

SHORT COMMUNICATIONS

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Concerning the κ Phase of Al–Cr–Ni

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Abstract

The structure of a new hexagonal phase aluminium–chromium–nickel, of reported composition $\text{Al}_{14.4}\text{Cr}_{3.4}\text{Ni}_{1.1}$, has recently been described and refined in space group $P6_3$; most of the atom sites were described as disordered between various pairs of metal atoms [Sato *et al.* (1997). *Acta Cryst.* **C53**, 1531–1533]. A simpler structure, in space group $P6_3/m$, leads to better refinement. In the revised structure most of the atom sites are ordered. There is no indication of Ni in any of these ordered sites, but one partially occupied site may contain Ni, octahedrally coordinated to six Al atoms. Disorder along a chain of four atoms, parallel to the c axis, prevents a determination of the exact chemical composition; the approximate cell contents are $\text{Al}_{177}\text{Cr}_{49}\text{Ni}$.

1. Comment

The structure of this hexagonal phase [$a = 17.674$ (3), $c = 12.516$ (3) Å], as recently reported by Sato *et al.* (1997; SYLHHS),† was a complicated one, with 40 different types of atom sites in space group $P6_3$. All these sites were refined as occupationally disordered between either Al and Cr, Al and Ni, or Cr and Ni; the occupation parameters and the final composition were restrained by a penalty function so as to approximate the analytical results (obtained by high-resolution transmission electron microscopy, HRTEM) of approximately $\text{Al}_{76}\text{Cr}_{18}\text{Ni}_6$. A particularly bothersome aspect of the reported structure involves the atom labeled Al32 [which was described as 78 (3)% Al, 22% Ni]; it lay at the center of an approximate octahedron, with six Al neighbors at 2.08–2.15 Å, unrealistically short distances. The reported structure clearly warranted further study.

The $P6_3$ coordinates and F_{obs} values were obtained electronically from the International Union of Crystallography (IUCr). The coordinates suggested the presence of a mirror plane and a model in space group $P6_3/m$ was readily derived. Full-matrix least-squares refinement progressed normally to an R of 0.041 for the 2452 ‘observed’ reflections, compared with 0.052 reported by SYLHHS for space group $P6_3$. The $P6_3/m$ coordinates are given in Table 1. For the six (in $P6_3/m$) sites presumed by SYLHHS to be disordered between Cr and Ni, Cr1–Cr6, composition parameters were refined; all six values indicated full occupancy (within s.u.’s of ~1%) by Cr. Most of the remaining sites were presumed to be occupied entirely by

Al. The site originally assigned as Al32 was studied with some care, since difference maps and population parameters suggested only partial occupancy by Al. If it is presumed that the site is fully occupied, the most satisfactory occupant is an O atom, for which the occupancy factor became 1.02 (3); the distances to the six neighboring Al atoms, 2.11 (1) Å, are reasonable for interstitial oxygen. However, the value of U_{iso} (refined in the same matrix) became negative, at -0.0006 (1) Å². An alternative description, which led to a slight improvement in R and to a reasonable U_{iso} value, is that the site is partially occupied by either Cr (occupancy factor 0.32) or Ni (0.25); for my final model I selected Ni, since it is slightly smaller than Cr. Some support for this partial-occupancy model comes from the U^{ij} ’s of the six neighboring atoms (three each of Al8 and Al13), since the displacement ellipsoids have their major axes directed parallel to the Ni–Al direction, suggesting that the Al atoms are displaced inwards when the ‘Ni’ atom is absent and outwards when it is present. An attempt to refine a split-atom model of this sort was partially successful, in that the population parameters became ~3:1 in favor of the inner site (corresponding to the Ni site being vacant three-quarters of the time); however, R was slightly worse and the distances from ‘Ni’ to the outer atoms were only 2.25 Å compared with an expected value of ~2.4 Å for octahedrally coordinated Ni (or Cr; Pauling, 1960). This situation remains unclear.

