

γ -Brasses with F Cells

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The crystal structures of phases with ideal compositions $\text{Sn}_{11}\text{Cu}_{41}$ and $\text{Sn}_3\text{Cu}_9\text{Ni}$ have been determined by X-ray diffraction from single crystals. Both phases have cubic γ -brass-type superstructures, $a = 17.98$ and $a = 18.01$ Å respectively, space group $F\bar{4}3m$. The structures are built up of four different clusters of 26 atoms, each containing site sets referred to as the inner tetrahedron (IT), outer tetrahedron (OT), octahedron (OH), and cubo-octahedron (CO). The large Sn atoms in both structures are located in sites OT, CO, none, and OH... in four successive clusters along $\langle 111 \rangle$, an ordering which uniquely prevents any close contact between the Sn atoms. Reasons for the formation of the F superstructure are discussed, as are observed Cu–Cu distances in the IT sites in these two structures.

Introduction

The γ -brass structure can be described as built up of clusters of 26 atoms which are created from an inner tetrahedron (IT) of four atoms, surrounded by an outer tetrahedron (OT) of four atoms, then an octahedron (OH) of six atoms and finally a cubo-octahedron (CO) of 12 atoms for a total of 26 atoms (Bradley & Jones, 1933). In cubic γ -brasses with the I cell ($a \sim 9$ Å), these 26-atom clusters pack together as pseudo atoms in the b.c. cubic arrangement; in those with the P cell ($a \sim 9$ Å) two different clusters, A and B, pack together in the CsCl arrangement and in those with the F cell ($a \sim 18$ Å) four different clusters, A, B, C, D, pack together in an arrangement not yet recognized as a superstructure of the b.c. cubic structure. On the other hand, no γ -brass arrangements corresponding to the Li_3Bi , NaTl or Heusler alloy, AlMnCu_2 , superstructures of a b.c. cube have yet been recognized. Neither are any close-packed arrangements of the

26-atom clusters of γ -brasses known. This results from the 'cubic' $\bar{4}$ and 3 symmetry axes of the clusters whose outer shell is a cubo-octahedron, since no sensible packing arrangement between clusters results along $\langle 110 \rangle$ when the clusters are aligned, as they must be, with the orthogonal axes defined by the atoms on OH sites, coinciding with the cubic cell axes, $\langle 100 \rangle$.

At least six γ -brasses have been reported to take the ~ 18 Å F cell: $\text{Sn}_{11}\text{Cu}_{41}$ (Westgren & Phragmén, 1926, 1928; Bernal, 1928; Hendus & Knödler, 1956; Knödler, 1957, 1964), $\text{Sn}_3\text{Cu}_9\text{Ni}$ (Booth, 1973), $\text{Sn}_2\text{Al}_2\text{Cu}_{12}$ (Leach & Raynor, 1954), $\text{Pt}_5\text{Zn}_{21}$ (Ekman, 1931), $\text{Ce}_5\text{Hg}_{21}$ (Berndt, 1967) and $\text{Pu}_5\text{Hg}_{21}$ (Berndt, 1966). Only γ -Pt–Zn, at a composition $\text{Pt}_3\text{Zn}_{10}$, has been reported examined by single-crystal methods (Johansson & Westman, 1970). In this paper we report single-crystal studies of phases with ideal compositions $\text{Sn}_{11}\text{Cu}_{41}$ and $\text{Sn}_3\text{Cu}_9\text{Ni}$ to establish the ordering of the atoms and to discover why the phases take the F rather than the I or P cells. Recently we became aware that

Table 1. *Crystal data for δ -Cu–Sn and $\text{Sn}_3\text{Cu}_9\text{Ni}$*

	δ -Cu–Sn	$\text{Sn}_3\text{Cu}_9\text{Ni}$
Crystal system	Cubic	Cubic
Space group	$F\bar{4}3m$	$F\bar{4}3m$
Cell constant (Å)	17.980 (7)	18.011 (8)
Composition		
(a) Nominal at. % from preparation	20.5 Sn, 79.5 Cu	23.1 Sn, 69.2 Cu, 7.7 Ni
(b) At. % for refined model	21.4 Sn, 78.6 Cu	22.0 Sn, 70.2 Cu, 7.8 Ni*
D_m	8.83 g cm ⁻³	8.68 g cm ⁻³
Chemical formula		
(a) From nominal composition and D_m	$\text{Sn}_{84.7}\text{Cu}_{328.3}$	$\text{Sn}_{92.9}\text{Cu}_{278.6}\text{Ni}_{31.0}$
(b) For refined model	$\text{Sn}_{88}\text{Cu}_{324}$	$\text{Sn}_{88.0}\text{Cu}_{280.8}\text{Ni}_{31.2}$ *
Atoms/unit cell		
(a) From nominal composition and D_m	413	402.5
(b) For refined model	412	400
D_x (For refined model composition)	8.86 g cm ⁻³	8.56 g cm ⁻³
$\mu(\text{Mo K}\alpha)$	391 cm ⁻¹	377 cm ⁻¹

* Refined model of $\text{Sn}_3\text{Cu}_9\text{Ni}$ actually used Cu atomic scattering factors for Ni atoms.

