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A Single-Crystal X-ray Diffraction Study of the ζ Bronze Structure, $Cu_{20}Sn_6$

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A new structure has been determined by single-crystal methods for ζ bronze, $Cu_{20}Sn_6$, previously reported from powder-diffraction work to have been a γ-brass defect superstructure with trigonal space group $P\bar{3}1m$. The single-crystal work shows cell constants $a=7{\cdot}330\pm0{\cdot}004$ and $c=7{\cdot}864\pm0{\cdot}005$ Å, with hexagonal space group $P6_3$ and one formula unit per unit cell. Intensity data were collected with an automatic single-crystal diffractometer using a θ–2θ scan and Zr-filtered Mo $K\alpha$ X-radiation. The structure was refined by Fourier methods and full-matrix least-squares calculations to a final weighted R_w value of 0·062. The previously reported model for the structure could be described in terms of nine layers of atoms perpendicular to **c** with two columns of tin atoms parallel to **c**. In contrast, our new structure has six main layers of atoms perpendicular to **c** with all the tin atoms in two of these layers separated by **c**/2. Rather than being related to γ-brass, the new $Cu_{20}Sn_6$ model can be visualized as a superstructure based on ζ Ag–Zn. Average interatomic distances for Cu–Cu and Cu–Sn are 2·65 Å, and 2·79 Å respectively, with no first neighbour Sn–Sn contacts present in the structure. The coordination shells around the various Cu atoms have 11 or 12 nearest neighbours whereas those around Sn atoms have 13 neighbours.

Introduction

An investigation of the crystal structure of the alloy $Cu_{20}Sn_6$ (ζ bronze) has been performed by single-crystal X-ray diffraction methods. This work was originally undertaken as part of a programme of study on alloy structures related to that of Cu_5Zn_8 (γ-brass). The archetype γ-brass structure crystallizes in a body-centred cubic lattice with typical cubic cell constant near 9 Å and 52 atoms per unit cell. γ-Brass structures have become rather well known as examples of electron compounds, whose stabilities are enhanced near a certain well defined value of the number of valence electrons per atom averaged over the contents of a unit cell (e/a ratio ideally $\frac{21}{13}$ for γ-brass phases).

A model structure for $Cu_{20}Sn_6$ ($e/a=\frac{22}{13}$) has previously been suggested by Carlsson & Hägg (1932), hereinafter referred to as CH, using evidence from powder X-ray diffraction experiments. Their proposed model can be regarded as a defect superstructure based on the γ-brass structure. It was anticipated that our present work would confirm the CH model and provide more reliable atomic coordinates from single-crystal work for comparison with other defect γ-brass structures currently under investigation. In contrast to these expectations, the single-crystal studies show a considerably different structure for $Cu_{20}Sn_6$ than had been inferred from the earlier powder diffraction results of CH.

Experimental

The Cu–Sn phase diagram in the region of the ζ phase (23·08 atomic % Sn) is shown in Fig. 1 (Raynor, 1944; Hansen, 1958). Appropriate amounts of 99·999 % pure Cu and Sn were melted at 850 °C in an evacuated quartz tube followed by rapid quenching to produce a mixture of γ and ε phases with small grain sizes. This sample was annealed for 6 days at 602 ± 2 °C to promote transformation to the ζ phase, and then rapidly quenched to prevent transformation to any lower temperature form. The sample was brittle and was composed of small crystallites. It was crushed into small fragments and several single crystals of the desired phase were selected according to X-ray diffraction patterns which showed cell constants characteristic of the ζ phase.

A series of Weissenberg and precession camera single-crystal X-ray diffraction photographs were obtained in an attempt to determine the space-group symmetry unambiguously. Previous results from the powder diffraction experiments of CH could be ambiguous because the overlap of powder lines would not have allowed comparison of individual intensities from crystallographic planes having identical d spacings. From these single-crystal diffraction photographs with hexagonal indexing, the trigonal Laue groups $\bar{3}$, $\bar{3}m1$, $\bar{3}1m$, and the hexagonal Laue groups $6/m$ and $6/mmm$ were in turn examined. The possibilities $\bar{3}1m$ and $6/mmm$ were eliminated by the observation that $|F(hkl)|\neq|F(khl)|$ for numerous reflexions, most notable cases being 430, 320, 231, 241, and 432. Less positive comparisons from diffraction films indicated that $|F(hkl)|=|F(hk\bar{l})|$ and $|F(\bar{h}kl)|=|F(h\bar{k}l)|$ favouring $6/m$ rather than $\bar{3}m1$ or $\bar{3}$ Laue groups. The possibilities $\bar{3}m1$ and $\bar{3}$ were eliminated by the observation of systematic absences only among $00l$ reflexions for l odd, whereas all space groups corresponding to $\bar{3}m1$ and $\bar{3}$ Laue groups which make any distinction whatsoever on the parity of l do so by requiring the more extensive condition that hhl or $h\bar{h}l$ are systematically absent for l odd. Laue group $6/m$ and the observed systematic absences

