton, Research Institute, Dayton, U.S.A.

Abstract. Ho$_{12}$Co$_7$ crystallizes with a new monoclinic structure type. Space group $P2_1/c$ (No. 14); $a=8\cdot327$ (6), $b=11\cdot191$ (4), $c=13\cdot871$ (5) Å, $\beta=138\cdot8$ (1)°; $Z=2$, $D_m=9\cdot51$, $D_x=9\cdot33$ g cm^{-3}; μ(Mo $K\alpha)=485$ cm^{-1}. Weissenberg films, Patterson method, absorption correction, least-squares refinement. $R=0\cdot08$ for 850 independent reflections. Gd$_{12}$Co$_7$, Tb$_{12}$Co$_7$, Dy$_{12}$Co$_7$ and Er$_{12}$Co$_7$ are isostructural with Ho$_{12}$Co$_7$. The four different types of Co-centered rare-earth polyhedra are identical to the four different types of Rh-centered rare-earth polyhedra found in Y$_3$Rh$_2$. They are a trigonal prism, a cube, an Archimedian antiprism and a truncated Archimedian antiprism.

Introduction. Phase diagrams for the systems Gd–Co, Dy–Co, Ho–Co, Er–Co and Y–Co have been reported by Buschow (1971). At 37 at.% Co all these diagrams show the presence of a phase labeled R$_x$Co (R=Gd, Dy, Ho, Er, Y) with congruent melting behavior. In fact three different compounds have been identified in the Y–Co system with compositions close to 40 at.% Co, namely hexagonal Y$_4$Co$_3$ (Lemaire, Schweizer & Yakinthos, 1969), orthorhombic Y$_3$Co$_2$ (Moreau, Parthé & Paccard, 1975) and monoclinic Y$_8$Co$_5$ (Moreau, Paccard & Parthé, 1976a). In the systems with Gd, Tb, Dy, Ho and Er only two compounds are found, one being isotypic with hexagonal Y$_4$Co$_3$ and the other crystallizing with an unknown crystal structure. The purpose of this paper is to present the results of a structure determination of this phase, for which the exact composition has been found to be R$_{12}$Co$_7$ with 36·8 at.% Co.

The alloys were made from commercially available elements of high purity: rare earth 99·9% and Co

99·99%. Samples of Ho$_{12}$Co$_7$ were prepared by conventional arc-melting techniques and then annealed for 7 days at 750°C. From the crushed button, a single crystal was isolated, with a pseudo-cylindrical shape: a long axis of 0·157 mm and a diameter varying between 0·067 and 0·095 mm. The diffraction study was carried out on this crystal.

Weissenberg photographs showed the crystal to be monoclinic with the unequivocal space group $P2_1/c$ (systematic absences, $h0l$ with l odd and $0k0$ with k odd).

Lattice constants and intensities were measured on Weissenberg films with Zr-filtered Mo $K\alpha$ radiation. Intensities were estimated by comparison with a standard. A cylindrical absorption correction was made with a calculated value of $\mu R=2\cdot3$, corresponding to an average diameter of 0·081 mm. An empirical correction based on the comparison of several equivalent reflections was also applied to take into account the varying diameter of the cylinder.

The volume of the unit cell together with density measurements and space-group restrictions indicate that there are two formula units of Ho$_{12}$Co$_7$ per cell. Consequently it might be expected that the Ho atoms are in six different crystallographic sites with a multiplicity of 4 (general position $4e$), and the Co atoms in three general sites with multiplicity 4 and one special site with multiplicity 2.

The measured intensities were used to compute a sharpened Patterson function. Examination of Harker sections allowed the positioning of the six Ho atoms. From an electron density map computed with the observed amplitudes and the phases due to the contribution of Ho atoms it was possible to locate all expected Co atoms. All positional and isotropic thermal parameters refined satisfactorily by least squares. The scattering factors of *International Tables for X-ray Crystal-*

* Present address: D.R.F./CENG, B.P. 85, 38041 Grenoble Cédex, France.

lography (1968) were used. The final $R(=\sum|\Delta F|/\sum|F_o|)$ calculated with 850 observed reflections was 0·081. The final atomic parameters are listed in Table 1. Interatomic distances around all Co atoms are given in Table 2. All distances are similar to those found in rare-earth–Co compounds, except one very short Co(1)–Co(3) distance of 2·32 Å. However, a slightly larger Co–Co distance of 2·35 Å has been found in Y₈Co₅ (Moreau, Paccard & Parthé, 1976a) and of 2·37 Å also in Y₈Co₅ and in Y₃Co₂ (Moreau, Parthé & Paccard, 1975). As this structure is of a new type a listing of the low-angle reflections with corresponding intensities for X-ray powder diagram identification is given in Table 3 (Yvon, Jeitschko & Parthé, 1969).*

Table 1. *Atomic parameters for* Ho₁₂Co₇ *with e.s.d.'s in parentheses*

The Debye–Waller factor is defined as $\exp[-B(\sin\theta/\lambda)^2]$.
Space group $P2_1/c$.

