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$Y_2Co_3Al_9$ with $Y_2Co_3Ga_9$ type structure: an intergrowth of CsCl- and Th_3Pd_5-type slabs

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Abstract

The structure of $Y_2Co_3Al_9$ was determined by the single-crystal diffraction method (λ(Mo Kα) = 0.71073 Å, μ = 19.931 mm^{-1}, F(000) = 1104, T = 293 K, wR = 0.037 for 555 unique reflections). This new aluminide has an orthorhombic structure of $Y_2Co_3Ga_9$ type, *oS*56, (63) *Cmcm* – hg^2feca, a = 12.740(2) Å, b = 7.4635(9) Å, c = 9.321(1) Å, V = 886.3(2) Å^3, Z = 4, M_r = 597.44, D_x = 4.478 mg mm^{-3}.

The $Y_2Co_3Al_9$ structure can be interpreted as being built up of two kinds of slabs cut from the simple structures CsCl (composition CoAl) and Th_3Pd_5 (composition Y_2Al_6): $Co_3Al_3 + Y_2Al_6 = Y_2Co_3Al_9$. The cobalt atoms are surrounded by eight aluminium atoms at contact distances, forming a distorted cube, and four yttrium atoms at relatively longer distances, the 12 atoms together forming an icosahedron. The yttrium atoms centre capped hexagonal prisms, the coordination numbers for the aluminium atoms are 10 or 11.

1. Introduction

The isothermal section at 873 K of the Y–Co–Al phase diagram up to 34 at.%Y was established by Rykhal' and Zarechnyuk [1]. Four compounds were found: $YCo_{1\rightarrow1.35}Al_{1\rightarrow0.65}$ with $MgZn_2$ type structure (see also ref. 2), $YCoAl_2$ with $MgCuAl_2$ type structure [3], and compounds approximately $YCoAl_4$ and YCo_2Al_7. For the latter two compounds orthorhombic cells were reported. The aim of the present work was to determine the crystal structure of the compound of approximate composition $YCoAl_4$.

2. Experimental details

A sample of nominal composition $YCoAl_4$ was prepared from high purity elements (yttrium 99.9% pure, cobalt and aluminium 99.99% pure) by arc melting under an argon atmosphere (weight loss 0.2%) and annealing at 1073 K for two weeks in a silica tube under an argon atmosphere at a

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pressure of 400 mmHg. A single crystal with irregular shape (mean radius 0.026 mm) was mounted on a Philips PW1100 automatic four-circle diffractometer (Mo Kα radiation, graphite monochromator). The unit cell parameters, refined from 2θ values of 21 reflections (Mo Kα, $\lambda = 0.71073$ Å, $16° < 2\theta < 34°$), are in good agreement with those reported in ref. 1. 1534 reflections were collected out to $\sin\theta/\lambda = 0.704$ Å^{-1} ($0 \le h \le 17$, $0 \le k \le 10$, $0 \le l \le 13$ and the antireflections) in the ω–2θ scan mode, yielding 719 unique reflections ($R_{int} = 0.058$). Two standard reflections, 0 0 -4 and -3 -1 -3, were measured with maximum intensity variations of 0.5% and 0.9% respectively. Absorption correction was made using the program LSABS, described in ref. 4, with minimum and maximum transmission factors of 0.4691 and 0.4794. The anomalous dispersion coefficients were taken from ref. 5. Systematic absences led to the following possible space groups: $Cmc2_1$, $C2cm$ ($=Ama2$) and $Cmcm$ [6]. The structure was solved in space group $Cmcm$ by the MULTAN87 program [7] and confirmed by a structure refinement based on $|F|$ values. 41 variables, including anisotropic atomic displacement parameters, refined to $R = 0.052$ and $wR = 0.037$ ($w = 1/\sigma^2(|F_{rel}|)$, $S = 1.851$), considering 555 contributing unique reflections with $|F_{rel}| > 3\sigma(|F_{rel}|)$. The maximum shift per e.s.d. in the last cycle was 0.8×10^{-4} and the final residual electron density was +3.8 (−4.9) electrons per Å^3. The programs used to refine the structure were all from the XTAL3.0 system [8]. The atomic positional parameters were standardized by using the STRUCTURE TIDY program [9]. The atomic positional and displacement parameters are given in Table 1 and the interatomic distances in Table 2.