then allow two possible space groups, $P6_3$ (C_6^6, No. 173) and $P6_3/m$ (C_{6h}^2, No. 176) (*International Tables for X-ray Crystallography*, 1969). The single-crystal structure determination subsequently favoured $P6_3$.

Room-temperature hexagonal lattice constants were refined by a least-squares program *CELLS* to fit 2θ values for 11 single-crystal reflexions measured on a General Electric XRD6 three-circle diffractometer using Zr-filtered Mo $K\alpha$ X-radiation ($\lambda=0{\cdot}71069$ Å). The refined cell constants were $a=7{\cdot}330\pm0{\cdot}004$ and $c=7{\cdot}864\pm0{\cdot}005$ Å, in reasonable agreement with the CH values of 7·331 and 7·870 Å (corrected from kX units). Cell constants and other crystal data have been summarized in Table 1.

Table 1. *Crystal data for* $Cu_{20}Sn_6$

Crystal system	Hexagonal
Space group	$P6_3$ (C_6^6, No. 173)*
Cell constants	$a=$ 7·330 (4) Å
	$c=$ 7·864 (5)
Unit-cell volume	$V=365{\cdot}9$ (4) Å^3
Density measured	$D_m=8{\cdot}95$ (7) g cm^{-3}
Density calculated	$D_x=9{\cdot}00$ (1)
Number of $Cu_{20}Sn_6$ units/cell	$Z=1$
Absorption coefficient	μ (Mo $K\alpha$)$=381$ cm^{-1}

* See text for discussion of $P6_3/m$ (C_{6h}^2, No. 176) space group considerations.

Intensity data were collected on the G.E. diffractometer equipped with scintillation counter and pulse-height analyser with a θ–2θ scan and Zr-filtered Mo $K\alpha$ radiation. The crystal used had the shape of a triangular prism with [$\bar{1}$20] as its prism axis aligned parallel to the φ axis of the goniostat. The triangular cross-section was isosceles with base 0·07 mm and height 0·16 mm, and the prism length was 0·30 mm. Background counts were taken on both sides of diffraction peaks and reflexions were scanned with a 2θ scan rate of 2° min^{-1} and a 2θ scan range of $\pm(0{\cdot}9+0{\cdot}3\tan\theta)$°. 1561 individual reflexions were measured in one-quarter hemisphere over the range $0{\cdot}025<\sin\theta/\lambda<0{\cdot}857$.

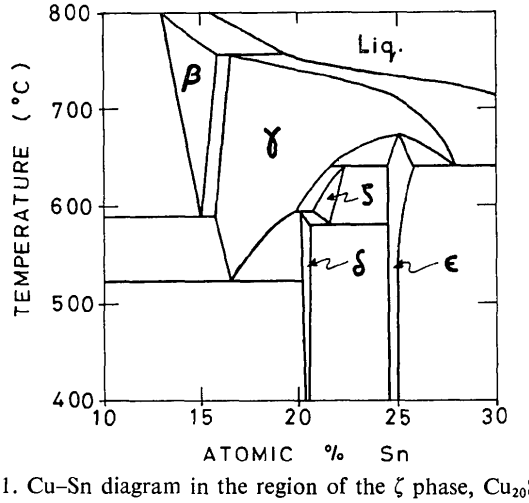

Fig. 1. Cu–Sn diagram in the region of the ζ phase, $Cu_{20}Sn_6$.

The measured intensities were corrected for background, Lorentz, and polarization effects by the program *DATAREP* on the University of Waterloo IBM 360-75 computer. The program also averaged crystallographically equivalent reflexions according to Laue group $6/m$ leaving 683 independent reflexions. 249 of these had values of I smaller than $3\sigma_I$ and were not used in the refinement (see Appendix). Most equivalent reflexions had measured values differing from their mean value by less than 10%. Since the crystal was quite small with mean $\mu R=1{\cdot}56$ for Mo $K\alpha$ radiation no absorption corrections were attempted.