$\text{Sn}_{11}\text{Cu}_{41}$ is also the subject of another single-crystal study (Arnberg, Jonsson & Westman, 1975), with results generally resembling those found by us. Mazzoleni (1953) reported that $\text{Sn}_3\text{Cu}_9\text{Ni}$ has a 9 \AA cell.

Experimental

The alloys were prepared from 99.99% pure Cu and Sn and 99.95% pure Ni, the $\delta\text{-Cu-Sn}$ alloy (20.5 at.% Sn) by melting the elements in an evacuated quartz tube at 800°C with subsequent annealing at 730°C (2 days) and 560°C ($5\frac{1}{2}$ days) before quenching in water. $\text{Sn}_3\text{Cu}_9\text{Ni}$ was first levitation-melted by induction heating and subsequently remelted at 900°C in an evacuated quartz tube, being finally annealed for 100 h at 800°C and then quenched in water. Small single crystals were selected from crushed portions of each alloy.

Rotation, Weissenberg and precession diffraction patterns of each alloy showed the intensity relationships of Laue class $m\bar{3}m$ and the systematic absences for an F -type lattice. The possible cubic space groups are $F432$ (No. 209), $F\bar{4}3m$ (No. 216), and $Fm\bar{3}m$ (No. 225) (*International Tables for X-ray Crystallography*, 1969). Since typical γ -brass structures can be described in terms of clusters of 26 atoms packed about point sites of $\bar{4}3m$ symmetry, the space group $F\bar{4}3m$ was chosen and later proved to be correct. The cell constants were determined initially from the photographs and later refined by least-squares methods with 2θ values measured on a General Electric XRD-6 single-crystal automated diffractometer using Ni-filtered $\text{Cu } K\alpha$ radiation ($\lambda_{K\alpha} = 1.5418 \text{ \AA}$). These and other crystal data are summarized in Table 1.

The crystal of $\delta\text{-Cu-Sn}$ used for intensity measurements was approximately spherical with a radius varying from 0.04 to 0.05 mm and a mean radius of

0.041 mm. The crystal of $\text{Sn}_3\text{Cu}_9\text{Ni}$ was approximately cylindrical with a radius varying from 0.036 to 0.047 mm and with a mean radius 0.042 mm and length 0.092 mm. In both cases the crystals were mounted with $[001]$ along the ϕ axis of the goniometer. The intensities were measured on the diffractometer with a scintillation counter, pulse-height analyser, Zr-filtered $\text{Mo } K\alpha$ radiation and a $\theta-2\theta$ scan. The scan range in 2θ was $\pm(0.9 + 0.3 \tan \theta)^\circ$. Standard errors in the intensities, σ , were obtained from counting statistics and, during later analysis of the data, it was possible to consider as reliable only those reflexions with intensities greater by $K\sigma$ than the background, with K values between 0 and 3 being used at various stages in the final refinement. Lorentz and polarization corrections were applied with the program *DATAPREP* on the University of Waterloo IBM 360/75 computer. In the refinement reported below for $\delta\text{-Cu-Sn}$, the threshold of observability was set at 1.5σ for all reflexions except the reciprocal-lattice rows $00l$ and $0kk$ for which 5σ was used because of strong streaks, leaving a total of 310 independent observed reflexions. For the reported refinement of $\text{Sn}_3\text{Cu}_9\text{Ni}$ the 1.5σ level was used for all reflexions, leaving 224 as observed.

Structure refinements and analyses

The cluster concept, first introduced by Bradley & Jones (1933), can be used to generate atomic coordinates of trial models for γ -brass-type structures. In the case of $18 \text{ \AA } F$ superstructures, the likely space group allowing individual clusters to retain their usual $\bar{4}3m$ point-group symmetry is $F\bar{4}3m$. Fig. 1 shows all the locations of the four crystallographically distinct clusters A, B, C, and D in the unit cell. The idealized atom coordinates in $F\bar{4}3m$ may then be generated by describing a cluster of atoms centred on each of these locations. It is only necessary to specify coordinates of one IT, OT, OH and CO atomic site in each of the four distinct clusters along $[111]$.

