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Y_8Co_5, a New Monoclinic Phase with Co Centred Trigonal Prisms

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Y_8Co_5 crystallizes with a new monoclinic structure type. Space group $P2_1/c$ (No. 14), $a=7{\cdot}058$ (2), $b=7{\cdot}286$ (2), $c=24{\cdot}277$ (8)Å, $\beta=102{\cdot}11$ (7)°, $Z=4$. Symbolic addition method, counter technique, absorption correction, least-squares refinement. $R=0{\cdot}09$ for 725 reflexions. The structure is built up from structural units consisting of trigonal prisms formed by Y atoms and centred by Co atoms. These units are linked in different ways, some sharing faces, some edges and some corners. Nevertheless the value of $3\frac{3}{4}$ for the trigonal prism linkage coefficient is in agreement with the overall composition of the compound. The structure may be characterized by layers of double prisms with an arrangement related to FeB.

Introduction

Phase diagrams for the system Y–Co have been published by Buschow (1971), and by Ray (1974) who refers to an earlier proposal by Strnat, Ostertag, Adams & Olson (1965). There is general agreement that for stoichiometries ranging from 0 to 50 at.% Co at least two intermetallic phases exist: Y_3Co with the orthorhombic $Gd_3Ni(Fe_3C, NiAl_3)$ type (Buschow & van der Goot, 1969) and Y_4Co_3 with the hexagonal Ho_4Co_3 type (Lemaire, Schweizer & Yakinthos, 1969). Buschow, however, pointed out that close to Y_4Co_3 there are two other unidentified phases. One of these has been identified as orthorhombic Y_3Co_2 (Moreau, Parthé & Paccard, 1975) which crystallizes with a shift structure variation of the monoclinic Dy_3Ni_2 structure type (Moreau, Paccard & Parthé, 1974).

We present the results of our structure determination on the third phase existing in the region from 30 at.% to 50 at.% Co and for which the exact composition is Y_8Co_5 with 38 at.% Co.

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Experimental

The alloys were made from commercially available elements of high purity: Y 99·9%, Co 99·99%. Samples were prepared by conventional arc melting techniques and were then heat treated in sealed quartz tubes at 700°C for two days. Initial stoichiometries were such that the Co content ranged from 30 at.% to 40 at.%. X-ray photographs from powdered samples were obtained on a Guinier camera with Cu $K\alpha$ radiation. Small crystals suitable for X-ray analysis were isolated by mechanical fragmentation from the sample containing 38 at.% Co. Weissenberg photographs showed the crystals to be monoclinic, space group $P2_1/c$ (systematic absences; $h0l$ with l odd and $0k0$ with k odd).

Lattice constants and intensities were measured with graphite-monochromated Mo $K\alpha$ radiation and a

Philips PW1100 computer-controlled, four-circle goniometer with θ–2θ scan. Lattice parameters (Table 1) were refined by least squares to fit 2θ values for 22 reflexions. The 1243 measured intensities were corrected for background, Lorentz and polarization factors with *LECTIX*, *TRIX* and *DATRDN* (Flack, 1974*a*). The crystal was a thin irregular platelet, $70\times30\times10$ μm. Absorption corrections were made by the experimental method of Flack (1974*b*, 1975).

Intensities of symmetry-equivalent reflexions are automatically collected at intervals of 20° in Ψ for the range 0° to 180° for each reflexion. These measurements were made on a set of 10 independent reflexions and for θ values ranging from $\theta=7°$ to $\theta=20°$.

Table 1. *Crystallographic data for* Y_8Co_5

Space group $P2_1/c$ (No. 14)
$a=$ 7·058 (2) Å
$b=$ 7·286 (2)
$c=$ 24·227 (8)
$\beta=$102·11 (7)°
$Z=4$
$F(000)=1788$
$D_x=5{\cdot}48$ g cm^{-3}
μ(Mo $K\alpha$)$=445$ cm^{-1}