	Equi-point	x	y	z	B (Å)²
Ho(1)	4e	0·8799 (7)	0·5704 (3)	0·8031 (4)	1·50 (7)
Ho(2)	4e	0·5982 (7)	0·2027 (3)	0·1729 (4)	1·44 (7)
Ho(3)	4e	0·9449 (7)	0·5719 (3)	0·5863 (4)	1·54 (7)
Ho(4)	4e	0·6879 (7)	0·2957 (3)	0·4604 (4)	1·63 (7)
Ho(5)	4e	0·8213 (7)	0·8400 (3)	0·6603 (4)	1·50 (7)
Ho(6)	4e	0·5565 (7)	0·0050 (3)	0·3472 (4)	1·59 (7)
Co(1)	4e	0·787 (2)	0·694 (1)	0·348 (1)	2·8 (2)
Co(2)	4e	0·678 (2)	0·089 (1)	0·594 (1)	1·6 (2)
Co(3)	4e	0·976 (2)	0·836 (1)	0·529 (1)	3·1 (3)
Co(4)	2b	½	0	0	2·3 (3)

The lattice parameters of Gd₁₂Co₇, Tb₁₂Co₇, Dy₁₂Co₇, Ho₁₂Co₇ and Er₁₂Co₇ are reported in Table 4. These parameters were obtained with *PARAM* (X-RAY system, 1972). The reflections were measured on films calibrated with Si, taken with a Guinier–de Wolff camera and Cu $K\alpha$ radiation. The variation of the cell parameters is a consequence of the normal lanthanide contraction. Patterns were difficult to obtain from powder specimens. Preparation of powders by crushing apparently destroyed the crystalline nature of the samples and powder patterns could only be obtained after heat treatment of the crushed melt. The resulting patterns lacked resolution but were adequate for identification of the structure involved.

Discussion. A projection of the Ho₁₂Co₇ structure on the (100) plane is shown in Fig. 1. One recognizes three types of Co-centered rare-earth polyhedra. Co(1) is at the center of a trigonal prism, Co(2) is surrounded by an Archimedian antiprism and Co(4) is at the center of a cube. For clarity of presentation the coordination figure around Co(3) has not been indicated. If 3·10 Å

---

* A list of structure factors and Table 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31807 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Interatomic distances of* Co *atoms in* Ho₁₂Co₇ *up to* 4 Å

All e.s.d.'s are less than 0·02 Å.

Co(1)–	Co(3)	2·32	Co(3)–	Co(1)	2·32
	*Ho(3)	2·82		†Ho(1)	2·79
	*Ho(5)	2·85		†Ho(2)	2·79
	*Ho(6)	2·89		†Ho(5)	2·92
	*Ho(1)	2·94		†Ho(6)	2·98
	*Ho(4)	2·95		†Ho(4)	3·07
	*Ho(2)	2·99		†Ho(1)	3·09
	Ho(4)	3·13		Ho(3)	3·12
	Ho(3)	3·41		Ho(6)	3·35
	Ho(6)	3·97		Ho(2)	3·57
				Co(3)	3·84

Co(2)–	‡Ho(1)	2·78	Co(4)–	2§Ho(1)	2·88
	Co(2)	2·81		2§Ho(2)	2·93
	‡Ho(6)	2·82		2§Ho(3)	3·02
	‡Ho(2)	2·86		2§Ho(4)	3·05
	‡Ho(5)	2·88			
	‡Ho(5)	2·89			
	‡Ho(6)	2·90			
	‡Ho(3)	2·93			
	‡Ho(4)	3·00			
	Ho(5)	3·94			

* Trigonal prism.
† Pentagon with one corner replaced by a pair of atoms perpendicular to the pentagon plane.
‡ Archimedian antiprism.
§ Cube.

Table 4. *Lattice constants for* R₁₂Co₇ *compounds with space group* $P2_1/c$

All e.s.d.'s are less than 0·05 Å. V=volume of the unit cell. n = number of atoms in the unit cell.

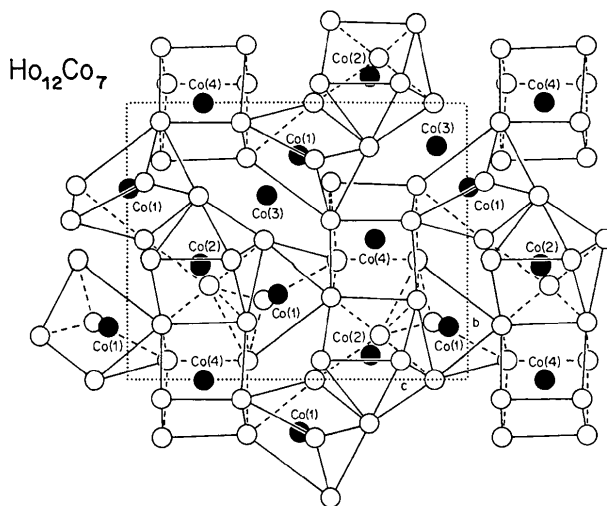|	a (Å)	b (Å)	c (Å)	β(°)	$(V/n)^{1/3}$
Gd₁₂Co₇	8·41	11·39	14·02	138·8	2·91
Tb₁₂Co₇	8·39	11·32	13·97	138·8	2·89
Dy₁₂Co₇	8·36	11·25	13·92	138·8	2·88
Ho₁₂Co₇	8·327	11·191	13·871	138·8	2·87
Er₁₂Co₇	8·30	11·16	13·82	138·7	2·86

