

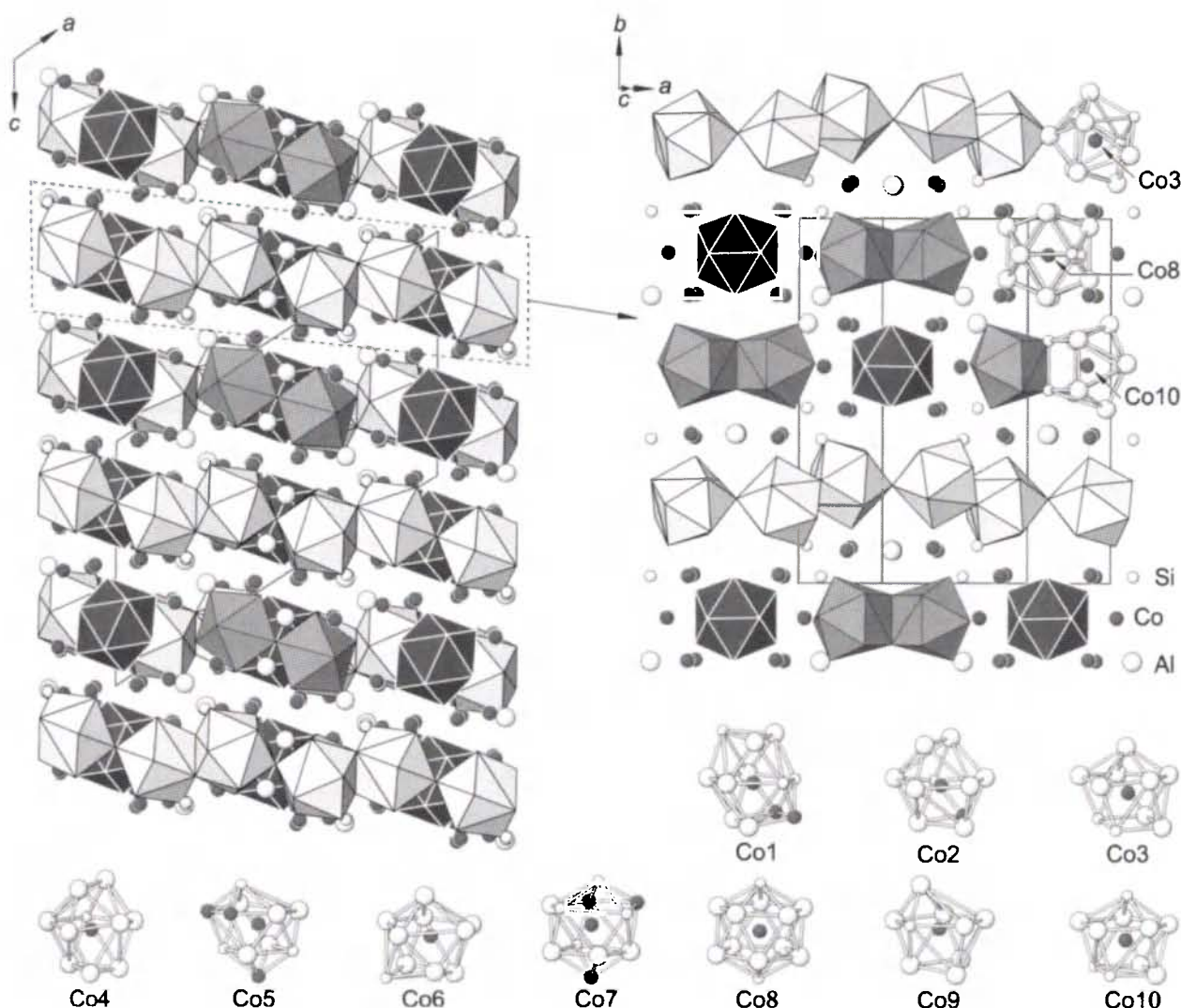
Crystal structures of cobalt aluminum silicide, $\text{Co}_{19+x}\text{Al}_{43+y}\text{Si}_{12-y}$ ($x = -0.14$, $y = 0.14$; $x = 0.49$, $y = -0.49$), the γ phase in the Co–Al–Si system