Structure solution

With single-crystal intensity data available, it seemed appropriate at an early stage to test how suitable the previously reported γ-brass defect model of CH might be. This trigonal $P\bar{3}1m$ structure had been based on an arrangement of atoms with the body diagonal of the 9Å body-centred cubic γ-brass archetype aligned along **c**. It could be described in terms of nine triangular layers of atoms per unit cell stacked along the c axis. In order to test this model, intensities were averaged according to the crystallographically equivalent reflexions for Laue group $\bar{3}m1$, and the model of CH was used as a starting point for least-squares refinement with the program *LSTSQR*. This model would not refine and gave unweighted R_1 values ($R_1\equiv\sum||F_o|-|F_c||/\sum|F_o|$) greater than 0·75. Hence this test gave further evidence that the previously proposed nine-layer model and space group $P\bar{3}1m$ were not correct, and completely new models using $P6_3$ or $P6_3/m$ space groups were examined next.

A three-dimensional Patterson function was calculated with the computer program *FOURIER* with the intensity data averaged according to $6/m$ Laue group. Peak distributions indicated: (*a*) that the structure was composed of six main layers since peaks at intervals of $\Delta z=\frac{1}{6}$ were prominent; (*b*) that many atoms were separated by the vector $0,0,\frac{1}{3}$; and (*c*) that the main layers had a triangular arrangement since atoms in the same layer were related by vectors Δx, Δy,0 with magnitudes of Δx and Δy approximately $\frac{1}{3}$ and $\frac{2}{3}$. Hence a model structure was devised in the more general non-centrosymmetric $P6_3$ space group having six main layers, each with an internal triangular arrangement of Cu atoms, and with the remaining Cu and Sn atoms filling interstitial locations within and between these six main layers. This model gave an unweighted R_1 of 0·27. New models with different arrangements of Cu and Sn were next attempted. In particular, Sn atoms were placed, not as in the CH model with columns of three interstitial Sn atoms running up **c**, but in a disordered fashion within the main layers and on some of the interstitial sites, thereby avoiding one anomaly of the CH structure for a c axis as short as 7·9 Å. Continued refinement indicated that the Sn atoms in fact occupied two of the six triangular

layers with Cu atoms in the other four layers and Cu atoms in all the occupied interstitial sites. This model gave a least-squares refined unweighted R_1 of 0·082. A weighting scheme of $w=(13{\cdot}95-0{\cdot}1728\ F_o+0{\cdot}00058\ F_o^2)^{-1}$ was introduced and further refinement gave a weighted $R_w\{R_w\equiv[\sum w(|F_o|-|F_c|)^2/\sum wF_o^2]^{1/2}\}$ of 0·062 leaving R_1 unchanged.

Although this analysis had been started assuming the more general non-centrosymmetric $P6_3$ space group, it became apparent with Sn occupying two of the six layers that much of the structure could be approximately described in the centrosymmetric $P6_3/m$ space group with the Sn layers on mirror planes at $z=0{\cdot}25$ and 0·75. The atoms not fitting $P6_3/m$ especially closely were the interstitial types Cu(1) which would have to move 0·18 Å to coincide with the origin, Cu(6) which would need to move 0·04 Å to the mirror plane at $z=0{\cdot}25$, and Cu(2) along with Cu(4) which would become related to Cu(2) in $P6_3/m$ both being required to move 0·06 Å. The triangular layers formed by Cu(3) and Cu(5) showed a difference of 0·11 Å between the locations of atoms which would be related by a mirror plane if the space group were $P6_3/m$. However, in spite of these apparently significant deviations from the centrosymmetric $P6_3/m$ space group, a series of least-squares refinement cycles were attempted using the constraints of $P6_3/m$. The resulting weighted R_w values were 0·072 in $P6_3/m$ compared to 0·062 in $P6_3$ using 14 and 21 variables respectively with 439 reflexions. Significance tests (Hamilton, 1965) suggest the $P6_3$ choice to be correct on the basis of the R factor ratios. Furthermore physical interpretations for the displacements away from the constraints of $P6_3/m$ can be made by considering the atomic packing in the structure. Reasons for such displacements are discussed in the next section. In view of these arguments, the non-centrosymmetric $P6_3$ space group has been adopted as the correct one.

