

The Structure of the Rhombohedral Gamma Brass Like Phase in the Copper-Mercury System

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The gamma-brass like intermediary phase in the copper-mercury system has a rhombohedral structure which may be described in space group $R\bar{3}m$. The copper-saturated crystals have the pseudo-cubic lattice parameters:

$$a = 9.4024 \pm 4 \text{ \AA}, \alpha = 90.425 \pm 5^\circ$$

The crystal structure may be described as an ordered version of the Cu_5Cd_8 structure type, with Hg in one sixfold and two threefold positions in the primitive unit of the body-centered cell. The stoichiometry of that atomic arrangement is Cu_7Hg_6 .

In 1929, Katoh¹ determined the range of homogeneity of the gamma-brass like phase in the Cu-Hg system, and reported the limits to be narrower than 50–55 atomic per cent copper. The edge of the crystallographic unit cell, assumed to be cubic, was observed to be approximately constant $9.419 \pm 6 \text{ \AA}$ (recalculated from kX) for different specimens of the amalgam.

Schoszberger⁸ also found the same cell dimensions and tried to fit a cubic structure model of Cu_7Hg_6 stoichiometry—related to the Cu_5Cd_8 structure—to the observed X-ray powder diffraction intensities yielded by this phase. The discrepancies were too large, however, and the model was eventually discarded.

In a recent investigation,² the present authors have shown that the symmetry of the phase is rhombohedral, with

$$a = 9.4067 \pm 7 \text{ \AA}; \alpha = 90.413 \pm 10^\circ$$

for a preparation in equilibrium with mercury. This article will present the results of a crystal structure investigation carried out on a preparation of the amalgam from which the mercury had been distilled off, and in which metallic copper was present. For that specimen, the following lattice parameters were found:

$$a = 9.4024 \pm 4 \text{ \AA}; \alpha = 90.425 \pm 5^\circ$$

EXPERIMENTAL

The methods of preparation of the phase, and of lattice parameter determination, were described in Ref. 2. In order to obtain a mercury free sample of the phase from which to select single crystals, we enclosed a batch of Hg-containing specimen in an evacuated pyrex capsule and distilled the mercury from the sample, which was initially held at 110°C, to the cool end of the capsule (at room temperature). A wad of cotton inserted in the capsule prevented the drops of mercury from running back and readhering to the specimen. The temperature of the hot end of the capsule was gradually lowered to 30°C over a period of three weeks.

Under the microscope, no mercury could be observed to remain in the preparation. A Guinier photograph of the sample showed copper metal to be present instead.

Weissenberg photographs of what appeared to be single crystals proved them to be polycrystalline twins. The photographically recorded X-ray reflexions were rather diffuse, and the complete diffraction pattern appeared to have cubic symmetry.

Some of the reflexions (of the $hh0$ type) from a very small twin—diameter ~ 0.007 mm—mounted on the Single Crystal Orienter of a General Electric X-ray Diffractometer ($\text{CuK}\alpha$ radiation) could be partially resolved into components diffracted by different single crystal regions within the aggregate. Most of the diffraction peaks, however, were broad and unresolved. The intensities of 335 such reflections were recorded and from these 77 independent “structure factors” were computed and used for the determination of an “average structure”, *i.e.* a cubic approximation to the real, rhombohedral structure. The absorption correction was found to be negligible.

In the last stages of the structure determination, intensities obtained from three Guinier photographs (exposure times $\frac{1}{2}$, 1 and 2 h with $\text{CuK}\alpha_1$ radiation) were used to differentiate between six plausible rhombohedral structure models. On these films the hkl , $\bar{h}kl$, $h\bar{k}l$, and $hk\bar{l}$ components of groups of reflexions could frequently be resolved. The intensities of the lines were determined by visual comparison with a ten-degree scale consisting of a range of exposures (1.5 to 32 min) of the 111 Guinier line from potassium chloride. In this fashion, 26 non-zero intensities of uniquely indexable diffraction lines were obtained. In addition, the intensities of 5 reflexions could be unambiguously set equal to zero (unobservable), whereas 19 line intensities must be considered to be sums of several non-identical components.

From the Guinier intensities, I , structure factors were computed according to the expression listed by Sagel³ (for $\beta=30^\circ$):

$$|F|^2 = \frac{I \cdot (1 + \cos^2 2\alpha) \cdot \sin\theta \cdot \sin 3\theta}{1 + \cos^2 2\alpha \cdot \cos 2\theta} \frac{1}{m}$$

and with $\alpha=13.32^\circ$. We have here included the multiplicity, m , into Sagel's formula.

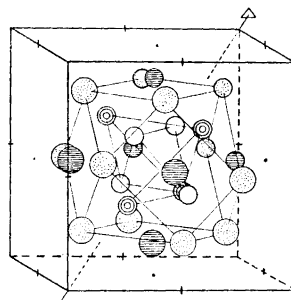
All numerical calculations were carried out with the IBM 1800 computer at this Institute.

In the SFLS⁴ structure refinement runs, atomic scattering factor tables, and dispersion corrections were taken from the *International Tables*.⁵

STRUCTURE DETERMINATION

In our previous publication² concerning the Cu-Hg gamma phase it was pointed out that its body-centered pseudo-cubic unit cell most probably contains ~ 52 atoms. Small defects would be very difficult to observe since no single-phase sample for density measurement and precise chemical analysis has been obtained. Several stoichiometric formulae have been proposed in the literature. Of those compatible with the rhombohedral symmetry (the primitive rhombohedral cell containing 26 atoms), $\text{Cu}_{15}\text{Hg}_{11}$ (57.7 atomic % Cu) and CuHg ($=\text{Cu}_{13}\text{Hg}_{13}$, 50.0 atomic % Cu) lie just outside the homogeneity range

Fig. 1. Atomic sites in one cluster (A) around the origin. Large circles indicate Hg and small circles Cu atoms. The direction of the threefold axis is indicated.



