Refinement of the γ-Cu$_9$Al$_4$ Structure

SVEN WESTMAN

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

The crystal structure of the cubic γ-Cu$_9$Al$_4$ phase has been refined, using single-crystal X-ray diffractometer data. The refined structure is described in terms of atomic clustering, coordination and bond lengths. Some of the structural features are discussed in terms of "bond number" regularities. The importance of Cu-Al bonding relative to Cu-Cu bonding *within* atomic clusters is demonstrated.

The refinement of the structure of Cu$_9$Al$_4$[1,2] was undertaken as part of the investigation of the γ-brass-like structures of the (possibly) three phases occurring at lower temperatures within the composition range 31—41 atomic % aluminium in the Cu-Al system.[3]

According to Bradley, Goldschmidt and Lipson[3] the homogeneity range of the undistorted cubic phase, the ideal composition of which is Cu$_9$Al$_4$, extends from 31.3 to 35.2 atomic % aluminium, after slow cooling. The unit cell edge is reported, by these authors, to increase from 8.685 to 8.703 Å between the above composition limits. Other authors report similar phase ranges at temperatures near 500°C.[4]

A phase analysis study at 660°C, by the present author[5] confirms the phase range found by Bradley *et al.*[3] The lattice parameter (measured at 20°C), however, increases from 8.700 Å at the lower limit (31.3 at. % Al) to 8.715 Å at the higher limit (somewhere between 35 and 36 atomic % Al).

The Cu$_9$Al$_4$ structure type is designated $D8_3$ by *Strukturbericht*. The atomic positional parameters, in space group $P\bar{4}3m$, given by Bradley and Jones[2] were used as a starting point in this investigation, and are reproduced alongside the refined parameters obtained.

An account of the result of the refinement has been published previously in a report from this Institute.[6] Since then, the lattice parameter a of the sample under investigation has been remeasured[5] on a more precisely aligned instrument. The new value is ~ 0.003 Å lower than the one previously measured. All interatomic distances and bond numbers have been recomputed using the lower value. The changes, though systematic, are well within the standard deviation ranges for all distances considered. The bond number discussion is in no way affected.

EXPERIMENTAL

Weighed amounts of copper (foil, 100.0 % Cu, J. T. Baker Chemical Co.) and aluminium (puriss, ribbon > 99,99 % Al, E. Merck A. G.) totaling 2 g were melted together by induction heating in a BeO crucible under vacuum ($< 1 \mu$). The pellets produced in this fashion were crushed in a steel mortar and the powder annealed at 660°C for ten days in evacuated silica capsules.

The alloy samples were analyzed electrolytically for copper according to standard practice. [7] The analyzed copper content was generally found to be around 0.5 atomic % less than the nominal composition.

X-Ray powder diffraction photographs of the alloys were taken, for phase analysis purposes and for lattice constant determination, with a Guinier focusing camera of 80 mm diameter, using monochromatized $CuK\alpha_1$ radiation ($\lambda = 1.54051$ Å). For accurate determination of lattice parameters, KCl was added as an internal standard. Its lattice parameter, $a = 6.2919$ Å at 20°C has been given by Hambling.[8] Details of the procedure have been reported elsewhere.[9]

The equipment used for single crystal work was a General Electric goniometer with a single crystal orienter (goniostat) and a proportional counter for determination of diffracted X-ray intensity. $CuK\alpha$ radiation was used for the measurements.

An irregular fragment of approximate dimensions $0.25 \times 0.06 \times 0.07$ mm was selected from a single-phase sample of analyzed composition $Al_{315}Cu_{685}$. Its shape was determined under the microscope and the coordinates of its corners established in the coordinate system used to describe its orientation on the goniostat. The data were used for the calculation of absorption corrections. The linear absorption coefficient in this case is 35 mm^{-1}.

The procedure for crystal alignment and intensity recording is described in detail by Furnas.[10] The integrated intensities were obtained by measurement, with a planimeter, of the peak areas in the intensity graph.

One half octant of the reciprocal lattice was covered, with occasional checks of other reflexions.

All data reduction and computation was carried out on the computers BESK and FACIT EDB of the Computer Division of the National Swedish Rationalization Agency. The programs used are listed in Ref. 6.

STRUCTURE REFINEMENT

The monophase preparation used in the search for single crystals was the one with the best approximation to ideal composition ($Al_4Cu_9 = Al_{308}Cu_{692}$). The analyzed composition of the sample was $Al_{315}Cu_{685}$. The lattice parameter calculated from its Guinier powder pattern is [5]

$$a = 8.7023 \pm 0.0005 \text{ Å} \qquad \text{(standard deviation)}$$

The positions of the copper and aluminium atoms reported by Bradley and Jones [2] were used as a starting point for structure factor calculations. Fourier maps showed the coordinates to be essentially correct. Therefore the least-squares refinement was started directly from this point.