After coordinates for a trial F cell were generated, a full-matrix least-squares refinement program *LSTSQOR* (a modified version of *ORFLS*, Oak Ridge full-matrix least-squares program) was used with average atomic scattering factors on all sites to refine the scale factor and overall isotropic temperature factor, followed by several cycles of coordinate and occupancy-factor refinement. Certain occupancy factors increased considerably from their idealized values indicating sites where Sn might be located, namely B CO, D OH and A OT. Tests in which the refinement was started with all coordinates fixed at idealized values, with Sn scattering factors used on B CO and with average scattering factors on other sites, led to increased occupancy factors for D OH and A OT and confirmed a model in which Sn atoms were

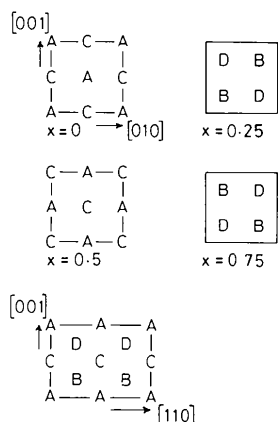


Fig. 1. Schematic diagrams of the $18 \text{ \AA } F$ cell of γ -brasses, showing locations of the four distinct cluster types in the cubic unit cell.

Table 2. Atomic coordinates and isotropic temperature factors for δ -Cu—Sn and $\text{Sn}_3\text{Cu}_9\text{Ni}$

Figures in parentheses are standard errors in the last digits quoted as derived in the least-squares refinement.

Cluster	Site	Point set	δ -Cu—Sn ($a_0 = 17.980 \text{ \AA}$)			$\text{Sn}_3\text{Cu}_9\text{Ni}$ ($a_0 = 18.011 \text{ \AA}$)				
			Atoms	x	z	$B (\text{\AA}^2)$	Atoms†	x	z	$B (\text{\AA}^2)$
A	IT	$x x x$	12 Cu*	0.0573 (7)		1.0 (3)	12 Cu*	0.0577 (11)		1.3 (4)
B	IT	$x x x$	16 Cu	0.3005 (5)		1.0 (2)	16 Cu	0.2988 (6)		0.3 (3)
C	IT	$x x x$	16 Cu	0.5504 (5)		0.5 (2)	16 Cu	0.5635 (9)		1.1 (4)
D	IT	$x x x$	16 Cu	0.8062 (6)		1.0 (2)	16 Cu	0.8046 (11)		2.6 (6)
A	OT	$x x x$	16 Sn	−0.0887 (3)		0.7 (1)	16 Sn	−0.0875 (5)		0.9 (3)
B	OT	$x x x$	16 Cu	0.1657 (7)		1.3 (3)	16 Cu	0.1638 (11)		1.2 (6)
C	OT	$x x x$	16 Cu	0.4166 (5)		0.6 (2)	16 Cu	0.4153 (10)		1.3 (5)
D	OT	$x x x$	16 Cu	0.6664 (6)		0.4 (2)	16 Cu	0.6647 (10)		1.3 (6)
A	OH	$0 0 z$	24 Cu	0.0	0.1763 (10)	1.2 (2)	24 Cu	0.0	0.1759 (12)	1.2 (4)
B	OH	$\frac{1}{2} \frac{1}{2} z$	24 Cu	0.25	0.4241 (8)	1.1 (2)	24 Cu	0.25	0.4249 (11)	0.7 (3)
C	OH	$\frac{1}{2} \frac{1}{2} z$	24 Cu	0.5	0.6765 (7)	0.5 (2)	24 Cu	0.5	0.6757 (12)	1.3 (4)
D	OH	$\frac{3}{4} \frac{3}{4} z$	24 Sn	0.75	0.9309 (4)	0.6 (1)	24 Sn	0.75	0.9299 (7)	1.3 (2)
A	CO	$x x z$	48 Cu	0.1562 (4)	0.0186 (6)	1.1 (2)	48 Cu	0.1580 (6)	0.0159 (9)	1.2 (3)
B	CO	$x x z$	48 Sn	0.4084 (3)	0.2680 (3)	1.5 (1)	48 Sn	0.4086 (5)	0.2678 (5)	1.9 (2)
C	CO	$x x z$	48 Cu	0.6465 (5)	0.5278 (6)	1.8 (2)	36 Cu*	0.6510 (9)	0.5255 (12)	1.3 (4)
D	CO	$x x z$	48 Cu	0.9087 (4)	0.7631 (5)	1.0 (2)	48 Cu	0.9106 (7)	0.7600 (8)	1.4 (3)

* A partial occupancy was found on this site.