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Abstract

$\text{Al}_{43.14}\text{Co}_{18.86}\text{Si}_{11.86}$, monoclinic, $C12/c1$ (no. 15), $a = 20.010(2)$ Å, $b = 19.1498(7)$ Å, $c = 12.8227(8)$ Å, $\beta = 123.56(1)^\circ$, $V = 4094.6$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.035$, $wR_{\text{ref}}(F^2) = 0.079$, $T = 293$ K.

$\text{Al}_{42.51}\text{Co}_{19.49}\text{Si}_{12.49}$, monoclinic, $C12/c1$ (no. 15), $a = 20.025(2)$ Å, $b = 19.173(2)$ Å, $c = 12.835(1)$ Å, $\beta = 123.63(1)^\circ$, $V = 4103.2$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.044$, $wR_{\text{ref}}(F^2) = 0.108$, $T = 293$ K.

Source of material

The title compound was observed during a systematic phase equilibria investigation in the Co–Al–Si system [1]. Samples were prepared from the pure elements by arc melting in inert gas atmosphere. Subsequent heat treatment (4 weeks at 800 °C) was carried out in alumina crucibles placed into evacuated silica ampules. Electron probe microanalysis shows that the homogeneity range of the γ phase is considerable: at 800 °C the Si content varies from 8.6 at.% to 17.0 at.% and the Co content varies between 25.6 at.% and 26.6 at.% [1]. Single crystals were isolated from three individual samples with the nominal compositions $\text{Co}_{22}\text{Al}_{62}\text{Si}_{16}$, $\text{Co}_{26}\text{Al}_{62}\text{Si}_{12}$ and $\text{Co}_{28}\text{Al}_{56}\text{Si}_{16}$. The data sets shown

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here correspond to the single crystals isolated from the samples with the nominal compositions Co₂₂Al₆₂Si₁₆ and Co₂₈Al₅₆Si₁₆, i.e. from the Co-poor and Co-rich sides of the homogeneity range. At the annealing temperature, the γ phase in Co₂₂Al₆₂Si₁₆ is in equilibrium with the liquid and in Co₂₈Al₅₆Si₁₆ it is in equilibrium with χ and δ .

Experimental details

Samples were characterized by X-ray powder diffraction (Huber Image Plate Guinier camera G670, CoK α radiation, $\lambda = 1.788965$ Å, $5^\circ \leq 2\theta \leq 100^\circ$, LaB₆ as internal standard, $a = 4.1569$ Å).

Discussion

The γ phase is one of five new complex ternary compounds that were found during the phase diagram investigation of the Co-Al-Si system. At 800 °C it is in equilibrium with the adjacent binary compounds CoAl₃ and Co₂Al₉, with the ternary phases δ , ϕ and χ and with liquid phase [1]. It adopts an own structure type with no obvious structural relations to the adjacent phases in the binary system [2-6]. Important common structural motifs of these compounds, like the existence of condensed pentagonal prismatic channels [7] or the existence of a "cluster" formed by two trigonal prisms around cobalt and a distorted rectangular prism around aluminum [8] are not found in the title compound. One possibility to visualize the complex structure of the γ phase is based on the coordination of Co atoms. Six out of ten Co positions are coordinated only by Al and Si (Co3, Co4, Co6, Co8, Co9 and Co10) while the other four positions have also Co atoms in their first coordination sphere. The most regular coordination polyhedra (figure, bottom) include an icosahedron around Co8 and capped pentagonal arrangements (coordination number 10) around Co3

and Co10 which are arranged in slabs within the structure (figure, top).

