Crystal structure of cobalt aluminum silicide, $Co_{10+x}Al_{23}Si_{9-2x}$ (x = 0.14), *the φ phase in the Co-Al-Si system*

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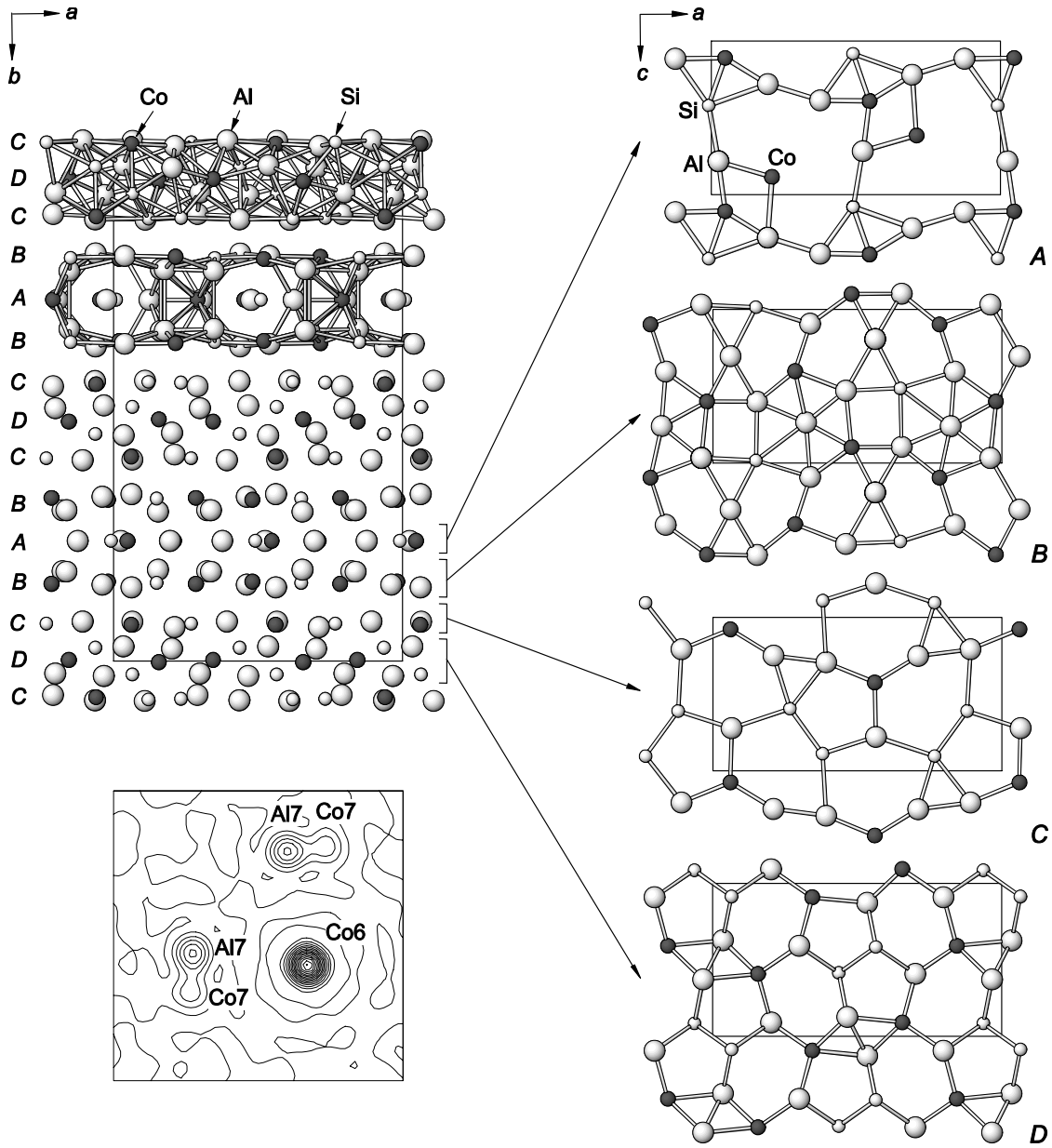

Abstract

$Al_{23}Co_{10.14}Si_{8.72}$, orthorhombic, *Pnma* (no. 62), a = 13.852(3) Å, b = 23.055(5) Å, c = 7.340(2) Å, V = 2344.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.035, $wR_{ref}(F^2)$ = 0.081, T = 293 K.