† Ni sites unspecified.

Table 3. Interatomic distances (\AA) for the coordination shells about each atom in δ -Cu—Sn and $\text{Sn}_3\text{Cu}_9\text{Ni}$ Atomic species and distance values appear first for δ -Cu—Sn followed by those for $\text{Sn}_3\text{Cu}_9\text{Ni}$. Estimated standard errors are $\pm 0.03 \text{ \AA}$. Ni sites are unspecified.

Number	Cluster A		Cluster B		Cluster C		Cluster D					
	A IT (Cu*;Cu*) to:		B IT (Cu;Cu) to:		C IT (Cu;Cu) to:		D IT (Cu;Cu) to:					
3	A IT	2.91	2.94	B IT	2.57	2.48	C IT	2.56	3.24	D IT	2.86	2.78
3	A OT	2.74	2.72	B OT	2.57	2.61	C OT	2.55	2.72	D OT	2.61	2.64
3	A OH	2.59	2.59	B OH	2.57	2.59	C OH	2.60	2.59	D OH	2.66	2.65
3	A CO	2.61	2.66	B CO	2.81	2.85	C CO	2.48	2.33	D CO	2.72	2.82
1	B OT	3.38	3.31	C OT	3.62	3.64	D OT	3.61	3.16	A OT	3.27	3.36
	A OT (Sn; Sn) to:			B OT (Cu; Cu) to:			C OT (Cu; Cu) to:			D OT (Cu; Cu) to:		
3	A IT	2.74	2.72	B IT	2.57	2.61	C IT	2.55	2.72	D IT	2.61	2.64
3	A OH	2.75	2.74	B OH	2.68	2.72	C OH	2.70	2.71	D OH	2.75	2.76
3	A CO	2.58	2.59	B CO	2.63	2.63	C CO	2.56	2.61	D CO	2.58	2.57
3	D CO	2.67	2.75	A CO	2.66	2.67	B CO	2.68	2.66	C CO	2.54	2.53
1	D IT	3.27	3.36	A IT	3.38	3.31	B IT	3.62	3.64	C IT	3.61	3.16
	A OH (Cu; Cu) to:			B OH (Cu; Cu) to:			C OH (Cu; Cu) to:			D OH (Sn; Sn) to:		
2	A IT	2.59	2.59	B IT	2.57	2.59	C IT	2.60	2.59	D IT	2.66	2.65
2	A OT	2.75	2.74	B OT	2.68	2.72	C OT	2.70	2.71	D OT	2.75	2.76
1	C OH	2.65	2.67	D OH	2.61	2.61	A OH	2.65	2.67	B OH	2.61	2.61
4	A CO	2.85	2.88	B CO	2.88	2.89	C CO	2.73	2.79	D CO	2.89	2.92
2	D CO	2.56	2.55	A CO	2.60	2.57	B CO	2.53	2.54	C CO	2.74	2.65
2	B CO	2.85	2.86	C CO	3.23	3.10	D CO	2.80	2.74	A CO	2.86	2.81
	A CO (Cu; Cu) to:			B CO (Sn; Sn) to:			C CO (Cu; Cu*) to:			D CO (Cu; Cu) to:		
1	A IT	2.61	2.66	B IT	2.81	2.85	C IT	2.48	2.33	D IT	2.72	2.82
1	A OT	2.58	2.59	B OT	2.63	2.63	C OT	2.56	2.61	D OT	2.58	2.57
1	B OT	2.66	2.67	C OT	2.68	2.66	D OT	2.54	2.53	A OT	2.67	2.75
2	A OH	2.85	2.88	B OH	2.88	2.89	C OH	2.73	2.79	D OH	2.89	2.92
1	B OH	2.60	2.57	C OH	2.53	2.54	D OH	2.74	2.65	A OH	2.56	2.55
1	D OH	2.86	2.81	A OH	2.85	2.86	B OH	3.23	3.10	C OH	2.80	2.74
2	A CO	3.50	3.62	B CO	3.57	3.59	C CO	3.02	3.20	D CO	3.70	3.83
2	B CO	2.67	2.68	C CO	2.82	2.78	D CO	2.59	2.53	A CO	2.72	2.70
2	D CO	2.72	2.70	A CO	2.67	2.68	B CO	2.82	2.78	C CO	2.59	2.53
2	C CO	3.65	3.52	D CO	3.33	3.30	A CO	3.65	3.52	B CO	3.33	3.30

* A partial occupancy was found on this site (see Table 2).

predominantly ordered on these three sites. This behaviour in the initial refinements was common to both the δ -Cu-Sn and the Sn₃Cu₉Ni data sets. A model having been established for the ordering of Sn atoms, final refinement steps were carried out as described separately below. In all refinements, scattering factors were taken from *International Tables for X-ray Crystallography* (1968), the self-consistent wave function values being used for Cu and Ni and the Thomas-Fermi-Dirac statistical model values for Sn. Corrections for anomalous scattering with Mo *K* α radiation were taken from *International Tables for X-ray Crystallography* (1968) for Sn and Ni and from Cromer (1965) for Cu.