The γ phase exhibits a significant range of homogeneity connected with Al/Si substitution. It is possible to distinguish positions mainly occupied by Al atoms from those positions mainly occupied by Si atoms, as the smallest Co—Al distances are larger than 2.40 Å while the smallest Co—Si distances are found below 2.40 Å. The identification of Al and Si positions yields an ideal chemical formula Co₁₉Al₄₃Si₁₂. The real extension of the γ phase at 800 °C (determined by EPMA) is Co_{19-2x}Al_{43+y}Si_{12-y} with $-0.5 \leq y \leq 3$ [1]. This clearly indicates that a certain amount of Al/Si substitution is possible at these positions. The mechanism of nonstoichiometry connected with the small but significant variability of the Co content was investigated on three single crystals with different Co content. According to our refinements, the γ phase is stable between the compositions Co_{18.86}Al_{43+y}Si_{12-y} and Co_{19.49}Al_{43+y}Si_{12-y} which is in excellent agreement with the experimental determination of the phase boundaries of the γ phase by EPMA ($0 \leq x \leq 0.7$) [1]. The Co deficiency is due to a reduced occupation at the position Co7 (93 % occupation refined). This deficiency is connected with positional splitting observed at the adjacent Si7/Al7 position: the occupation of the position by a Co atom is connected with a Si atom at the position Si7, while the position Al7 is occupied in case of an empty position Co7. The structure refinement of a single crystal obtained from the Co-rich end of the composition range shows that the deviation to the Co-rich side of the ideal composition is due to the partial occupation of an additional Co position, Co11, with the atomic coordinates $x = 0.0558, y = 0.0951, z = 0.3181$. This partial occupation is limited to 28 % and it is connected with multiple splitting of adjacent Al and Si positions. It should be pointed out that the Al/Si ratio is in general not connected with the Co content.

1. Cobalt aluminum silicide, Co_{18.86}Al_{43.14}Si_{11.86}

Table 1. Data collection and handling.

Crystal:	metallic, irregular, size 0.065 × 0.080 × 0.175 mm
Wavelength:	Mo K α radiation (0.7107 Å)
μ :	87.14 cm ⁻¹
Diffractometer, scan mode:	Rigaku AFC7 & Mercury CCD, ϕ/ω
$2\theta_{\max}$:	66°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	21130, 7439
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6655
$N(\text{param})_{\text{refined}}$:	340
Programs:	SHELXL-97 [9], CSD [10], ATOMS [11]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Co(1)	8f		0.68390(2)	0.48022(2)	0.81530(4)	0.0096(2)	0.0096(2)	0.0109(2)	0.0024(1)	0.0067(1)	0.0027(1)
Co(2)	8f		0.56605(3)	0.29179(2)	0.55130(4)	0.0122(2)	0.0086(2)	0.0065(2)	-0.0041(1)	0.0006(1)	0.0005(1)
Co(3)	8f		0.63720(2)	0.28157(2)	0.92616(3)	0.0058(2)	0.0059(1)	0.0069(2)	0.0002(1)	0.0035(1)	0.0004(1)
Co(4)	8f		0.07493(2)	0.59770(2)	0.04170(3)	0.0094(2)	0.0067(2)	0.0079(2)	-0.0010(1)	0.0051(1)	-0.0001(1)
Co(5)	8f		0.57770(2)	0.47623(2)	0.04918(4)	0.0094(2)	0.0098(2)	0.0103(2)	-0.0005(1)	0.0049(1)	0.0007(1)
Co(6)	8f		0.31510(2)	0.28892(2)	0.18086(4)	0.0074(2)	0.0089(2)	0.0099(2)	-0.0012(1)	0.0053(1)	-0.0025(1)
Co(7)	8f	0.931(2)	0.83271(3)	0.90603(2)	0.88581(4)	0.0082(2)	0.0073(2)	0.0078(2)	0.0007(1)	0.0040(2)	0.0000(1)
Co(8)	4e		½	0.59701(3)	¼	0.0075(2)	0.0099(2)	0.0071(2)	0	0.0035(2)	0
Co(9)	8f		0.82104(2)	0.58982(2)	0.69962(3)	0.0072(2)	0.0070(2)	0.0074(2)	0.0003(1)	0.0040(1)	0.0001(1)
Co(10)	8f		0.61451(2)	0.09832(2)	0.40112(3)	0.0056(2)	0.0057(1)	0.0063(2)	-0.0000(1)	0.0026(1)	0.0001(1)
Si(1)	4e		½	0.16617(5)	¼	0.0070(4)	0.0071(4)	0.0066(4)	0	0.0033(4)	0