Electron density and difference electron density calculations were performed as a final check and no inconsistencies were found. The final atomic coordinates and isotropic thermal vibration parameters for $Cu_{20}Sn_6$ in space group $P6_3$ are given in Table 2. Observed structure amplitudes and calculated structure factors are shown in Table 3. In all calculations, atomic scattering factors for Cu and Sn were taken from *International Tables for X-ray Crystallography* (1968), with corrections for anomalous scattering also included. A correction parameter for secondary extinction was also varied during least-squares refinement but it remained within its own error limit of zero.

Discussion

The interatomic distances and the atom coordinations are described in Table 4. The average Cu–Cu and Cu–Sn distances throughout the structure are 2·65 and 2·79 Å respectively, with no first neighbour Sn–Sn con-

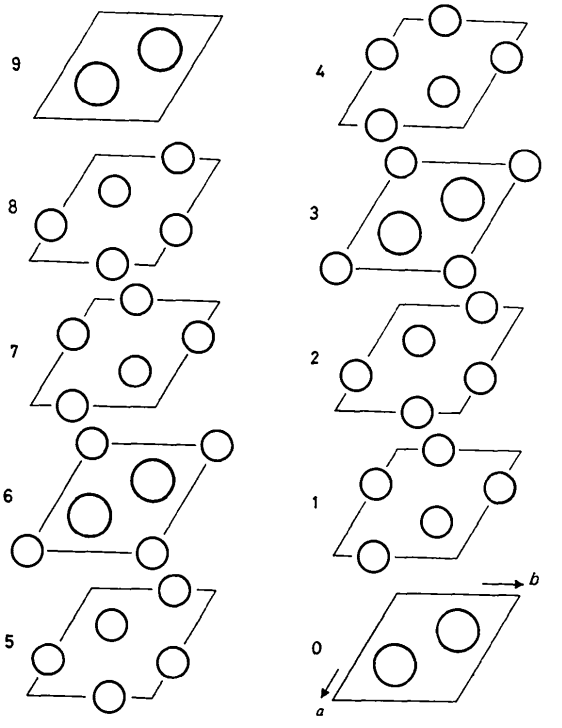

Fig. 2. Carlsson & Hägg (1932) nine-layer model for $Cu_{20}Sn_6$. Numbers indicate the layer height in ninths of c. This model was derived as a defect γ-brass structure viewed as a b.c.c. arrangement of atoms. The perfect b.c.c. arrangement would have atoms at all four corners of the cell outline at $z=0$ and $z=1$. The idealized cubic γ-brass arrangement would have vacancies at 000, 110, $10\frac{1}{3}$, and $01\frac{1}{3}$. The CH model shows vacancies at 000, 100, 010 and 110. Large circles represent the CH ordering of Sn atoms, which leads to Sn–Sn contacts as short as 2·62 Å and makes the CH model subject to suspicion.

Table 2. *Structural parameters for* $Cu_{20}Sn_6$

Atom	Crystallographic site	x	y	z	B (Å^2)
Cu(1)	2(*a*)	0	0	−0·0223 (14)	1·27 (11)
Cu(2)	2(*b*)	$\frac{2}{3}$	$\frac{1}{3}$	−0·0900 (23)	1·54 (27)
Cu(3)	6(*c*)	0·6472 (15)	−0·0179 (11)	−0·0845 (12)	0·86 (11)
Cu(4)	2(*b*)	$\frac{1}{3}$	$\frac{2}{3}$	0·0737 (17)	0·57 (17)
Cu(5)	6(*c*)	0·3574 (13)	0·0350 (10)	0·0831 (12)	0·72 (9)
Cu(6)	2(*b*)	$\frac{2}{3}$	$\frac{1}{3}$	0·2450 (26)	0·67 (8)
Sn	6(*c*)	0·6800 (3)	−0·0200 (4)	0·25*	0·77 (3)

* Sn z was fixed at 0·25 to define the origin in space group $P6_3$.