Structure determination and refinement

The phases of the 155 largest ($E>1{\cdot}5$) normalized structure factors were determined by symbolic addition with *LSAM* (Main, Woolfson & Germain, 1972). From the various sets of phases generated, the one with the highest absolute figures of merit was chosen. The E map calculated with these 155 reflexions revealed 8 Y and 5 Co atoms, all in general positions, and with reasonable interatomic distances. This was in agreement with calculations based on the atomic volume of the elements which indicated that the unit cell could accommodate four Y_8Co_5 units. Moreover this stoichiometry agreed with the original composition of the sample from which the crystal was chosen. Allowing variation of positional and isotropic thermal parameters the structure refined satisfactorily with *CRYLSQ* (X-RAY System, 1972). Relativistic Hartree–Fock scattering factors were used (Cromer & Mann, 1968). Anomalous dispersion corrections were taken from *International Tables for X-ray crystallography* (1974). The value of $R(\equiv\sum|\Delta F|/\sum|F_o|)$ was 0·09 with 725 observed reflexions for which $|F_o|>2\sigma_F$. A difference map did not show any significant electron density representing missing atoms in the structure.* The final positional and thermal parameters are listed in Table 2.

* A table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31228 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Atomic parameters for* Y_8Co_5 *with e.s.d.'s in parentheses*

Isotropic temperature factor is $\exp[-8\pi^2U(\sin\theta/\lambda^2]$. Space group $P2_1/c$. All atoms in equipoint 4(*e*).

	x	y	z	U (Å^2) $\times 10^2$
Y(1)	0·360 (1)	0·185 (1)	0·963 (1)	1·2 (2)
Y(2)	0·471 (1)	0·173 (1)	0·823 (1)	1·2 (2)
Y(3)	0·308 (1)	0·815 (1)	0·298 (1)	1·1 (2)
Y(4)	0·212 (1)	0·835 (1)	0·441 (1)	1·3 (2)
Y(5)	0·000 (1)	0·181 (1)	0·337 (1)	1·2 (2)
Y(6)	0·188 (1)	0·182 (1)	0·196 (1)	1·0 (2)
Y(7)	0·685 (1)	0·956 (1)	0·415 (1)	0·9 (2)
Y(8)	0·141 (1)	0·976 (1)	0·064 (1)	1·5 (2)
Co(1)	0·025 (1)	0·142 (1)	0·479 (1)	1·6 (3)
Co(2)	0·835 (1)	0·028 (1)	0·133 (1)	1·1 (3)
Co(3)	0·637 (1)	0·029 (1)	0·282 (1)	1·6 (3)
Co(4)	0·097 (1)	0·030 (1)	0·765 (1)	1·3 (3)
Co(5)	0·489 (1)	0·884 (1)	0·905 (1)	1·5 (3)

As this structure is of a new type, a listing of the low-angle reflexions with corresponding intensities for X-ray powder diagram identification is given in Table 3 (Yvon, Jeitschko & Parthé, 1969).

Table 3. *Calculated powder data for* Y_8Co_5 *for* Cr $K\alpha$ *radiation* ($\lambda=2{\cdot}29092$ Å)