Table 2. Continued.

m	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
1)	4e		0	0.46804(5)	$\frac{3}{4}$	0.0070(4)	0.0081(4)	0.0083(4)	0	0.0043(4)	0
1)	8f		0.24855(4)	0.28292(4)	0.58442(7)	0.0055(3)	0.0072(3)	0.0074(3)	-0.0006(2)	0.0030(3)	-0.0003(2)
1)	8f		0.28137(5)	0.48166(4)	0.32596(7)	0.0079(3)	0.0093(3)	0.0094(3)	-0.0016(3)	0.0050(3)	-0.0010(2)
1)	8f		0.77969(5)	0.39701(4)	0.83303(7)	0.0086(3)	0.0119(3)	0.0102(3)	0.0008(3)	0.0045(3)	-0.0008(2)
1)	8f		0.47493(5)	0.59306(4)	0.53411(7)	0.0078(3)	0.0082(3)	0.0098(3)	0.0008(3)	0.0044(3)	-0.0002(2)
1)	8f	0.931	0.74851(7)	0.90919(7)	0.9618(1)	0.0123(5)	0.0408(7)	0.0307(6)	-0.0013(4)	0.0125(5)	-0.0010(5)
1)	8f		0.96992(5)	0.58897(4)	0.82462(8)	0.0051(3)	0.0103(3)	0.0067(3)	-0.0006(3)	0.0023(3)	0.0009(3)
2)	8f		0.37575(5)	0.16806(4)	0.26325(8)	0.0089(4)	0.0094(3)	0.0084(3)	0.0002(3)	0.0047(3)	0.0010(3)
3)	8f		0.12923(5)	0.28703(4)	0.23645(8)	0.0088(4)	0.0078(3)	0.0085(4)	0.0013(3)	0.0041(3)	-0.0005(3)
4)	8f		0.87898(5)	0.47373(4)	0.76986(8)	0.0097(4)	0.0078(3)	0.0099(4)	0.0001(3)	0.0056(3)	0.0012(3)
5)	8f		0.46534(5)	0.28735(4)	0.32108(8)	0.0073(4)	0.0079(3)	0.0063(3)	-0.0008(3)	0.0028(3)	0.0004(3)
5)	8f		0.71646(5)	0.28741(4)	0.67432(8)	0.0073(4)	0.0065(3)	0.0085(3)	0.0009(3)	0.0047(3)	0.0005(2)
7)	8f	0.069	0.746(1)	0.904(1)	0.902(2)	0.0123(5)	0.0408(7)	0.0307(6)	-0.0013(4)	0.0125(5)	-0.0010(5)
3)	8f		0.54710(6)	0.17019(5)	0.47909(8)	0.0133(4)	0.0131(4)	0.0110(4)	0.0045(3)	0.0066(3)	-0.0005(3)