Table 3. *Observed and calculated structure factors for* $Cu_{20}Sn_6$

Asterisks denote reflexions with measured intensities less than $3\sigma_I$. With these excluded from the refinement $R_w = 0{\cdot}062$. With these included $R_w = 0{\cdot}073$ as discussed in the Appendix.

h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c
0 0 1	1	1	1 0 1	1	1	2 0 1	1	1	3 0 1	1	1	4 0 1	1	1	5 0 1	1	1	6 0 1	1	1	7 0 1	1	1
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Table 4. *Atomic coordination and distances in* $Cu_{20}Sn_6$

	Number			Number	
Cu(1)–Cu(3)	3	2·57 Å	Cu(5)–Cu(1)	1	2·64 Å
–Cu(5)	3	2·64	–Cu(2)	1	2·61
–Sn	3	2·90	–Cu(3)	1	2·62
–Sn	3	3·12	–Cu(3)	1	2·69
			–Cu(3)	1	2·75
Cu(2)–Cu(3)	3	2·51	–Cu(3)	1	2·92
–Cu(4)	1	2·65	–Cu(4)	1	2·62
–Cu(5)	3	2·61	–Cu(6)	1	2·57
–Cu(6)	1	2·63	–Sn	1	2·63
–Sn	3	2·73	–Sn	1	2·67
			–Sn	1	2·79
Cu(3)–Cu(1)	1	2·57	–Sn	1	2·90
–Cu(2)	1	2·51			
–Cu(4)	1	2·62	Cu(6)–Cu(2)	1	2·63
–Cu(5)	1	2·62	–Cu(3)	3	2·67
–Cu(5)	1	2·69	–Cu(4)	1	2·59
–Cu(5)	1	2·75	–Cu(5)	3	2·57
–Cu(5)	1	2·92	–Sn	3	2·64
–Cu(6)	1	2·67			
–Sn	1	2·64	Sn–Cu(1)	1	2·90
–Sn	1	2·72	–Cu(1)	1	3·12
–Sn	1	2·76	–Cu(2)	1	2·73
–Sn	1	2·86	–Cu(3)	1	2·64
			–Cu(3)	1	2·72
Cu(4)–Cu(2)	1	2·65	–Cu(3)	1	2·76
–Cu(3)	3	2·62	–Cu(3)	1	2·86
–Cu(5)	3	2·62	–Cu(4)	1	2·80
–Cu(6)	1	2·59	–Cu(5)	1	2·63
–Sn	3	2·80	–Cu(5)	1	2·67
			–Cu(5)	1	2·79
			–Cu(5)	1	2·90
			–Cu(6)	1	2·64

tacts. The coordination shells around the various Cu atoms have 11 or 12 nearest neighbours whereas those around Sn atoms have 13 neighbours.

The structure proposed by CH for ζ Cu–Sn which they based on a defect γ-brass arrangement of atoms is considerably different from the new structure determined here. On the basis that $Cu_{20}Sn_6$ had an e/a ratio ($\frac{22}{13} = 1{\cdot}692$) close to the value for γ-brass types ($\frac{21}{13} = 1{\cdot}615$) and that $Cu_{20}Sn_6$ displayed powder patterns similar to those of γ-brass structures, the atomic arrangement of CH seemed quite reasonable in view of the fact that the powder patterns with superposed lines did allow an interpretation in a trigonal space group which is easily obtained from the archetype 9Å γ-brass body-centred cubic unit cell. The actual CH model can be visualized by means of an early description of γ-brass, due to Bradley & Thewlis (1926), as a $3 \times 3 \times 3$ arrangement of twenty-seven 3Å body-centred cubes with atoms at the corners and body-centre of the resulting 9Å cube omitted and other atoms shifted slightly. This idealized γ-brass model can be cast onto a trigonal structure with nine layers perpendicular to the cubic [111] direction stacking up **c** of the hexagonal reference frame. Fig. 2 shows the CH model of $Cu_{20}Sn_6$ derived by introducing some additional vacant sites into the above trigonal γ-brass description. For comparison Fig. 3(*a*) shows the results of the new structure determined for $Cu_{20}Sn_6$ with six main distorted triangular layers and with interstitial sites occupied both within and between these triangular layers. The contrast between the CH model and the single-crystal structure determination is evident. Although arguments based on powder diffraction evidence made the CH model plausible, their ordering of Sn onto sites giving columns with Sn–Sn contacts as short as 2·62 Å was highly suspect. The new structure does not have this objectionable feature and in fact no first-neighbour Sn–Sn contacts occur. We conclude that the CH model is incorrect and that ζ Cu–Sn cannot in fact be regarded as a defect b.c.c. or γ-brass arrangement (CH; Hansen, 1958; Pearson, 1972) despite the fact that it possesses an e/a ratio close to that which enhances the stability of γ phases.