3. Discussion

$Y_2Co_3Al_9$ is the first aluminide identified with the $Y_2Co_3Ga_9$ structure type [10]. Until now isotypes of this structure type have only been found

TABLE 1

Structure data for $Y_2Co_3Al_9$ with $Y_2Co_3Ga_9$ type, *oS*56, (63) *Cmcm* — hg^2feca, $a = 12.740(2)$ Å, $b = 7.4635(9)$ Å, $c = 9.321(1)$ Å, $V = 886.3(2)$ Å^3, $Z = 4$, $wR = 0.037$

Atom	Wyckoff position	x	y	z	$U_{eq} \times 100$ (Å^2)
Al(1)	16(h)	0.1685(2)	0.1673(4)	0.0714(2)	0.70(6)
Al(2)	8(g)	0.1065(3)	0.4450(5)	¼	0.84(9)
Y	8(g)	0.33886(9)	0.3328(2)	¼	0.60(3)
Al(3)	8(f)	0	0.3323(6)	0.5433(4)	0.80(9)
Co(1)	8(e)	0.3289(1)	0	0	0.53(4)
Al(4)	4(c)	0	0.1249(7)	¼	0.7(1)
Co(2)	4(a)	0	0	0	0.63(7)

The equivalent isotropic atomic displacement parameters are expressed as $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}{}^* a_i a_j{}^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$. E.s.d.s are given in parentheses.

TABLE 2

Interatomic distances up to 4 Å in $Y_2Co_3Al_9$

Y–Al(2)	2.977(4)	Al(3)–Co(2)	2.513(5)
Y–Al(4)	2.994(4)	Al(3)–2Co(1)	2.545(3)
Y–2Al(1)	2.997(2)	Al(3)–Al(3)	2.630(6)
Y–2Al(1)	3.001(3)	Al(3)–2Al(1)	2.696(4)
Y–2Al(1)	3.002(3)	Al(3)–2Al(2)	2.884(4)
Y–2Al(3)	3.073(3)	Al(3)–2Y	3.073(3)
Y–Al(2)	3.076(4)	Al(3)–Al(4)	3.142(5)
Y–2Co(2)	3.347(1)	Al(3)–2Al(2)	3.166(4)
Y–2Co(1)	3.400(1)	Al(3)–Al(3)	3.853(5)
Y–2Co(1)	3.408(1)	Al(3)–Al(4)	3.919(6)
Al(1)–Co(1)	2.486(3)	Al(4)–2Co(2)	2.510(2)
Al(1)–Co(2)	2.571(3)	Al(4)–4Al(1)	2.735(2)
Al(1)–Co(1)	2.571(3)	Al(4)–2Al(2)	2.748(6)
Al(1)–Al(3)	2.696(4)	Al(4)–2Y	2.994(4)
Al(1)–Al(4)	2.735(2)	Al(4)–2Al(3)	3.142(5)
Al(1)–Al(1)	2.758(4)	Al(4)–2Al(3)	3.919(6)
Al(1)–Al(2)	2.773(4)		
Al(1)–Al(1)	2.829(4)	Co(1)–2Al(1)	2.486(3)
Al(1)–Y	2.997(2)	Co(1)–2Al(2)	2.505(1)
Al(1)–Y	3.001(3)	Co(1)–2Al(3)	2.545(3)
Al(1)–Y	3.002(3)	Co(1)–2Al(1)	2.571(3)
Al(1)–Al(1)	3.330(3)	Co(1)–2Y	3.400(1)
Al(1)–Al(2)	3.706(4)	Co(1)–2Y	3.408(1)
Al(2)–2Co(1)	2.505(1)	Co(2)–2Al(4)	2.510(2)
Al(2)–Al(2)	2.715(5)	Co(2)–2Al(3)	2.513(5)
Al(2)–Al(4)	2.748(6)	Co(2)–4Al(1)	2.571(3)
Al(2)–2Al(1)	2.773(4)	Co(2)–4Y	3.347(1)
Al(2)–2Al(3)	2.884(4)		
Al(2)–Y	2.977(4)		
Al(2)–Y	3.076(4)		
Al(2)–2Al(3)	3.166(4)		
Al(2)–2Al(1)	3.706(4)		

E.s.d.s are given in parentheses.

with cobalt-based gallides for rare earth elements from neodymium to lutetium (europium excepted). In the original work the structure of $Y_2Co_3Ga_9$ was presented as an $(hccc)_2$ stacking along the [0 0 1] direction of close-packed aluminium, cobalt and yttrium atom layers, one third of the rare earth atoms in the yttrium atom layers being replaced by aluminium atoms in the ratio 1:3.