Intensity calculated from 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	$10^3\cdot\sin^2\theta$	INTENSITY	H	K	L	$10^4\cdot\sin^2\theta$	INTENSITY
0	0	2	9.35	103.9	2	1	-5	159.70	60.3
0	1	1	27.06	56.0	1	2	-5	168.04	513.9
1	0	0	27.55	12.7	0	1	8	174.37	579.8
1	0	-2	30.17	0.6	2	0	4	174.56	3.0
0	1	2	34.07	28.9	1	1	-8	174.98	0.9
0	0	4	37.41	19.5	2	1	3	176.17	204.4
1	0	2	43.64	101.0	1	2	4	177.31	74.2
0	1	3	45.76	62.6	2	1	-6	178.69	292.9
1	1	-1	51.24	246.8	0	2	6	183.05	480.7
1	0	-4	51.49	22.6	1	2	-6	190.40	123.2
1	1	0	52.27	2.2	1	1	7	190.42	624.2
1	1	-2	54.89	39.2	2	1	4	199.28	255.4
1	1	1	57.98	66.1	1	2	5	201.72	27.1
0	1	4	62.13	8.1	2	1	-7	202.35	32.9
1	1	-3	63.21	7.8	1	0	8	204.15	160.3
1	1	2	68.36	7.5	2	2	-1	204.68	45.0
1	1	-4	76.21	25.0	2	2	-2	204.96	137.4
1	0	4	78.44	36.1	2	0	-8	205.98	208.7
0	1	5	83.18	7.0	2	2	0	209.08	18.4
1	1	3	83.42	13.5	2	2	-3	209.91	212.0
0	0	6	84.18	5.1	1	1	-9	211.36	0.1
1	0	-6	91.53	11.5	0	2	7	213.45	72.5
1	1	-5	93.89	14.9	0	1	9	214.12	14.1
0	2	0	98.87	0.1	1	2	-7	217.43	714.9
0	2	1	101.21	6.5	2	2	1	218.15	0.0
1	1	4	103.15	16.3	2	2	-4	219.55	357.9
2	0	-2	106.09	0.3	0	3	1	224.80	26.2
0	2	2	108.22	21.0	2	1	5	227.06	228.6
0	1	6	108.90	8.6	1	0	-10	227.71	163.9
2	0	0	110.21	10.9	1	1	8	228.86	15.3
1	1	-6	116.24	37.7	2	1	-8	230.69	45.6
0	2	3	119.92	45.3	1	2	6	230.81	162.8
2	0	-4	120.68	10.6	0	3	2	231.81	34.0
1	2	-1	125.39	12.3	2	2	2	231.90	49.6
1	2	0	126.42	36.7	0	0	10	233.83	10.4
1	1	5	127.57	53.3	2	2	-5	233.86	127.5
1	2	-2	129.04	166.7	2	0	6	234.80	0.3
2	1	-1	130.53	110.1	3	0	-2	237.11	0.1
2	1	-2	130.81	14.5	0	3	3	243.50	11.4
1	0	6	131.94	58.4	3	0	-4	244.96	53.6
1	2	1	132.13	333.1	3	0	0	247.96	0.0
2	0	2	133.03	16.3	0	2	8	248.52	118.0
2	1	0	134.92	2.2	1	3	-1	248.98	10.5
2	1	-3	135.76	153.3	1	2	-8	249.13	28.1
0	2	4	136.28	22.1	1	3	0	250.01	2.7
1	2	-3	137.36	3.4	2	2	3	250.33	80.9
0	1	7	139.30	0.1	1	1	-10	252.43	8.9
1	2	2	142.51	77.8	1	3	-2	252.63	3.2
1	1	-7	143.27	0.8	2	2	-6	252.84	70.4
2	1	1	144.00	10.5	1	3	1	255.72	943.0
2	1	-4	145.39	169.7	0	1	10	259.55	0.7
0	0	8	149.65	320.4	2	1	6	259.52	56.3
1	0	-8	150.26	21.8	0	3	4	259.87	59.7
1	2	-4	150.36	362.9	1	3	-3	260.95	1.1
2	0	-6	153.97	573.5	3	1	-2	261.83	92.0
1	1	6	156.66	210.7	3	1	-3	263.42	276.1
0	2	5	157.33	234.9	2	1	-9	263.71	43.7
1	2	3	157.57	52.3	1	2	7	264.57	9.6
2	1	2	157.75	1000.0	3	1	-1	264.92	376.2
					1	3	2	266.10	21.3

Discussion

A study of the crystal structures of rare earth (or Y)-transition element compounds R_mT_n with $m\geq n$ has revealed the prominence of a characteristic structural element: the trigonal prism formed by R and centred by T atoms [see for example Parthé (1970); Moreau, Paccard & Parthé (1974)]. These trigonal prisms occur also in Y_8Co_5 with all Co atoms at the prism centres. The interatomic distances between Co atoms and its neighbours up to 3·70 Å are given in Table 4. The six closest Y atoms form the surrounding trigonal prism.

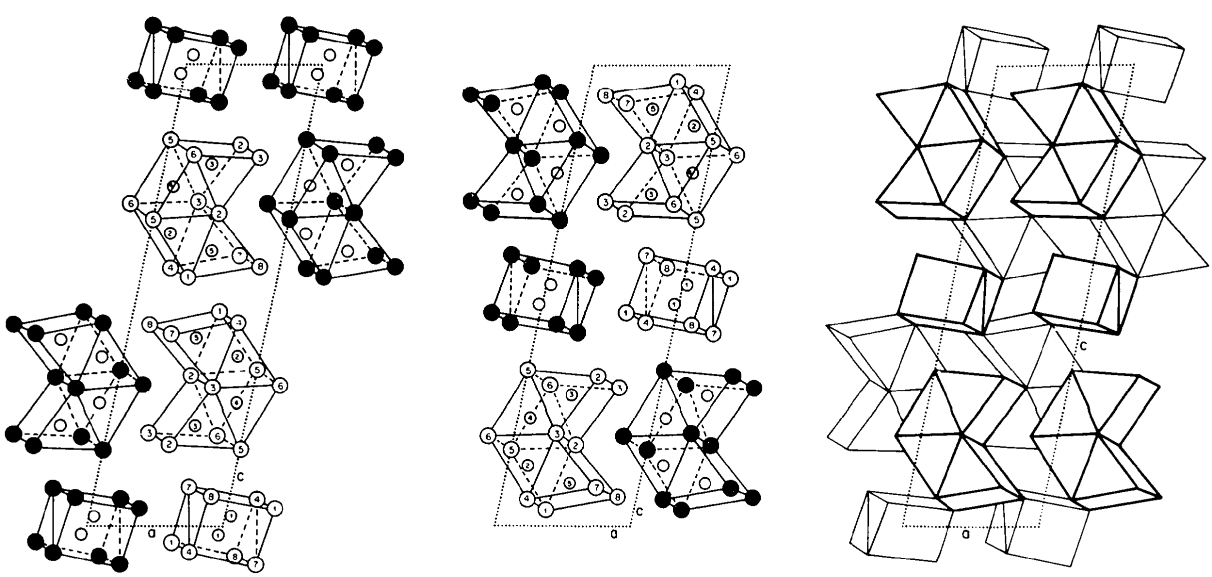
Table 4. *Interatomic distances of* Co *atoms in* Y_8Co_5 *up to* 3·70 Å