Inspection of Fig. 3(*a*) and the *z* coordinates of Table 2 show that the interstitial Cu atoms Cu(2), Cu(4), and Cu(6) actually lie slightly below the plane of their respective triangular layers, and that Cu(1) is considerably below the half-way point between the Cu(3) and Cu(5) triangular layers. These are the major deviations in the refined structure which destroy $P6_3/m$ symmetry, and the directions of these shifts seem to correlate with one another through the atomic packing interactions. The interstitial atoms also influence the triangular layers by enlarging certain triangles and producing the distortions of these layers. The reasons for the shifts from what could be $P6_3/m$ symmetry may be argued by noting that Cu(6) is unique in having three Sn neighbours which are among the shortest Cu–Sn contacts in the whole structure (2·64 Å). Since the triangular layer containing larger Sn atoms cannot accommodate an interstitial Cu atom within that layer quite as easily as a triangular Cu layer might, the three close

Cu(6)–Sn contacts might be relieved by Cu(6) moving slightly out of the Sn plane. This shift can then influence shifts in the same direction for interstitial atoms Cu(2) and Cu(4). That Cu(1), shown as a cross-hatched circle in Fig. 3(*a*), is the only interstitial site occupied *between* rather than *within* the triangular layers is explained by the fact that it is unique in having both its nearby triangular layers composed of smaller Cu atoms. The downward direction for its shift follows that of the other interstitial shifts and is enhanced in magnitude by the fact that the triangle of Cu(3) atoms below it is larger than the triangle of Cu(5) atoms above it. In fact a least-squares refinement test starting with all atoms except Cu(1) constrained in their $P6_3/m$ arrangement resulted in the identical structure reported in Table 2. The same procedure starting with a positive Cu(1) z coordinate resulted in the enantiomorphous structure. The explanations for the observed shifts in terms of the atomic packing together with the above refinement tests and the R factor ratio test all lead us to conclude that the non-centrosymmetric $P6_3$ space group description is correct.

Instead of showing a relationship to γ-brass, $Cu_{20}Sn_6$ is better regarded as a superstructure based on ζ Ag–Zn (Edmunds & Qurashi, 1951; Bergman & Jaross, 1955; Edmunds, 1955). ζ Ag–Zn has the centrosymmetric trigonal space group $P\bar{3}$ (C_{3i}^1, No. 147) with cell constants $a=7{\cdot}6360$, $c=2{\cdot}8179$ Å and formula AgZn with $Z=4{\cdot}5$. Fig. 3(*b*) shows three repeat units along **c** of this ζ Ag–Zn structure. Its unit cell has distorted triangular layers at $z=\frac{1}{4}$ and $\frac{3}{4}$ randomly occupied by Zn and Ag in the ratio of 1·5 to 4·5, and these layers have been drawn beside their counterparts in $Cu_{20}Sn_6$ of Fig. 3(*a*). Three Zn atoms occur interstitially in ζ Ag–Zn, one within each of these layers and the third shown as cross-hatched exactly between two of the triangular layers. The ζ Ag–Zn packing thus repeats along **c** after just two triangular layers since an identical interstitial site between layers is then generated. The $Cu_{20}Sn_6$ packing with larger Sn atoms forming every third triangular layer provides an interstitial site between two Cu triangular layers only after every third layer. Since the triangular layers themselves must alternate with a repeat of orientation after every two layers, the true c repeat in $Cu_{20}Sn_6$ occurs only after $2\times3=6$ layers have been completed. In ζ Ag–Zn no evidence has been found for shifts of interstitial atoms out of their idealized sites in contrast to the displacements described above in $Cu_{20}Sn_6$. This seems reasonable since in ζ Ag–Zn the triangular layers are all reported to have a disordered but uniform composition of Ag and Zn so there is no mechanism as in $Cu_{20}Sn_6$ whereby a predominantly larger atom in one triangular layer can promote such displacements. Since there is little difference in the sizes of Zn and Ag atoms, random disordering is more likely to occur in ζ Ag–Zn, whereas the vast difference in the sizes of Cu and Sn suggests that ordering rather than random occupancy is essential in $Cu_{20}Sn_6$. We conclude that despite the small differences among its interstitial atom locations, the interpretation of $Cu_{20}Sn_6$ as an ordered superstructure based on ζ Ag–Zn seems valid.