The structure of $Y_2Co_3Al_9$ can also be described as an intergrowth along the *c* axis of two kinds of slabs, each formed of three consecutive monoatomic layers. Two aluminium atom layers and one cobalt atom layer, all with triangular meshes, produce a slab approximately 1.3 Å thick shown on the left-hand side of Fig. 1. A similar slab, shown in Fig. 2, can be obtained by cutting the structure of CoAl, crystallizing with the cubic CsCl type structure [11], perpendicular to the cubic body diagonal. The same two aluminium

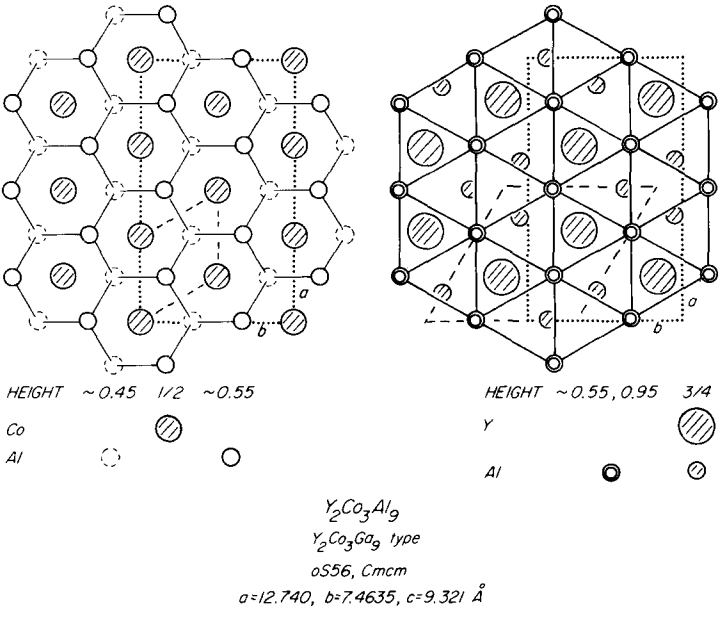

Fig. 1. Projections along the [0 0 1] direction of the two kinds of slabs found in the $Y_2Co_3Al_9$ structure. The cobalt atoms of the CsCl-type slab and the yttrium and aluminium atoms in the central plane of the Th_3Pd_5-type slab are marked by stripes. Dotted lines indicate the unit cell, dashed lines the translation unit of the slabs.

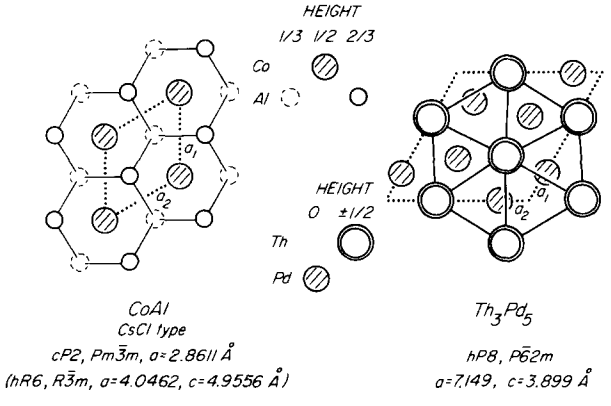

Fig. 2. Projections of CoAl along the [1 1 1] direction and Th_3Pd_5 along the [0 0 1] direction. For CoAl, only atoms at $1/3 \leq z \leq 2/3$ of the triple hexagonal cell are shown.

layers together with one mixed yttrium and aluminium atom layer form a slab approximately 3.3 Å thick, shown on the right-hand side of Fig. 1. This slab can be derived from the hexagonal Th_3Pd_5 type structure [12], a vacancy derivative of AlB_2 where 1/6 of the trigonal prisms are empty. A projection of Th_3Pd_5 along the [0 0 1] direction is shown in Fig. 2. With respect to binary $Th_3Pd_5 \equiv Th_3Pd_3Pd_2$, the composition of the slab in $Y_2Co_3Al_9$ is

$Y_2Al_6 \equiv Al_3Al_3Y_2$. At present, ordered substitution variants of Th_3Pd_5 are not known, however, similar slabs are found in the trigonal $ErNi_3Al_9$ type structure [13]. The composition of the intergrowth structure is obtained in the following way: $Co_3Al_3 + Y_2Al_6 = Y_2Co_3Al_9$. There are four slabs in the translation unit, the cobalt atoms being located at $z = 0$ and $z = 1/2$ and the yttrium atoms at $z = 1/4$ and $z = 3/4$. The three-fold axes of the CsCl-type slabs and the six-fold axes of the Th_3Pd_5-type slabs are parallel but do not coincide in the intergrowth structure, leading to orthorhombic symmetry.

The coordination polyhedron around the yttrium site is a hexagonal Co_6Al_6 prism, with all faces capped by additional atoms (including three yttrium atoms at distances greater than 4 Å). The cobalt sites centre Y_4Al_8 icosahedra whereas the aluminium atoms have lower coordination numbers (10 or 11). Not considering Y–Co contacts (interatomic distances greater than 3.3 Å), the coordinations of the cobalt sites are reduced to Al_8 cubes, as in the CoAl structure. Hexagonal prisms around the large atoms are also found in other structure types of ternary aluminium-rich compounds, for example $PrNi_2Al_5$ [14] and $BaFe_2Al_9$ [15]. However, in these structures the transition metal atoms occupy sites at the centres of tricapped trigonal prisms.

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