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

Co(1)–Co(1)	2·35
*Y(1)	2·78
*Y(4)	2·80
*Y(8)	2·81
*Y(4)	2·85
*Y(7)	2·90
*Y(7)	3·00
Y(5)	3·44
Y(8)	3·45
Co(2)–Co(5)	2·37
Co(4)	2·44
*Y(5)	2·81
*Y(4)	2·85
*Y(6)	2·86
*Y(1)	2·90
*Y(2)	2·98
*Y(3)	2·99
Y(8)	3·00
Co(3)–Co(4)	2·43
*Y(2)	2·75
*Y(6)	2·82
*Y(5)	2·85
*Y(3)	2·89
Co(3)–*Y(2)	2·91
*Y(3)	2·93
Y(7)	3·22
Y(6)	3·58
Co(4)–Co(3)	2·43
Co(2)	2·44
*Y(6)	2·84
*Y(6)	2·85
*Y(5)	2·87
*Y(5)	2·89
*Y(2)	2·92
*Y(3)	2·94
Y(3)	3·15
Co(5)–Co(2)	2·37
*Y(8)	2·75
*Y(4)	2·81
*Y(7)	2·82
*Y(2)	2·86
*Y(1)	2·87
*Y(3)	3·00
Y(1)	3·19
Y(6)	3·70

Except for Co(2) the seventh nearest Y atom is considerably further away. Four prisms, around Co(2), Co(3), Co(4) and Co(5), share one prism edge (parallel to the threefold prism axes) and form, to a first approximation, a semicircular structural unit with its main axis almost parallel to **b**. Each unit is connected along **b** with a unit below by means of a common prism base edge and similarly connected to a four-prism unit above. A centre of symmetry relates two prisms around two Co(1) atoms. They share a rectangular face and thus form a double prism whose main axis is almost parallel to **a**. The prism linkage can be seen in Fig. 1(*a*), (*b*), and (*c*) which presents a projection of the Y_8Co_5 structure along **b**.

Another description of the structure is given in Fig. 2(*a*) and (*b*) which shows the arrangement of the prisms in layers parallel to (001). In Fig. 2(*a*) the prisms around Co(3) and Co(4) at $z \sim \frac{1}{4}$ are joined by one rectangular face to form double prisms. The arrangement of these double prisms in zigzag chains is similar to the one found in the FeB type structure except that in FeB there are infinite bands of prisms instead of double prisms. In Fig. 2(*b*) are shown the double prisms around Co(2) and Co(5), both at $z \sim \frac{3}{8}$, and around two Co(1) atoms at $z \sim \frac{1}{2}$. If one considers only the Co(2)–Co(5) double prisms in this layer, the arrangement is similar to the FeB type but with every other double prism missing. The Co(1)–Co(1) double prism fills up the empty space but with a 90° rotation of its trigonal axis compared to FeB. As a consequence the Co(1)–Co(1) and Co(2)–Co(5) double prisms are displaced along **c**.



(*a*) (*b*) (*c*)

Fig. 1. The linkage of the trigonal prisms in Y_8Co_5 demonstrated in a projection along **b**. Large circles represent Y atoms, small circles at the centres of the prisms the 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 $\frac{1}{4} \le y_{Co} \le \frac{3}{4}$. (*b*) Arrangement of prisms centred by Co atoms with $\frac{3}{4} \le y_{Co} \le \frac{5}{4}$. (*c*) Superposition of drawings (*a*) and (*b*).