The space group is $P\bar{4}3m$ (No. 215). The 52 atoms per unit cell are in the following special positions:

Cu(1) in 6(f), Cu(2) in 6(g), Cu(3) in 4(e), Cu(4) in 4(e),
Cu(5) in 4(e), Cu(6) in 12 (i);
Al(7) in 4(e) and, finally Al(8) in 12 (i).

In five cycles of refinement, using Cruickshank's weighting scheme with $w = 1/(20 + |F_o| + 0.004 \, |F_o|^2)$, the value of the residual, $R = \Sigma ||F_o| -$

$|F_c|/\Sigma|F_o|$, as indicated by the L. S. program dropped from 19.2 % to 12.7 % and remained stationary during the sixth and last cycle. Over the last three cycles, the values of the atomic coordinates generally oscillated with insignificant amounts.

The thermal parameters still showed some tendency to »creep», though appreciably less than their standard deviations. A further refinement was, however, deemed to be of doubtful value. The magnitudes of the B's should, e.g., be severely influenced by the accuracy of the absorption corrections, which is probably not very high, owing to the size and irregular shape of the crystal.

If any significance at all is to be attached to the thermal parameters, the tendency for copper to have, in general, the greater magnitude of B (Table 1) might be an indication of partial substitution of aluminium for copper, or vice versa. No attempts were made, however, to proceed with the refinement along these lines. There was no indication of preferential substitution in position 12(i) as claimed by Bradley, Goldschmidt and Lipson.[3]

Table 1. Fractional atomic coordinates, and temperature factors. The values in parantheses are those of Bradley and Jones.

Atom	x	σ_x	z	σ_z	B (Å^2)	σ_B
Cu(1)	0.3561 (0.356)	0.0006			0.935	0.088
Cu(2)	0.8559 (0.856)	0.0007			1.230	0.095
Cu(3)	0.8305 (0.828)	0.0005			1.184	0.063
Cu(4)	0.3248 (0.331)	0.0005			1.220	0.063
Cu(5)	0.6052 (0.601)	0.0004			0.825	0.053
Cu(6)	0.3145 (0.312)	0.0005	0.0329 (0.036)	0.0004	1.043	0.063
Al(7)	0.1151 (0.112)	0.0009			−0.215	0.098
Al(8)	0.8089 (0.812)	0.0010	0.5362 (0.536)	0.0009	0.498	0.136

A comparison of observed and calculated structure factors is given in the DIS report.[6] It appeared that the strongest reflexions observed, viz. (330), (411), (600), and (444) have $|F_o|$ very much less than $|F_c|$. If it be assumed that these reflexions are appreciably affected by extinction, they should be excluded from the refinement (the program did so automatically for 330) and from the calculation of R.

In that case, a value of $R = 9.3$ % is obtained. A weight analysis of the structure factor fit is given in Ref. 6.

The refined atomic coordinates and isotropic temperature factors are given in Table 1, together with the starting parameters taken from Bradley and Jones.[2] It will be observed from the table, that the largest shift of position obtained in the refinement is that of Cu(4), which is of the order of 0.1 Å.

GEOMETRICAL DESCRIPTION OF THE STRUCTURE

The γ-Cu_9Al_4 structure may be described [11] in terms of two geometrically similar clusters of 26 atoms each. (In γ-brass the clusters are identical.)

One cluster, A, with its center at the origin, 0,0,0; contains 22 copper atoms, *viz.* 6 Cu(1), 4 Cu(3), 12 Cu(6), and 4 aluminium atoms, *viz.* 4 Al(7). The cluster is shown in Fig. 1.
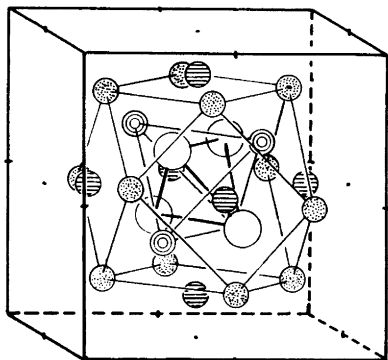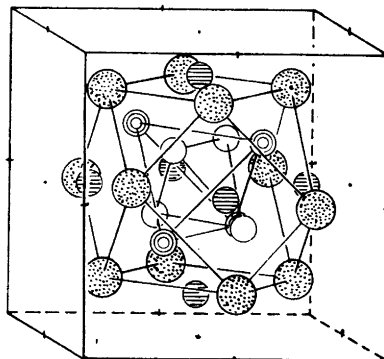

= Cu(1) in 0.356 0   0   etc.