The characteristic layering found for Sn atoms in the structure prompted our speculation that ζ Cu–Sn might have some interesting superconducting properties. Measurements made on a small lump of our alloy did not indicate any superconducting T_c above 1·09 K (Smith, 1974). Possibly these speculations should be followed up using more carefully prepared samples.

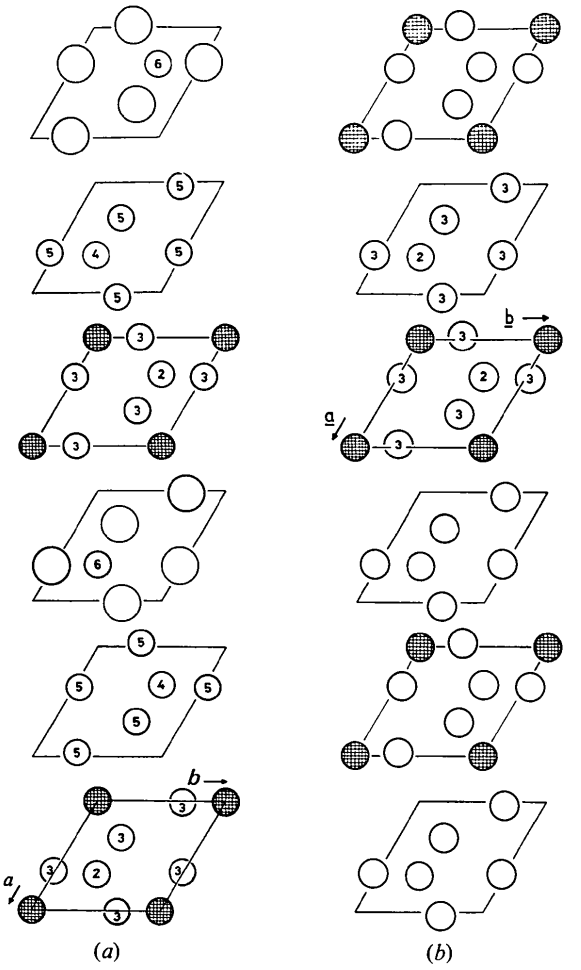

Fig. 3. (*a*) The six main layers of the presently determined $Cu_{20}Sn_6$ structure stacking up **c**. Approximate z coordinates of the distorted triangular layers are from bottom to top −0·08, 0·08, 0·25, 0·42, 0·58 and 0·75. Small and large circles represent Cu and Sn atoms respectively. Cross-hatched circles are Cu(1) atoms which lie between the layer in which they are drawn and the next layer above. The numbering of other Cu atoms corresponds to the labelled types in Table 2. (*b*) The structure of ζ Ag–Zn (Edmunds & Qurashi, 1951) with its two layer repeat for comparison with the six-layer sequence of ζ Cu–Sn in (*a*). The two layers with numbered atoms have z coordinates of −0·25 and 0·25 in the ζ Ag–Zn cell. Cross-hatched circles are Zn atoms which lie between the layer in which they are drawn and the next layer above. No atoms are present at $z=0{\cdot}5$ between the distorted triangular layers. Atoms numbered 2 are also Zn sites, and those labelled 3 are randomly occupied by 75% Ag plus 25% Zn.

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APPENDIX

Treatment of weak reflexions

The intensity data collected for $Cu_{20}Sn_6$ have been used to test certain philosophies concerning the treatment of weak reflexions when counter measurements are used. Hirshfeld & Rabinovich (1973) have warned that the arbitrary exclusion of weak intensities biases the input data in a manner which can create systematic errors in the refined parameters. The refinement reported above was based on 439 reflexions with a criterion of $3\sigma_I$ as the threshold of observability. We have also performed a parallel refinement with 638 reflexions under a zero threshold criterion. The resulting structural parameters do agree with those in Table 2 within their respective errors. However with the larger data set there was a tendency for the temperature factors to become more uniform among all sites. The final R_1 was 0·127 and R_w was 0·073 for the larger data set compared to values of 0·082 and 0·062 reported above. We conclude from this test that the differences in the refined coordinates are insignificant but that certain systematic differences in the temperature factors have occurred. As expected the R values increase upon inclusion of more weak reflexions. We consider that such tests are useful in that they may at least provide confidence that no large or unpreictabled effects arising through omission of these weak reflexions could have led to an incorrect structure.

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