It is of interest to compare the structure of monoclinic Y_8Co_5 with the three other structures of similar composition: hexagonal Y_4Co_3, orthorhombic Y_3Co_2 and orthorhombic Y_3Co. For a comparative analysis of structures with trigonal prisms one may classify the structures according to the following scheme: (1) Do all R atoms participate in the formation of trigonal prisms? The answer is yes for all three structure types. (2) Are all T atoms at the centres of trigonal prisms? This is the case for Y_3Co, Y_3Co_2 and Y_8Co_5; however in Y_4Co_3 there is one extra Co atom which is octahedrally coordinated. (3) What is the value of the trigonal prism linkage coefficent, LC, which aids in the comparison of different structure types having trigonal prisms as prominent structural features? To calculate this coefficient, it is necessary to consider only prisms centred by T atoms. For each crystallographically different site of atom R one determines the number of trigonal prisms to which R belongs. LC is this number averaged over all R atom sites. The minimum value of LC is 1 which corresponds to an isolated trigonal prism. The maximum number is 12, which corresponds to a space completely filled with trigonal prisms. The value of LC is related to the overall composition of the trigonal prism framework according to $[R_6T_{LC}]$. If there are no extra T atoms outside the trigonal prisms the composition of the trigonal prism framework (enclosed in square brackets) is naturally equal to the composition of the compound: $R_6T_{LC}=[R_6T_{LC}]$.

In Y_8Co_5 the eight crystallographically different Y atoms participate altogether 30 times in the formation of trigonal prisms as demonstrated in Table 5. As all eight sites are of equal multiplicity LC is $30/8=15/4$. In due consideration of the fact that no Co atoms are outside the trigonal prisms, the total composition may be expressed by

$$Y_8Co_5=[Y_8Co_5]\,.$$

Table 5. *The participation of the* Y *atoms in the formation of the five different trigonal prisms in* Y_8Co_5

	Y(1)	Y(2)	Y(3)	Y(4)	Y(5)	Y(6)	Y(7)	Y(8)	
Co(1)	1	–	–	2	–	–	2	1	6
Co(2)	1	1	1	1	1	1	–	–	6
Co(3)	–	2	2	–	1	1	–	–	6
Co(4)	–	1	1	–	2	2	–	–	6
Co(5)	1	1	1	1	–	–	1	1	6
	3	5	5	4	4	4	3	2	30

The structures of Y_3Co, Y_3Co_2 and Y_4Co_3 have LC= 2, 4 and 4 respectively. In Fig. 3 are shown projections of structural units which, when properly linked, form the prism frameworks in Y_3Co, Y_3Co_2 and Y_4Co_3. Near each prism corner is written the number of prisms which share this corner. The corresponding composition formulae for these intermetallic phases are