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Source of material

The title compound was identified in several Al-rich samples during an investigation of the Co-Al-Si phase diagram [1]. Samples were prepared from the pure elements by arc melting and subsequent heat treatment in alumina crucibles placed into evacuated silica ampules. After slow cooling from 1050 °C to 800 °C (5 K/h) in order to promote crystal growth from the melt the samples were

annealed for 4 weeks at 800 °C. Single crystals suitable for X-ray structure analysis were isolated from a crushed sample with the nominal compositions $Co_{22}Al_{58}Si_{20}$ which also contained small amounts of liquid phase at the annealing temperature.

Experimental details

Samples were characterized by X-ray powder diffraction (Huber Image Plate Guinier camera G670, Co$K_{\alpha 1}$ radiation, λ = 1.788965 Å, 5° ≤ 2θ ≤ 100°, LaB_6 as internal standard, a = 4.1569 Å).

Discussion

The title compound $Co_{10+x}Al_{23}Si_{9-2x}$ (x = 0.14, φ phase) is the most Co-poor of five new complex ternary compounds that were found during the investigation of the Co-Al-Si system [1]. It adopts an own structure type with some structural relations to the phases in the adjacent binary Co-Al system. The crystal structures of Al-rich binary compounds in the Co-Al system like o-Co_4Al_{13} [2], m-Co_4Al_{13} [3], h-Co_4Al_{13} [4] and Co_2Al_5 [5] are closely related to quasicrystals like the decagonal $CoAl_3$ [6]. An important common structural motif of these compounds is the existence of condensed pentagonal prismatic channels which are arranged in different ways depending on the structure adopted [7]. A similar motif can also be seen in the φ phase which shows pentagonal prismatic channels along the c axis of the structure around the atomic positions Co5, Al9 and Si3 (figure, left). Another common structural motif which connects the binary Co-Al phases with the ternary compound $Co_4Al_{7+x}Si_{2-x}$ reported recently [8] is the existence of a "cluster" formed from by two trigonal prisms around cobalt and a distorted rectangular prism around the aluminum. This structural motif is not found in the title compound.

The structure of the φ phase may be represented by four different types of layers stacked perpendicular to the long b axis of the unit cell. These layers are shown in the right part of figure, and include the flat A layer situated within the mirror plane at y = ¼ as well as the puckered B, C and D layers. The atoms forming the centers of the condensed pentagonal prismatic channels are situated within the A layer, while the atoms forming the surrounding channels are situated in the A and B layers, respectively. The C and D layers together form a kind of slab which is separated from the columns by a small, but noticeable gap (figure, left).

The φ phase shows a remarkable defect structure. In contrast to the usual behavior of mixed Al/Si ternary compounds, only a very limited amount of mixed Al/Si occupation is found in this compound. All main group element positions can be identified as Al or Si positions based on their nearest distances to adjacent Co which are below 2.40 Å in the case of Si and higher than 2.40 Å for Al positions. The chemical formula (ignoring the split positions around Co6) is $Co_{10}Al_{23}Si_9$. According to our analysis of the electron density map around Co6 (figure, bottom left) the Co6 position is not occupied by 100 % Co atoms, but shows 14 % vacant sites. An occupied Co6 position is connected with an occupied position Al7 and an occupied position Si5 (86 % occupation refined). In the case of a vacant site at the Co6 position, the position Co7 is occupied instead of Al7 and this is connected with an occupation of Al5 and Al6 (14 % occupation refined). The position Al9 remains unoccupied in this case. Both alternatives yield realistic interatomic distances for all involved atoms and offer a consistent interpretation of the difference electron density map in the defect part of the structure. Furthermore, the refined overall composition according to our model ($Co_{24.2}Al_{55.0}Si_{20.8}$) is in excellent agreement with the composition of the φ phase found by EPMA at 800 °C ($Co_{24.6(1)}Al_{54.9(1)}Si_{20.5(1)}$ [1]). A small homogeneity range was reported for the φ phase [1], probably caused by the different ratio of the two environment alternatives around Co6/Co7 sites.

Table 1. Data collection and handling.