Continued refinement of δ -Cu-Sn with unit weights led to $R_1 = 0.076$ ($R_1 = \sum ||F_o| - |F_c|| / \sum F_o$, summations over the reflexions observed above threshold). Corrections for absorption were applied with a spherical approximation for the crystal and $\mu R = 1.86$ for Mo *K* α radiation. A Cruickshank-type weighting scheme, $w = (1825 - 1.0F_o + 0.0243F_o^2)^{-1}$, was introduced and an extinction parameter was refined. The extinction correction was a modified Zachariasen (1963) form. The isotropic temperature factor of A IT had the largest value and this was interpreted as a partial occupancy of that site. With *B* of A IT fixed at the average value 0.9 \AA^2 , the occupancy factor of A IT refined to about $\frac{2}{3}$ of its ideal value, indicating 412 atoms per unit cell rather than 416 if all 16 sites were fully occupied. The final refined parameters for δ -Cu-Sn are given in Table 2, and Table 3 gives the calculated interatomic distances. Table 4 gives the observed and calculated structure factors for δ -Cu-Sn corresponding to a final weighted R_w value of 0.094 $\{R_w = [\sum w(|F_o - F_c|)^2 / \sum w|F_o|^2]^{1/2}$, summations over reflexions observed above threshold}, with $R_1 = 0.070$.

Continued refinement of Sn₃Cu₉Ni with Sn on B CO, D OH and A OT and Cu on all other sites led to $R_w = 0.096$, but with large isotropic temperature factors of 3.0 and 5.0 \AA^2 on the A IT and C CO sites, whereas all other sites had values in the range 0.1 to 1.8 \AA^2 . This was interpreted as a partial occupancy of these two sites. Approximate absorption corrections for a cylindrical crystal were then applied to the data for a $\mu R = 1.66$ for Mo *K* α radiation. Refinement was continued by fixing the temperature factors of A IT and C CO at an average value of 1.26 \AA^2 and varying their occupancy factors. A final Cruickshank-type weighting scheme, $w = (187.5 - 1.0F_o + 0.002F_o^2)^{-1}$, was used and an extinction parameter was refined. This refinement yielded $R_w = 0.105$. A calculation of interatomic distances showed an unusually short IT-IT distance for Cu atoms of 2.48 \AA in the B cluster (Cu-Cu in contact is expected to be 2.56 \AA). Either this site is in compression within the structure, or it may be occupied by Ni atoms which have an expected Ni-Ni contact distance of 2.48 \AA . A model with Ni atoms on B IT

did not reduce R_w but led to $B(B \text{ IT}) = 0.02 \text{ \AA}^2$. As another possibility for ordered Ni sites, D IT was tested since it had the largest remaining *B* value of 2.56 \AA^2 . Again R_w did not improve although $B(D \text{ IT})$ reduced to 2.17 \AA^2 . No definite conclusions about the locations of the Ni atoms can be drawn. With Cu scattering factors for both Cu and Ni, our final refined parameters for Sn₃Cu₉Ni appear in Table 2 with calculated distances in Table 3 and structure factors in Table 4.

In both final models partial occupancy of certain sites is found. In δ -Cu-Sn the fractional occupancy of A IT is consistent with the measured density $D_m = 8.83 \text{ g cm}^{-3}$ since the stoichiometry of the refined model Cu₃₂₄Sn₈₈ gives a calculated density of $D_x = 8.86 \text{ g cm}^{-3}$. This stoichiometry corresponds to 21.4 at.% Sn and is within the δ range of the phase diagram (Hansen, 1958), although close to the Sn-rich boundary. These vacancies in A IT and possibly some in C CO, which has the next largest *B* value, are interpreted as the mechanism which allows some composition variation across the δ phase while maintaining a relatively fixed valence-electron concentration as the atomic percentage of the higher-valency element increases. That A IT should be vacant rather than other IT sites is probably because the central parts of the A cluster already possess large Sn atoms in A OT sites. (Reasons for Sn in A OT are discussed in the next section.) It is interesting to note that the partially occupied sites in Sn₃Cu₉Ni, which has a similar Sn distribution, occur in A IT and also in C CO. Such additional vacancies found in our refinement of

Table 4. *Observed and calculated structure amplitudes for Sn₁₁Cu₄₁ and Sn₃Cu₉Ni*

For Sn₁₁Cu₄₁, 310 independent reflexions were above the threshold of observability and were used in the final refinement. 278 were below the threshold and were not used. For Sn₃Cu₉Ni the corresponding numbers of reflexions are 224 above and 82 below threshold.