= Cu(3) in -0.170 -0.170 -0.170 etc.

= Cu(6) in 0.315 0.315 0.033 etc.

= Al(7) in 0.115 0.115 0.115 etc.

Fig. 1. The cluster, A, of atoms around the origin, 000.

= Cu(2) in 0.856 0.500 0.500 etc.

= Cu(4) in 0.325 0.325 0.325 etc.

= Cu(5) in 0.605 0.605 0.605 etc.

= Al(8) in 0.809 0.809 0.536 etc.

Fig. 2. The cluster, B, of atoms around the center, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

The other cluster, B, centered on $\frac{1}{2},\frac{1}{2},\frac{1}{2}$; consists of 14 copper atoms and 12 aluminium atoms, *viz.* 6 Cu(2), 4 Cu(4), 4 Cu(5), and 12 Al(8). It is depicted in Fig. 2.

Interatomic distances in the structure, of magnitude less than 3 Å, have been computed. They are given, with standard deviations, in Table 2. The corresponding distances, calculated from the coordinates reported by Bradley and Jones,[2] are also listed.

The coordination numbers of corresponding atoms in cluster A and B are the same, namely:

A	B	$C.N.$
Cu(1)	Cu(2)	13
Cu(3)	Cu(4)	12
Al(7)	Cu(5)	12
Cu(6)	Al(8)	11

Table 2. Interatomic distances and their standard deviations. The values in column B & J are those of Bradley and Jones.[2] N = number of distances within one unit cell.

N	Atoms	d (Å)	a_d	B & J	Bond number
3	Cu(1) — Cu(1)	2.505	± 0.010	2.51	0.555
12	Cu(1) — Cu(3)	2.644	± 0.005	2.66	0.326
24	Cu(1) — Cu(6)	2.776	± 0.004	2.76	0.196
3	Cu(2) — Cu(2)	2.508	± 0.012	2.51	0.550
12	Cu(2) — Cu(4)	2.669	± 0.004	2.64	0.296
12	Cu(2) — Cu(5)	2.537	± 0.005	2.54	0.492
12	Cu(2) — Cu(6)'	2.754	± 0.007	2.80	0.214
12	Cu(2) — Cu(6)''	2.480	± 0.006	2.50	0.612
12	Cu(3) — Cu(6)	2.507	± 0.005	2.50	0.552
12	Cu(4) — Cu(5)	2.588	± 0.006	2.50	0.404
12	Cu(4) — Cu(6)	2.543	± 0.006	2.58	0.481
6	Cu(5) — Cu(5)	2.589	± 0.005	2.49	0.403
6	Al(7) — Al(7)	2.833	± 0.022	2.76	0.274
12	Cu(1) — Al(7)	2.531	± 0.004	2.53	0.663
12	Cu(1) — Al(8)'	2.826	± 0.012	2.80	0.214
12	Cu(1) — Al(8)''	2.532	± 0.012	2.50	0.661
24	Cu(2) — Al(8)	2.737	± 0.007	2.76	0.301
12	Cu(3) — Al(7)	2.566	± 0.008	2.58	0.580
12	Cu(3) — Al(8)	2.575	± 0.009	2.55	0.560
12	Cu(4) — Al(8)	2.468	± 0.010	2.51	0.844
12	Cu(5) — Al(8)	2.578	± 0.013	2.66	0.554
12	Cu(6) — Al(7)	2.556	± 0.010	2.55	0.603
24	Cu(6) — Al(8)'	2.602	± 0.006	2.59	0.505
24	Cu(6) — Al(8)''	2.577	± 0.007	2.59	0.552

DISCUSSION

The only aluminium-aluminium contact is Al(7) — Al(7) in cluster A. The contact distance, 2.833 ± 0.022 Å is apparently slightly less than the interatomic distance in the pure element, 2.863 Å at 20°C.[12] This is entirely natural, considering that the coordination number of Al(7) is 11 instead of 12 as in the close-packed metal. Application of a coordination correction factor [13] of 0.99 to the interatomic distance in the element indicates that the contact distance in the alloy should be approximately 2.83 Å.