9)	8f		0.37261(5)	0.40350(4)	0.25928(8)	0.0071(4)	0.0062(3)	0.0081(3)	-0.0001(3)	0.0038(3)	-0.0004(2)
10)	8f		0.61682(5)	0.66546(4)	0.92079(8)	0.0083(4)	0.0094(3)	0.0071(3)	-0.0009(3)	0.0037(3)	0.0005(3)
11)	8f		0.46601(5)	0.48159(4)	0.82104(8)	0.0076(4)	0.0087(3)	0.0077(3)	0.0003(3)	0.0025(3)	0.0003(3)
12)	8f		0.11932(5)	0.35099(4)	0.40955(8)	0.0121(4)	0.0088(3)	0.0105(4)	0.0005(3)	0.0073(3)	0.0002(3)
13)	8f		0.21082(6)	0.10256(4)	0.48350(8)	0.0110(4)	0.0093(4)	0.0083(4)	0.0015(3)	0.0041(3)	-0.0007(3)
14)	8f		0.38143(5)	0.47964(4)	0.08241(8)	0.0112(4)	0.0097(4)	0.0089(4)	0.0011(3)	0.0066(3)	-0.0002(3)
15)	8f		0.81403(7)	0.71131(5)	0.02527(9)	0.0285(5)	0.0104(4)	0.0083(4)	0.0079(4)	0.0052(4)	0.0002(3)
16)	8f		0.17056(6)	0.48048(5)	0.47546(9)	0.0225(5)	0.0105(4)	0.0125(4)	0.0071(4)	0.0067(4)	0.0017(3)
17)	8f		0.54772(6)	0.03229(5)	0.48246(9)	0.0137(4)	0.0119(4)	0.0141(4)	-0.0013(3)	0.0098(3)	0.0019(3)
18)	4e	$\frac{1}{2}$	0.26835(8)	$\frac{3}{4}$		0.0083(6)	0.0198(6)	0.0161(6)	0	-0.0007(5)	0
19)	8f		0.20657(5)	0.17796(4)	0.65519(8)	0.0115(4)	0.0097(3)	0.0084(3)	-0.0002(3)	0.0060(3)	0.0004(3)
20)	8f		0.20478(6)	0.39717(5)	0.13166(8)	0.0125(4)	0.0193(4)	0.0069(4)	0.0013(3)	0.0030(3)	-0.0011(3)
21)	8f		0.56156(6)	0.23146(5)	0.0052(1)	0.0206(5)	0.0123(4)	0.0259(5)	0.0017(3)	0.0197(4)	0.0037(3)
22)	8f		0.11239(5)	0.13989(4)	0.24295(8)	0.0112(4)	0.0093(4)	0.0099(4)	-0.0003(3)	0.0043(3)	0.0000(3)
23)	8f		0.05492(6)	0.13182(5)	0.43759(9)	0.0114(4)	0.0138(4)	0.0166(4)	-0.0047(3)	0.0053(4)	0.0030(3)