Crystal:	metallic, irregular, size 0.125 × 0.065 × 0.050 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	82.99 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC-7 and Mercury CCD, ω/φ
$2\theta_{max}$:	63.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	31867, 4064
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3822
$N(param)_{refined}$:	222
Programs:	SHELXL-97 [9], CSD [10], ATOMS [11]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
Al(6)	4c	0.140	0.1258(9)	¼	0.299(2)	0.025(2)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)	8d		0.21540(3)	0.33941(2)	0.90223(6)	0.0126(2)	0.0079(2)	0.0116(2)	0.0008(1)	–0.0016(1)	–0.0004(1)
Co(2)	8d		0.43936(3)	0.42464(2)	0.57628(5)	0.0068(2)	0.0069(2)	0.0076(2)	–0.0001(1)	0.0004(1)	–0.0001(1)
Co(3)	8d		0.34412(3)	0.50222(2)	0.09220(5)	0.0075(2)	0.0121(2)	0.0099(2)	0.0019(1)	0.0006(1)	0.0017(1)
Co(4)	8d		0.48021(3)	0.66492(2)	0.89966(5)	0.0107(2)	0.0104(2)	0.0101(2)	0.0012(1)	–0.0013(1)	–0.0023(1)
Co(5)	4c		0.45277(4)	¼	0.60913(8)	0.0125(3)	0.0083(2)	0.0127(3)	0	0.0029(2)	0
Co(6)	4c	0.860(2)	0.29049(5)	¼	0.38610(9)	0.0093(3)	0.0072(3)	0.0130(3)	0	–0.0023(2)	0
Co(7)	8d	0.140	0.2083(2)	0.1607(1)	0.2775(4)	0.003(1)	0.003(1)	0.005(1)	0.0018(8)	–0.0001(8)	0.0022(8)
Al(1)	4c		0.30536(9)	¼	0.7807(2)	0.0092(5)	0.0105(5)	0.0154(6)	0	0.0014(4)	0
Al(2)	8d		0.43523(6)	0.41850(4)	0.2224(1)	0.0087(4)	0.0102(4)	0.0101(4)	0.0020(3)	0.0001(3)	0.0002(3)
Al(3)	8d		0.16311(7)	0.31377(4)	0.5940(1)	0.0141(4)	0.0168(4)	0.0093(4)	–0.0030(3)	–0.0023(3)	0.0014(3)
Al(4)	4c		0.12419(9)	¼	0.8849(2)	0.0071(5)	0.0043(4)	0.0116(5)	0	0.0002(4)	0
Al(5)	8d	0.140	0.328(1)	0.3516(7)	0.510(2)	0.024(7)	0.028(7)	0.032(6)	–0.021(5)	–0.003(5)	–0.010(5)
Al(7)	8d	0.860	0.17701(9)	0.18650(6)	0.2387(2)	0.0135(5)	0.0187(6)	0.0108(5)	–0.0043(5)	0.0021(4)	–0.0029(4)
Al(8)	8d		0.10796(7)	0.41739(4)	0.7929(1)	0.0080(4)	0.0123(4)	0.0182(4)	0.0012(3)	0.0017(3)	0.0050(3)
Al(9)	4c	0.860	0.5241(1)	¾	0.7160(2)	0.0190(7)	0.0019(5)	0.0070(6)	0	–0.0032(5)	0
Al(10)	8d		0.43827(8)	0.34673(4)	0.8063(1)	0.0269(5)	0.0112(4)	0.0118(4)	0.0006(4)	–0.0037(4)	0.0025(3)
Al(11)	8d		0.03932(9)	0.34114(4)	0.0307(2)	0.0277(5)	0.0099(4)	0.0201(5)	0.0017(4)	0.0069(4)	0.0014(3)

Table 3. Continued.

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Al(12)	8*d*		0.34671(7)	0.31042(4)	0.1030(1)	0.0064(4)	0.0193(4)	0.0085(4)	–0.0004(3)	–0.0005(3)	0.0013(3)
Al(13)	8*d*		0.28980(7)	0.42942(5)	0.7486(2)	0.0109(4)	0.0293(5)	0.0244(5)	0.0071(4)	0.0081(4)	0.0128(4)
Al(14)	8*d*		0.29847(7)	0.47447(4)	0.4082(1)	0.0086(4)	0.0143(4)	0.0095(4)	0.0001(3)	0.0008(3)	–0.0003(3)
Al(15)	8*d*		0.46580(7)	0.46920(4)	0.8730(1)	0.0159(4)	0.0150(4)	0.0096(4)	0.0012(3)	–0.0002(3)	–0.0033(3)
Si(1)	8*d*		0.38004(6)	0.57974(4)	0.8892(1)	0.0110(4)	0.0105(3)	0.0131(4)	–0.0007(3)	–0.0006(3)	0.0017(3)
Si(2)	8*d*		0.23273(6)	0.42179(4)	0.0959(1)	0.0139(4)	0.0104(3)	0.0112(3)	–0.0013(3)	–0.0001(3)	–0.0012(3)
Si(3)	4*c*		0.4904(1)	¾	0.0817(2)	0.0219(6)	0.0073(4)	0.0127(5)	0	0.0006(4)	0
Si(4)	8*d*		0.43596(6)	0.52788(3)	0.5853(1)	0.0078(3)	0.0083(3)	0.0092(3)	0.0002(3)	0.0001(2)	–0.0005(2)
Si(5)	8*d*	0.860	0.3508(2)	0.33772(9)	0.4854(3)	0.0223(9)	0.0202(8)	0.0255(9)	–0.0011(6)	–0.0050(6)	–0.0006(6)

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