Sn ₁₁ Cu ₄₁				Sn ₁₁ Cu ₄₁				Sn ₁₁ Cu ₄₁				Sn ₁₁ Cu ₄₁				Sn ₁₁ Cu ₄₁				Sn ₁₁ Cu ₄₁																							
hkl	F _o	F _c	F _o /F _c	hkl	F _o	F _c	F _o /F _c	hkl	F _o	F _c	F _o /F _c	hkl	F _o	F _c	F _o /F _c	hkl	F _o	F _c	F _o /F _c	hkl	F _o	F _c	F _o /F _c	hkl	F _o	F _c	F _o /F _c	hkl	F _o	F _c	F _o /F _c												
001	9.6	9.6	1.00	002	19.2	19.2	1.00	003	28.8	28.8	1.00	004	38.4	38.4	1.00	005	48.0	48.0	1.00	006	57.6	57.6	1.00	007	67.2	67.2	1.00	008	76.8	76.8	1.00												
010	12.0	12.0	1.00	011	14.4	14.4	1.00	012	16.8	16.8	1.00	013	19.2	19.2	1.00	014	21.6	21.6	1.00	015	24.0	24.0	1.00	016	26.4	26.4	1.00	017	28.8	28.8	1.00	018	31.2	31.2	1.00	019	33.6	33.6	1.00	020	36.0	36.0	1.00

$\text{Sn}_3\text{Cu}_9\text{Ni}$ provide a mechanism to maintain valence-electron concentrations with fewer atoms per unit cell when the percentage of low-valency Cu atoms is smaller than in δ -Cu-Sn.

Discussion

(a) Ordering of atoms in structures with the F cell

The ordering in the $\text{Sn}_{11}\text{Cu}_{41}$ structure can be accounted for uniquely on the condition that the larger Sn atoms shall not be close neighbours. Recent experimental evidence shows that this condition has been met in the nearby ζ -Cu-Sn phase (Brandon, Pearson & Tozer, 1975). Close contacts in γ -brass can be defined generally by building up the 26-atom clusters in a hard-sphere model. In the inner tetrahedron each IT atom is in contact with three IT atoms. Each of the surrounding OT atoms is then in contact with three IT atoms. Next the octahedron atoms each make contact with two IT atoms. Finally each CO atom is in contact with one OT and one OH atom, thus giving the close contacts shown in Table 5(a). When the clusters are packed together the close contacts shown in Table 5(b) occur, where a prime represents atoms in a neighbouring cluster. That these are indeed close contacts is confirmed by the interatomic distances in the $\text{Sn}_{11}\text{Cu}_{41}$ structure which show them equal to or closer than the radii sums of Sn and/or Cu.

In addition there are several other contacts to be regarded as close (\sim equal to the radii sums) when they

	A	B	C	D
IT		3		
OT		3		
OH		3		
CO		3		

(a)

	A	B	C	D
IT		3		
OT			3	
OH		3		
CO	3	3		

(b)

	A	B	C	D
IT		2		
OT		2		
OH			1	1
CO	2	4	2	

(c)

	A	B	C	D
IT		1		
OT		1	1	
OH	1	2	1	
CO	2		2	

(d)

Fig. 2. Close neighbours of a Sn atom that would occur if it were located on an (a) IT, (b) OT, (c) OH or (d) CO site in the $\text{Sn}_{11}\text{Cu}_{41}$ structure.

Table 5. Close contacts

(a)		(b)	
IT-3 IT		OT-3 CO'	
OT-3 IT	IT-3 OT	OH-1 OH'	2 CO'
OH-2 IT	IT-3 OH		
CO-1 IT	IT-3 CO	CO-1 OT'	1 OH'
1 OT	OT-3 OT		2 CO'
			2 CO''