Cobalt aluminum silicide, $\text{Co}_{19.49}\text{Al}_{42.51}\text{Si}_{12.49}$

Table 3. Data collection and handling.

stal:	metallic, irregular, size $0.055 \times 0.085 \times 0.125$ mm
wavelength:	Mo K_{α} radiation (0.7107 Å) 89.44 cm^{-1}
fractometer, scan mode:	Rigaku AFC7 & Mercury CCD, ϕ/ω
ax:	56.86°
kl measured, $N(hkl)_{\text{unique}}$:	12247, 4169
erion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3083
aram) refined:	359
grams:	SHELXL-97 [9], CSD [10], ATOMS [11]

Table 4. Atomic coordinates and displacement parameters (in $\text{\AA}^2$).

m	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
1)	8f		0.68296(5)	0.48020(4)	0.81336(8)	0.0156(5)	0.0131(4)	0.0177(5)	0.0037(3)	0.0120(4)	0.0034(3)
2)	8f		0.56775(6)	0.29016(4)	0.54965(8)	0.0270(6)	0.0168(4)	0.0105(5)	-0.0117(4)	0.0011(4)	0.0011(3)
3)	8f		0.63697(5)	0.28174(4)	0.92703(7)	0.0094(4)	0.0099(4)	0.0119(4)	-0.0001(3)	0.0061(4)	-0.0003(3)
4)	8f		0.07480(5)	0.59773(4)	0.04168(7)	0.0128(5)	0.0121(4)	0.0126(5)	-0.0018(3)	0.0078(4)	-0.0006(3)
5)	8f		0.57707(5)	0.47522(4)	0.04709(7)	0.0110(5)	0.0178(4)	0.0156(5)	0.0015(3)	0.0072(4)	0.0052(3)
6)	8f		0.31484(5)	0.28887(4)	0.17965(7)	0.0102(5)	0.0120(4)	0.0136(4)	-0.0004(3)	0.0069(4)	-0.0018(3)
7)	8f	0.963(5)	0.8321(3)	0.9052(1)	0.8864(4)	0.011(1)	0.0111(5)	0.0116(5)	0.0019(4)	0.0050(5)	0.0002(3)
8)	4e	$\frac{1}{2}$	0.59961(5)	$\frac{3}{4}$		0.0105(6)	0.0134(5)	0.0119(6)	0	0.0060(5)	0
9)	8f		0.82040(5)	0.58956(4)	0.69881(8)	0.0110(4)	0.0107(4)	0.0123(4)	0.0001(3)	0.0071(4)	0.0002(3)
10)	8f		0.61419(5)	0.09793(3)	0.40134(8)	0.0076(4)	0.0101(4)	0.0110(4)	-0.0005(3)	0.0051(4)	-0.0002(3)
11)	8f	0.280(3)	0.0558(2)	0.0951(1)	0.3181(3)	0.012(2)	0.009(1)	0.017(2)	-0.000(1)	0.009(1)	-0.001(1)
)	4e	$\frac{1}{2}$	0.1656(1)	$\frac{3}{4}$		0.010(1)	0.012(1)	0.012(1)	0	0.007(1)	0
)	4e	0	0.4683(1)	$\frac{3}{4}$		0.008(1)	0.009(1)	0.015(1)	0	0.006(1)	0
)	8f		0.2487(1)	0.28277(7)	0.5845(1)	0.0086(9)	0.0106(7)	0.0108(8)	0.0004(6)	0.0045(7)	-0.0002(6)

Table 4. Continued.