The interatomic distances between neighboring copper atoms range from 2.480 Å to 2.776 Å, the extreme values 2.776 (Cu(1)—Cu(6), 2.754 (Cu(2)—Cu(6)'), 2.505 (Cu(1)—Cu(1)), and 2.480 (Cu(2)—Cu(6)'') occurring in the irregular coordination shells around the 13-coordinated atoms Cu(1) and Cu(2). The over-all average Cu—Cu contact distance, $\Sigma N \cdot d / \Sigma N$, is 2.620 Å. Excluding contacts with the 13-coordinated atoms, *i.e.* considering only the Cu(3)—Cu(6), Cu(4)—Cu(5), Cu(4)—Cu(6), and Cu(5)—Cu(5) contacts, the average Cu—Cu distance becomes 2.552 Å. The interatomic distance in copper metal is 2.556 Å.[12]

The functionally similar distances Cu(1)—Cu(1) (cluster A — cluster A') and Cu(2)—Cu(2) (cluster B — cluster B') are equal in magnitude: 2.505 ±

0.010 Å and 2.508 $\pm$ 0.012 Å, respectively. It is a noteworthy fact that Cu(1)—Cu(3) in cluster A is shorter, by 0.025 Å, than its structural equivalent in cluster B, Cu(2)—Cu(4).

The over-all average copper-aluminium contact distance is 2.605 Å, which is less than both the average Al—Al (2.833 Å) and Cu—Cu (2.620 Å) distances. It should be noted that the Cu—Al distance in Cu_2Al is of similar magnitude: 2.59 Å, according to Friauf.[14] In order to avoid the obscuring effects of varying coordination number, it will be well to compare copper-copper distances within cluster A with the crystallographically similar copper-aluminium distances within cluster B, and *vice versa:*

$$
\begin{aligned}
Cu(1)-Al(7) &: 2.531 \text{ Å} \leq Cu(2)-Cu(5) : 2.537 \text{ Å} \\
Cu(2)-Al(8) &: 2.737 \text{ Å} < Cu(1)-Cu(6) ; 2.776 \text{ Å} \\
Cu(3)-Al(7) &: 2.566 \text{ Å} < Cu(4)-Cu(5) : 2.588 \text{ Å} \\
Cu(4)-Al(8) &: 2.468 \text{ Å} < Cu(3)-Cu(6) : 2.507 \text{ Å}
\end{aligned}
$$

Thus it appears that, *within* the separate clusters, the extent of copper-aluminium bonding is greater than that of either copper-copper or aluminium-aluminium bonding. This is as one might expect.

However, comparing corresponding Cu—Cu and Cu—Al distances *between* clusters:

$$
\begin{aligned}
Cu(1)-Al(8)'' &: 2.532 \text{ Å} > Cu(2)-Cu(6)'' : 2.480 \text{ Å} \\
Cu(1)-Al(8)' &: 2.826 \text{ Å} > Cu(2)-Cu(6)' : 2.754 \text{ Å}
\end{aligned}
$$

it would seem that here the copper-copper bonding assumes relatively greater importance, although the Cu(1)—Al(8)'' distance is still shorter than the Cu—Cu distance in the metallic element.

The preceding considerations will contribute to an understanding of the nonequality of the Cu(1)—Cu(3) and Cu(2)—Cu(4) distances. Comparing the coordination around structurally equivalent atoms:

Distance Cu(1) —		*Distance Cu(2)* —
	within clusters	
Cu(6) × 4	>	Al(8) × 4
Al(7) × 2	=	Cu(5) × 2
	between clusters	
Al(8) × (2+2)	>	Cu(6) × (2+2)
Cu(1) × 1	=	Cu(2) × 1

Distance Cu(3) —		*Distance Cu(4)* —
	within clusters	
Cu(6) × 3	>	Al(8) × 3
Al(7) × 3	<	Cu(5) × 3
	between clusters	
Al(8) × 3	>	Cu(6) × 3

Both Cu(1) and Cu(3) appear to be less firmly bonded to the rest of their environment than Cu(2) and Cu(4), respectively. It is therefore quite reasonable for Cu(1)—Cu(3) (2.644 Å) to be somewhat shorter than its functional counterpart Cu(2)—Cu(4) (2.669 Å).

There are two structurally similar types of Cu—Al distance *within* the clusters, namely Cu(5)—Al(8): 2.578 $\pm$ 0.013 Å and Al(7)—Cu(6): 2.556 $\pm$ 0.010 Å. Their standard deviation ranges overlap, and they may therefore be considered to be nearly equal. The two remaining, structurally distinct, types of Cu—Al contact, *between* clusters, *viz.* Cu(6)—Al(8)' : 2.602 Å and Cu(6)—Al(8)'': 2.577 Å, have no Cu—Cu structural equivalents. The four last distances discussed are slightly less than average for the structure. They are all distinctly shorter than the mean, 2.710 Å, of the interatomic distances in the two elements.