Also unclear is the distribution of atoms along the threefold axis at $x = y = 0$. The electron density distribution along this line shows a somewhat broad peak at $z = 0$ (and $z = 0.5$) and a larger broader peak at $z = 0.25$ (0.75), suggesting that there are four atoms in a somewhat disordered array along this 12.5 Å axis. The peak at $z = 0$ can be represented satisfactorily by an isotropic Al atom, Al19, disordered between two positions ~0.4 Å apart, on either side of $z = 0.0$. The peak at $z = 0.25$ is more complicated and I have represented it by four quarter-populated sites, two of Cr (Cr7) and two of Al (Al20); while the total number of electrons seems approximately correct, the resulting U_{iso} ’s are unusual (Table 1) and other interpretations are surely possible, perhaps involving Ni atoms. My refinement in $P6_3/m$ included anisotropic U^{ij} ’s for four atoms; isotropic U ’s seemed adequate for the remainder. Two of the anisotropic atoms are those coordinated to ‘Ni’; the other two, Cr6 and Al18, are coordinated to the atoms along the chain at $x = y = 0$, and undoubtedly join them in disorder.

In view of the disorder, the exact composition of the crystal is uncertain. What can be said is that this revised structure indicates, at best, only a small amount of Ni in the crystal studied; the approximate composition is $\text{Al}_{177}\text{Cr}_{49}\text{Ni}$. This is at odds with the analytical results reported by SYLHHS, who

† T. Haibach and W. Steurer have informed me that they were not involved in that structure determination, and were not aware that a manuscript had been prepared.

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$$
 for Cr6, Al8, Al13 and Al18, U_{iso} for all others.

	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$	No. in unit cell
Cr1	0.10866 (5)	0.40289 (5)	0.07749 (6)	0.0042 (1)	12
Cr2	0.42386 (7)	0.14663 (7)	1/4	0.0040 (2)	6
Cr3	0.22396 (7)	0.26463 (8)	1/4	0.0046 (2)	6
Cr4	0.18527 (7)	0.49372 (7)	1/4	0.0051 (2)	6
Cr5	0.53589 (7)	0.08028 (8)	1/4	0.0043 (2)	6
Cr6	0.13942 (6)	0.00908 (5)	0.05036 (7)	0.0090 (1)	12
Cr7	0	0	0.2313 (4)	0.0004 (9)	1
Al1	0.27634 (10)	0.03529 (10)	0.13523 (12)	0.0062 (3)	12
Al2	0.01879 (13)	0.39011 (13)	1/4	0.0022 (3)	6
Al3	0.41243 (10)	0.20513 (10)	0.07009 (13)	0.0068 (3)	12
Al4	0.29496 (10)	0.27786 (10)	0.06803 (13)	0.0090 (3)	12
Al5	0.08024 (10)	0.53822 (10)	0.13636 (13)	0.0074 (3)	12
Al6	0.13073 (10)	0.26164 (10)	0.05933 (14)	0.0094 (3)	12
Al7	0.48443 (10)	0.39688 (10)	0.06964 (13)	0.0069 (3)	12
Al8	0.57614 (11)	0.22628 (11)	0.13670 (13)	0.0105 (3)	12
Al9	0.43593 (10)	0.06077 (10)	0.06432 (12)	0.0067 (3)	12
Al10	0.49875 (15)	0.30793 (15)	1/4	0.0071 (4)	6
Al11	0.38147 (15)	0.38228 (14)	1/4	0.0071 (4)	6
Al12	0.26831 (10)	0.42233 (10)	0.13648 (13)	0.0078 (3)	12
Al13	0.24593 (10)	0.56425 (11)	0.05757 (14)	0.0110 (3)	12
Al14	0.30951 (15)	0.18987 (15)	1/4	0.0076 (4)	6
Al15	0.12278 (14)	0.32793 (14)	1/4	0.0036 (4)	6
Al16	0.34776 (15)	0.58098 (15)	1/4	0.0070 (4)	6
Al17	0.02892 (16)	0.15168 (16)	1/4	0.0118 (5)	6
Al18	0.14114 (14)	0.12231 (14)	0.13675 (17)	0.0239 (5)	12
Al19	0	0	0.0148 (5)	0.0094 (11)	2
Al20	0	0	0.1767 (13)	0.022 (3)	1
Ni1	2/3	1/3	0.0419 (4)	0.0053 (7)	1

found appreciably greater amounts of Ni. A plausible explanation is that the sample, which was prepared from a melt, was not homogeneous. In any event, further experiments would be necessary to uncover the reason for the discrepancy in composition.

References

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