Fig. 1. A projection of the Ho₁₂Co₇ structure on the (100) plane showing three of the four different types of Co-centered rare-earth polyhedra.

is to be considered the upper limit of the acceptable co-ordination distances, Co(3) is surrounded by six Ho atoms. The coordination can be described by two equivalent figures: either a truncated Archimedian antiprism with two opposite corners through the center of the antiprism missing or a pentagon with one corner being replaced by a pair of atoms along a direction perpendicular to the pentagon plane. The occurrence of these different coordination polyhedra with $Ho_{12}Co_7$ is rather unexpected, since the compounds on both sides, Ho_3Co and Ho_4Co_3, have a much simpler construction. They are all composed of Co-centered trigonal rare-earth prisms. However, in Ho_4Co_3 one of the nine Co atoms per unit cell is at the center of an octahedron. The structure of Y_3Rh_2 (Moreau, Paccard & Parthé, 1976b) is characterized by the same four types of transition metal-centered rare-earth polyhedra found in $Ho_{12}Co_7$.

The R_3Rh_2 alloys are brittle whilst those of the $R_{12}Co_7$ phase show typical plastic behavior. Hence there seems to be no correlation between the mechanical properties and the type of coordination polyhedra of the transition metal atoms.

References

Buschow, K. H. J. (1971). *Philips Res. Rep.* **26**, 49–64.
International Tables for X-ray Crystallography (1968). Vol. III, 2nd ed., pp. 210–212. Birmingham: Kynoch Press.
Lemaire, R., Schweizer, J. & Yakinthos, J. (1969). *Acta Cryst.* B**25**, 710–713.
Moreau, J.-M., Paccard, D. & Parthé, E. (1976a). *Acta Cryst.* B**32**, 496–500.
Moreau, J.-M., Paccard, D. & Parthé, E. (1976b). *Acta Cryst.* B**32**, 1767–1771.
Moreau, J.-M., Parthé, E. & Paccard, D. (1975). *Acta Cryst.* B**31**, 747–749.
X-RAY system (1972). Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
Yvon, K., Jeitschko, W. & Parthé, E. (1969). *A Fortran IV Program for the Intensity Calculation of Powder Patterns.* Université de Genève, Geneva.

N-2-(6'-Methyl)pyridyl-4-ethoxycarbonyl-2H,3H-pyrrole-2-one

By K. Simon* and James A. Ibers

Department of Chemistry, Northwestern University, Evanston, Illinois 60201, U.S.A.

Abstract. $C_{13}H_{14}N_2O_3$, monoclinic, $P2_1/c$ C_{2h}^5, $a = 8.840$ (2), $b = 7.880$ (2), $c = 17.814$ (4) Å, $\beta = 97.21$ (1)°, $D_x = 1.32$ (1), $D_c = 1.328$ g cm^{-3}, $Z = 4$. The compound was prepared and kindly supplied by Vasvári-Debreczy and Mészáros at the Chinoin Research Laboratories, Budapest. Recrystallization from $CHCl_3$ yielded suitable crystals. The final R index is 0.048 for the full-matrix least-squares refinement of 164 variables based on 2074 observations. The dihedral angle between the best planes of the five and six-membered rings is 5.2°.

Introduction. As part of a systematic study of pharmaceutically interesting N-(pyridyl)pyrrole derivatives Dvortsák, Náray-Szabó & Vasvári-Debreczy (1975) have correlated PMR chemical shift data with quantum mechanical calculations of charge distributions. The present crystal structure study was undertaken to

provide details on the conformation in the solid state of one such derivative.

Details of data collection on a Picker FACS-I diffractometer are given in Table 1 and parallel those described earlier (Corfield, Doedens & Ibers, 1967). The unit-cell parameters were determined from a least-squares refinement of 12 reflections in the range $50 < 2\theta$ (Cu $K\alpha_1$) $< 58°$. No decomposition occurred during data collection. The data were processed in the usual way, using a value of p of 0.04 in the estimation of standard deviations. The structure was solved by direct methods and refined by full-matrix least-squares methods utilizing the 2074 reflections above background. In the refinement the quantity $\sum w(|F_o| - |F_c|)^2$ was minimized, where $w = 4F_o^2/\sigma^2(F_o^2)$. Scattering factors for the nonhydrogen atoms were taken from Cromer & Waber (1974) while those for H were from Stewart, Davidson & Simpson (1965). From the initial E map the positions of all nonhydrogen atoms were clear. On a subsequent difference Fourier map the positions of all the H atoms were discernible. These

---

* Present address: Chinoin Pharmaceutical and Chemical Works, H-1325 Budapest, Hungary.