The preceding arguments can be systematized and substantiated by appeal to Pauling's bond number concept.[15] The interatomic distance for bond number n being designated D(n), Pauling gives the relation:

$$D(n) = D(1) - 0.600 \; \log \; n$$

Values of D(1) for the types of contact discussed have been calculated from the univalent radii tabulated in *The Nature of the Chemical Bond*.[15]

$$r(1)_{Al} = 1.248 \text{ Å} \qquad r(1)_{Cu} = 1.176 \text{ Å}$$

Thus:

$$D(1)_{Al-Al} = 2.496 \text{ Å}, \qquad D(1)_{Cu-Cu} = 2.352 \text{ Å} \quad \text{and}$$
$$D(1)_{Cu-Al} = 2.424 \text{ Å}$$

The bond number values calculated from these data and the interatomic distances obtained in the present investigation are listed in Table 2.

The figures bring out the relative importance of Cu—Al bonding within clusters:

Cu—Cu bond	n	Equivalent Cu—Al bond	n'	n/n'
		within clusters		
Cu(1)—Cu(6)	0.196	Cu(2)—Al(8)	0.301	~ 0.7
Cu(2)—Cu(5)	0.492	Cu(1)—Al(7)	0.663	~ 0.7
Cu(3)—Cu(6)	0.552	Cu(4)—Al(8)	0.844	~ 0.7
		between clusters		
Cu(2)—Cu(6)'	0.214	Cu(1)—Al(8)'	0.214	~ 1.0
Cu(2)—Cu(6)''	0.612	Cu(1)—Al(8)''	0.661	~ 0.9

A considerable amount of interest also attaches to the sum of bond numbers for the contacts between one atom and its environment.

Cluster A	$\Sigma \, n$	Cluster B	$\Sigma \, n$	$\Sigma \, n_{Cu}/\Sigma \, n_{Al}$
Cu(1)	5.08	Cu(2)	4.99	
Cu(3)	6.07	Cu(4)	6.07	
Al(7)	6.37	Cu(5)	5.56	0.87
Cu(6)	4.98	Al(8)	5.56	0.90

The tabulation brings out the notable feature that $\Sigma \, n$ is very nearly the same for structurally corresponding Cu atoms in the two clusters A and B,

even though their environments differ chemically (Cu(3) coordinates 6 Cu + 6 Al, whereas Cu(4) coordinates 9 Cu + 3 Al). This regularity has some bearing on the discrepancy between the magnitudes of the crystallographically equivalent contact distances Cu(1)—Cu(3) and Cu(2)—Cu(4). Had those distances been equal, this would have yielded almost exactly the same $\Sigma\, n$ for Cu(1) and Cu(2), but would have produced a difference in $\Sigma\, n$ for Cu(3) and Cu(4). The Cu(1)—Cu(3) distance being the shorter makes $\Sigma\, n$ for Cu(3) and Cu(4) equal to within 0.01 unit. Thus; it would appear that the difference in contact distance ought to be in the direction found. The regularity in $\Sigma\, n$, or the validity of the bond number concept, seems to be too limited to allow of an accurate prediction of its magnitude.

Pursuing the bond number discussion further, it appears, that $\Sigma\, n$ is smaller by a factor of ~ 0.9 for a copper atom in one cluster than for its aluminium counterpart in the other cluster.

If the bond numbers are summed over all the atoms in the unit cell (36 Cu + 16 Al), $\Sigma\, \Sigma\, n = 283$. If the atoms are all accorded their usual metallic valencies, given by Pauling as 5.56 and 3, respectively, $\Sigma\, \Sigma\, n$ would be $= 248$. Aluminium can yield no more than 3 valence electrons. Under the prevailing conditions, therefore, copper would have to contribute an average of 6.53 electrons per atom to the bonding. Approximately one (1.23) of these 6.53 electrons per copper atom is, in Paulings parlance, transferred to aluminium to bring its metallic valence up to around 6 — *i.e.* 5.6 for Al(8) and 6.4 for Al(7).

In order to fit into this bonding scheme, aluminium will have to make use of nearly two (average 1.76) of its five $3d$ orbitals, as in the aluminates.

The physical significance of the bond number concept must not be overemphasized, however. It should be observed that, with the low electronegativity difference, ~ 0.4, between Cu and Al the ionic character of the bonds ought to be rather small. The bonding scheme described places an average formal negative charge of 2.76 units on aluminium, which runs counter to the direction of the electronegativity difference.

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