occur between Cu and Sn atoms, but not when they occur only between Cu atoms (Table 6). Thus, in summary, a Sn atom on an IT, OT, OH or CO site would have the close contacts indicated in Fig. 2. The F cell has, in order along $[111]$, four clusters A,B,C,D each with four site sets IT, OT, OH and CO and, as Fig. 2 indicates, Sn can be put in any of the OT, OH or CO sites without incurring Sn as a near neighbour, since there are no intracluster OT-OT, OH-OH or CO-CO contacts. It is more convenient in arriving at the unique result that is obtained if we first put 48 Sn in B CO where they are found experimentally. The close contacts of a Sn atom on this site are then those indicated by the numbers of contacts in Fig. 3(a). Further Sn atoms can now be put in A OT, D OT, D OH or D CO without making Sn-Sn close neighbours. If they were put into D CO (or if 44 Sn are put each into B CO and D CO to preserve the composition $\text{Sn}_{11}\text{Cu}_{41}$), the B and D clusters would be identical and the structure would reduce to the P cell. If, on the other hand, 24 Sn are put into D OH, then the close neighbours are as shown in Fig 3(b) and it is apparent that the only remaining site where Sn atoms can be located without creating Sn-Sn close neighbours is A OT [Fig. 3(c)]. The total number of Sn atoms now located is $48 + 24 + 16 = 88$, giving the formula $\text{Sn}_{11}\text{Cu}_{41}$ and indeed the ordering found experimentally, which at first sight appeared highly idiosyncratic. Thus the ordering is accounted for on the basis that Sn atoms shall not be close neighbours. It can furthermore be shown that this condition cannot be satisfied in the P or I cells at this composition; hence the adoption of the F cell. Similar ordering occurs in Sn_3NiCu_9 .

A further consequence of the observed ordering of $\text{Sn}_{11}\text{Cu}_{41}$ in the F cell is an increase in the number of unlike Sn-Cu contacts that are obtained compared to the maximum number obtainable with any ordering in the I cell. The importance of maximizing the number of unlike contacts as a factor in the stability of γ -brass structures is discussed in Brandon, Brizard, Pearson & Tozer (1977).

	A	B	C	D
IT		1		
OT		1	1	2
OH	1	2	1	
CO	2		2	

(a)

	A	B	C	D
IT		1		2
OT		1	1	2
OH	1	2	1	
CO	2	2	2	4

(b)

	A	B	C	D
IT		3	1	2
OT			1	1
OH	1	3	3	1
CO	4	3	4	3

(c)

Fig. 3. Close neighbours of a Sn atom in the $\text{Sn}_{11}\text{Cu}_{41}$ structure located (a) on the B CO site, (b) on B CO and D OH sites, (c) on B CO, D OH and A OT sites.

Table 6. Close contacts between Cu and Sn atoms

OT-3 OH	OH-2 OT	CO-2 OH
	4 CO	1 OH'
	2 CO''	

Several γ phases said to take the F cell have the composition M_5N_{21} which also permits the condition to be satisfied that the M atoms shall not be close neighbours if they are located in sites OT, OH, OH, OT, ... in successive clusters along [111]. Fig. 4 (a) to (d) shows them in A OT, B OH, C OH and D OT. In this case the structure contains $16 + 24 + 24 + 16 = 80$ M atoms corresponding to the formula M_5N_{21} . The phases Ce_5Hg_{21} , Pu_5Hg_{21} and Pt_5Zn_{21} reported to have F cells are predicted to have this type of ordering. The ordering in γ -PtZn has been determined (Johansson & Westman, 1970), but the single crystal was said to have the composition Pt_3Zn_{10} , so that some Pt-Pt near neighbours must occur in the F cell. Pt was reported to be located mainly in the following sites: A OT, B OH, C OH, D OT, B OT and C OT which resembles the arrangement predicted above. In this case, since Pt and Zn atoms are practically the same size, it is for reasons other than size that the Pt atoms tend to avoid each other.

Other variations of ordering on OT and OH sites so that no close contacts occur between the M atoms give formulae M_9N_{43} and M_8N_{44} if each site set is fully occupied by one component only. If in the ordering found for $M_{11}N_{41}$, a further 16 M are added in C IT [see Fig. 3(c)], the formula $M_{13}N_{39}$ (MN_3) is satisfied, but there are now M - M contacts within the inner tetrahedron of the C cluster. The γ phase $Al_2Sn_2Cu_{12}$ which has the F cell (Leach & Raynor, 1954) may be of this type if Al and Sn are regarded as M atoms.