Atom	Site	Occ.	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Si(4)	8f		0.2816(1)	0.48196(8)	0.3266(2)	0.0105(9)	0.0136(7)	0.0137(8)	-0.0011(7)	0.0074(7)	-0.0012(6)
Si(5)	8f		0.7799(1)	0.39720(8)	0.8333(2)	0.0121(9)	0.0162(8)	0.0147(9)	0.0000(7)	0.0071(8)	-0.0003(6)
Si(6)	8f		0.4743(1)	0.59385(8)	0.5336(2)	0.0101(9)	0.0160(8)	0.0152(9)	0.0008(7)	0.0053(8)	-0.0019(6)
Si(7)	8f	0.963	0.7481(1)	0.9066(1)	0.9616(2)	0.017(1)	0.058(2)	0.038(1)	-0.001(1)	0.016(1)	-0.002(1)
Al(1)	8f		0.9700(1)	0.58864(8)	0.8243(2)	0.008(1)	0.0149(8)	0.0118(9)	-0.0004(7)	0.0056(8)	0.0003(7)
Al(2)	8f		0.3756(1)	0.16805(8)	0.2630(2)	0.011(1)	0.0140(8)	0.0123(9)	0.0005(7)	0.0060(8)	0.0016(7)
Al(3)	8f		0.1286(1)	0.28731(8)	0.2361(2)	0.014(1)	0.0101(8)	0.0141(9)	0.0013(7)	0.0081(8)	-0.0010(7)
Al(4)	8f		0.8788(1)	0.47340(8)	0.7691(2)	0.012(1)	0.0124(8)	0.0134(9)	0.0015(7)	0.0067(8)	0.0033(7)
Al(5)	8f		0.4656(1)	0.28635(8)	0.3205(2)	0.010(1)	0.0103(8)	0.0099(9)	0.0004(7)	0.0048(8)	0.0005(6)
Al(6)	8f		0.7176(1)	0.28695(8)	0.6757(2)	0.012(1)	0.0095(8)	0.0146(9)	0.0005(7)	0.0090(8)	-0.0007(6)
Al(7)	8f	0.037	0.83(2)	0.91(1)	0.88(3)	0.017(1)	0.058(2)	0.038(1)	-0.001(1)	0.016(1)	-0.002(1)
Al(8)	8f		0.5465(1)	0.16884(9)	0.4783(2)	0.020(1)	0.0201(9)	0.016(1)	0.0059(8)	0.0105(9)	0.0001(7)
Al(9)	8f		0.3725(1)	0.40291(8)	0.2596(2)	0.0093(9)	0.0097(8)	0.0115(9)	-0.0005(7)	0.0064(8)	-0.0010(6)
Al(10)	8f		0.6165(1)	0.66553(9)	0.9194(2)	0.011(1)	0.0143(8)	0.0120(9)	-0.0002(7)	0.0062(8)	0.0010(7)
Al(11)	8f		0.4663(1)	0.48505(9)	0.8217(2)	0.009(1)	0.0165(8)	0.0118(9)	0.0019(7)	0.0049(8)	0.0012(7)
Al(12)	8f		0.1191(1)	0.35124(9)	0.4097(2)	0.017(1)	0.0155(8)	0.0177(9)	0.0008(8)	0.0112(9)	-0.0008(7)
Al(13)	8f		0.2103(1)	0.10305(8)	0.4822(2)	0.017(1)	0.0137(8)	0.0129(9)	0.0029(7)	0.0082(9)	0.0009(7)
Al(14)	8f		0.3804(1)	0.47867(8)	0.0822(2)	0.014(1)	0.0132(8)	0.0125(9)	0.0007(7)	0.0088(8)	-0.0003(7)
Al(15)	8f		0.8162(2)	0.71222(9)	0.0248(2)	0.042(2)	0.0184(9)	0.013(1)	0.0129(9)	0.007(1)	0.0011(8)
Al(16)	8f		0.1716(1)	0.48087(9)	0.4756(2)	0.032(1)	0.0195(9)	0.019(1)	0.0083(9)	0.011(1)	0.0014(8)
Al(17)	8f		0.5480(1)	0.03129(9)	0.4824(2)	0.020(1)	0.0169(9)	0.019(1)	-0.0047(8)	0.0123(9)	-0.0003(7)
Al(18)	4e	½	0.2729(1)	¾	0.011(2)	0.025(1)	0.022(2)	0	0	0.004(1)	0
Al(19)	8f		0.2066(1)	0.17792(8)	0.6555(2)	0.017(1)	0.0118(8)	0.0148(9)	-0.0001(7)	0.0108(8)	0.0013(7)
Al(20)	8f		0.2044(1)	0.39762(9)	0.1320(2)	0.016(1)	0.026(1)	0.012(1)	0.0008(8)	0.0062(9)	-0.0002(7)
Al(21)	8f		0.5593(1)	0.2310(1)	0.0018(2)	0.025(1)	0.032(1)	0.028(1)	-0.0040(9)	0.020(1)	0.0009(9)
Al(22)	8f		0.1127(1)	0.14053(9)	0.2387(2)	0.016(1)	0.0180(9)	0.022(1)	0.0034(8)	0.0039(9)	-0.0025(8)
Al(23)	8f	0.720	0.0563(3)	0.1273(2)	0.4302(5)	0.016(2)	0.024(2)	0.039(3)	-0.009(2)	0.005(2)	0.014(2)
Si(23)	8f	0.280	0.0523(7)	0.1473(5)	0.468(1)	0.011(4)	0.012(4)	0.024(5)	0.007(3)	0.004(4)	0.007(3)

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