$$Y_3Co = [Y_3Co]$$
$$Y_3Co_2 = [Y_3Co_2]$$
$$3Y_4Co_3=4[Y_3Co_2]+Co\,.$$

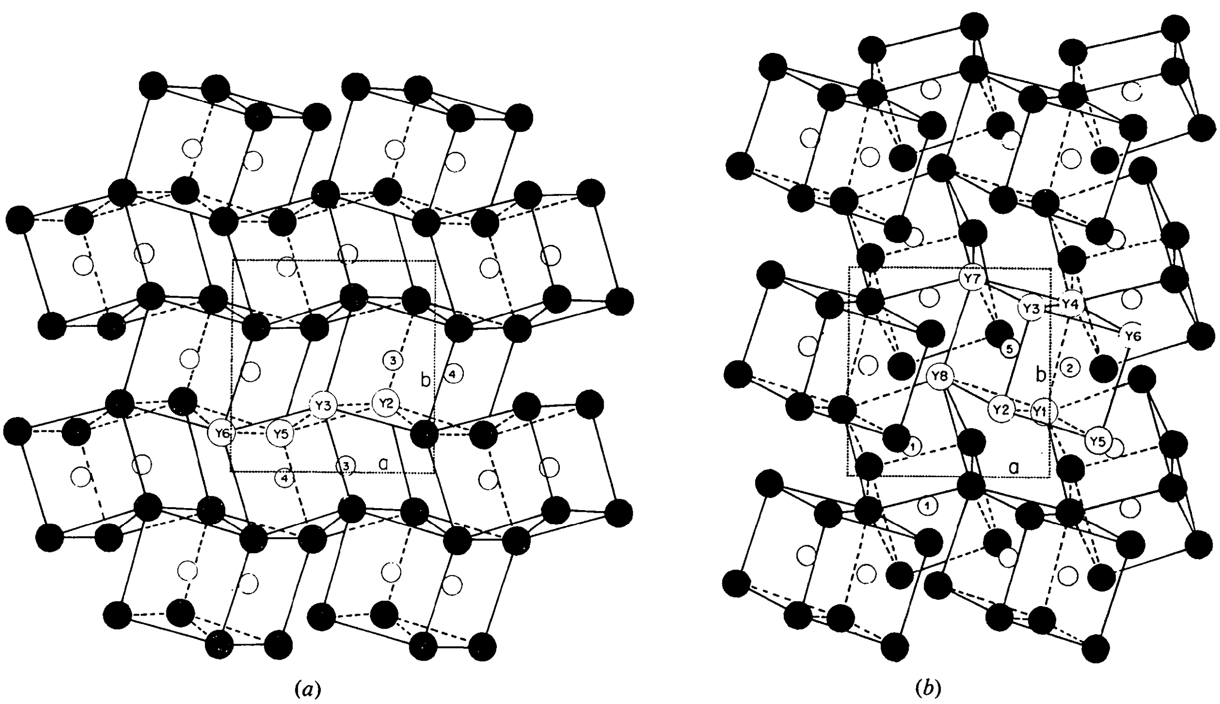


Fig. 2. The prism arrangement seen perpendicular to (001). (*a*) Prisms centred by Co atoms at $z_{Co}\simeq\frac{1}{4}$. (*b*) Prisms centred by Co atoms at $z_{Co}\simeq\frac{3}{8}$ and $\frac{1}{2}$..

In Y_3Co and Y_8Co_5 the trigonal prisms are tilted with respect to each other as in FeB, while in Y_3Co_2 and Y_4Co_3 the prism base planes are parallel as in CrB. In Y_3Co_2 and Y_4Co_3 infinite columns of prisms are formed. The change occurring from one framework to another is the side by side arrangement of the columns.

With the use of the concept of the trigonal prism linkage coefficient, it is possible to relate the stoichiometry of this type of compound to the linkage of prisms in the crystal structure. Moreover in certain cases it should be possible to predict the way the prisms are joined together from the knowledge of the composition of the alloy.

The assistance of Dr H. D. Flack with the computer programming is acknowledged.

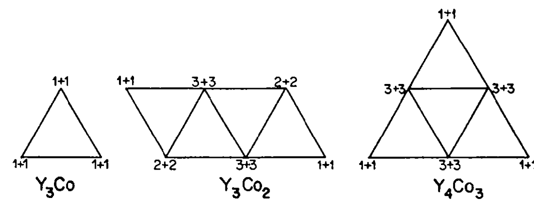


Fig. 3. Projection of structural units of prisms in Y_3Co, Y_3Co_2 and Y_4Co_3. The number near each corner indicates the number of lower and upper prisms which share this corner.

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The Carvoxime System. I. X-ray Study of *dl*-Carvoxime (m.p. 92°C)

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dl-Carvoxime, $C_{10}H_{15}NO$, (m.p. 92°C) is monoclinic $P2_1/c$, with $a=9{\cdot}856$ (3), $b=11{\cdot}848$ (3), $c=8{\cdot}480$ (3) Å, $\beta=98{\cdot}95$ (5)°, $Z=4$. The structure was determined from 1767 independent intensities measured with Mo $K\alpha$ radiation on an automatic four-circle diffractometer and refined by a block-diagonal least-squares procedure to $R=0{\cdot}057$. Contrary to previous expectations there is no substitutional disorder. In the crystal structure hydrogen bonding in which six-membered rings occur is found.

Introduction

Ever since its determination (Adriani, 1900) the phase diagram of the solid–liquid equilibrium in the system *d*-carvoxime + *l*-carvoxime has played a controversial role. The diagram, which is of type II according to Roozeboom's (1891, 1899) classification, suggests a continuous series of mixed crystals in which the 1:1 (the *dl*) composition, has the highest melting point. The possibility of such a type of phase diagram in a system of optical antipodes was excluded by Van Laar (1908) on thermodynamic grounds, which, however,