(b) Distances between Cu atoms on IT sites

In $Sn_{11}Cu_{41}$, Cu atoms occupy all four IT site sets where they are in 12 coordination. However, the Cu-Cu distances in A IT and D IT are 2.88 ± 0.03 Å, whereas they have the expected value of 2.56 ± 0.01 Å for CN 12 in the B IT and C IT sites. The observations for Sn_3Cu_9Ni also show a similar variation. This raises

	A	B	C	D
IT		2		
OT		2		
OH				1
CO	2	4	2	

(a)

	A	B	C	D
IT		2	2	
OT		2	2	
OH	1			1
CO	2	4	2	4

(b)

	A	B	C	D
IT	3	2	2	
OT		2	2	
OH	1	3		1
CO	2	3	6	2

(c)

	A	B	C	D
IT		2	2	3
OT		2	2	
OH	4			1
CO	5	6	3	5

(d)

Fig. 4. Close neighbours of an M atom in a γ -brass of formula M_5N_{21} which has the 18 Å F cell when M is located (a) on the B OH site, (b) on the B OH and C OH sites, (c) on the A OT, B OH and C OH sites and (d) on the A OT, B OH, C OH and D OT sites.

the interesting question of how the inner tetrahedron may be expanded, which is resolved by Fig. 5, showing projections of the three OT, three OH and three CO neighbours of an IT atom normal to the line (OW) running from the centre of the cluster through the IT atom. This line OW is the locus of movement of an IT atom as the inner tetrahedron expands or contracts. Because the plane of the three OT neighbours lies closer to the origin, O , than the IT atom, a thrust along the three OT-IT contacts will, in fact, expand the inner tetrahedron, rather than contract it as would naively be imagined since the OT atoms are themselves further from the origin than the IT atoms. Thrust along the three OH-IT contacts will have practically no effect on the inner tetrahedron since the three OH and IT atoms are nearly coplanar, whereas thrust along the three CO-IT contacts will contract the inner tetrahedron since the plane containing the three CO is further from the origin than IT. Thus thrusts along the OT-IT and CO-IT contacts tend to balance each other; an imbalance should lead either to an expanded or contracted inner tetrahedron, although contraction will be opposed by thrust along the three IT-IT contacts also. If the contacts concerned are shorter than the radii sums of the atoms involved for CN 12, we expect them to exert a thrust on the IT atoms, whereas if they are longer, the thrust is relaxed. Table 7 gives values of Δ , the difference of the radii sums, and the observed interatomic distances for the OT-IT and CO-IT contacts in each of the four clusters in the $Sn_{11}Cu_{41}$ structure. A positive value of Δ corresponds to a positive thrust and contacts shorter than the radii sums. The observed values of Δ account well enough for the observed Cu-Cu distances in the inner tetrahedra. In cluster A, where the IT sites are only partially occupied, the thrust along OT-IT, unopposed by one along CO-IT, accounts for the large Cu-Cu distance whereas the very sloppy CO-IT contact in cluster D also accounts for it there (it should be noted that these effects are measured after

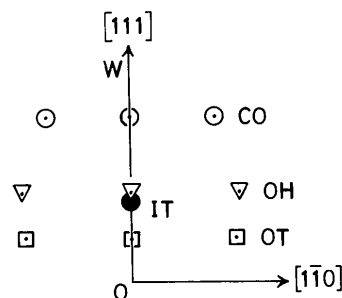


Fig. 5. Projection of the three OT, three OH and three CO neighbours of an IT atom onto a $(\bar{1}\bar{1}2)$ plane which passes through the origin of the cluster and the IT atom. OW is thus the locus of movement of the IT atom as the inner tetrahedron is expanded or reduced in size.

Table 7. Values of Δ and observed interatomic distances

Cluster	A	B	C	D
Observed Cu–Cu distance (Å)	2.91	2.57	2.56	2.86
Δ values OT–IT (Å)	+0.08	–0.01	+0.01	–0.05
Δ values CO–IT (Å)	–0.05	+0.01	+0.08	–0.16

CN 12 radii: Cu 1.278, Sn^{IV} 1.545 Å.

the expansion has occurred; they would be much more impressive if the Cu atoms were set at positions corresponding to an IT–IT distance of 2.56 Å. In cluster B there is little thrust along either contact and the normal Cu–Cu distance is found; in cluster C there is thrust inwards along CO–IT and the normal Cu–Cu distance observed might have been expected to be slightly shorter.

Similar arguments hold for the distances in clusters A, B and D of Sn₃Cu₉Ni. In cluster C the IT Cu–Cu distance is very large, 3.24 Å. This appears to be the result of only 75% occupancy in the C CO site and a consequential imbalance under loss of CO–IT contacts.

Conclusions

In the present state of our knowledge, ordering of γ -brasses in the superstructure with F symmetry occurs to avoid contacts between the component atoms present in smaller proportion, either because of their relatively large size or for other reasons. It occurs at compositions where this condition cannot be satisfied in the I or P cells if each site set is to be occupied by a single component only. In γ -brasses with composition M_5N_{21} and F cells, the ordering of the M atoms in neighbouring clusters along [111] is predicted to be in the OH, OH, OT, OT, ... sites.

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