●	= OH \approx	.35	.0	.0
⊙	= OT \approx	-.16	-.16	-.16
○	= CO \approx	.30	.30	.05
○	= IT \approx	.10	.10	.10

reported by Katoh,¹ and Cu_7Hg_6 ($=\text{Cu}_{14}\text{Hg}_{12}$, 53.9 atomic % Cu) is in the middle of that range.

The calculated density for this last stoichiometry, 13.1 g cm^{-3} compares favorably with Schoszberger's⁸ carefully determined experimental value, 13.0 g cm^{-3} .

The starting point for the structure determination was a cubic model (Fig. 1) in space group $I\bar{4}3m$ (No. 217), with atomic positions analogous with those in, *e.g.*, Cu_5Zn_8 , Cu_5Cd_8 , $\text{Ni}_4\text{Zn}_{22}$, *etc.* (IT=Inner Tetrahedral, OT=Outer Tetrahedral, OH=OctaHedral and CO=distorted Cubo-Octahedral position):

IT	8(c)	<i>xxx etc.</i>	$x \approx 0.10$
OT	8(c)	<i>xxx etc.</i>	$x \approx -0.17$
OH	12(e)	<i>x00 etc.</i>	$x \approx 0.35$
CO	24(g)	<i>xxz etc.</i>	$x \approx 0.30 \quad z \approx 0.05$

Assuming as initial positional parameters those of the Cu_5Cd_8 structure,⁶ for a completely disordered arrangement of Cu and Hg atoms (composition $\text{Cu}_{15}\text{Hg}_{11}$), a least-squares refinement of scale factor, positional and thermal parameters, using all the 77 "average" structure factors converged very poorly. When high- θ reflexions were excluded from the refinement, leaving 39 structure factors in the region $\sin\theta \leq 0.66$ a five-cycle run converged to an *R*-value of 19 %. The tetrahedral positions, then, had acquired large positive temperature factor values: $B_{\text{IT}}=7$, $B_{\text{OT}}=17$, whereas $B_{\text{OH}}=1$, which is fairly normal and $B_{\text{CO}}=-1$.

On the basis of this refinement it was concluded that the tetrahedral positions (IT and OT) were probably completely occupied by copper; that the copper/mercury ratio in the OH position was approximately 1:1, and that the CO position did most probably contain more Hg than Cu. The only reasonable stoichiometry of an ordered structure, in either of the two rhombohedral subgroups of $I\bar{4}3m$, *viz.* $R\bar{3}$ and $R3m$, consistent with the above requirements and with the composition of the phase is Cu_7Hg_6 , which results from an ar-

rangement with a 1:3 ratio of copper to mercury in the CO position. The exact nature of the possible arrangements will be made clear below.

Another least-squares refinement run, on an "average" cubic structure model with the above composition and distribution of atoms, ended up with a value of $R=16\%$ and with somewhat scattered thermal parameters which were, however, all fairly near $B=1$, within their standard deviations.

The more symmetrical of the two possible space groups, namely $R3m$ (No. 160) was first chosen for the description of the rhombohedral structure. The correctness of the choice is confirmed by the final agreement reached. In that space group, the positions of cubic symmetry are broken down into 1-, 3-, and 6-fold positions:

$$\begin{aligned} 6(c) & xyz \text{ etc.} \\ 3(b) & xxz \text{ etc.} \\ 1(a) & xxx \end{aligned}$$

In order to bring out the relationship between gamma-Cu,Hg and other, cubic, gamma phases we will retain, in the following, a pseudo-cubic body-centered unit cell containing two clusters of atoms. Thus, position 6(c) in that cell generates 12 equipoints.

The resulting distribution of atoms in one cluster (Fig. 1) will be:

- IT 4 Cu in one threefold and one onefold position
- OT 4 Cu in one threefold and one onefold position
- OH 3 Cu in one threefold position and
3 Hg in one threefold position
- CO 3 Cu in one threefold position and
9 Hg in one sixfold and one threefold position.

If one assumes the lower symmetry—space group $R3$ —the sixfold position decomposes into two threefold positions, and a larger number of possible structure models results. The stoichiometry, however, remains the same.

The following four rhombohedral trial structures, which may all be characterized as ordered versions of the Cu_5Cd_8 structure type, could now be constructed in space group $R3m$ (the numbers in parantheses following the IT, OT, OH, and CO symbols designate the number of equipoints of the positions):

Model:	A	B	C	D			
IT(1)	Cu	Cu	Cu	Cu	$x=+0.10$		
IT(3)	Cu	Cu	Cu	Cu	$x=-0.10$	$z=+0.10$	
OT(1)	Cu	Cu	Cu	Cu	$x=-0.16$		
OT(3)	Cu	Cu	Cu	Cu	$x=+0.16$	$z=-0.16$	
OH(3)	Cu	Hg	Hg	Cu	$x=0.00$	$z=+0.35$	
OH(3')	Hg	Cu	Cu	Hg	$x=0.00$	$z=-0.35$	
CO(3)	Cu	Cu	Hg	Hg	$x=+0.30$	$z=+0.06$	
CO(3')	Hg	Hg	Cu	Cu	$x=-0.30$	$z=+0.06$	
CO(6)	Hg	Hg	Hg	Hg	$x=+0.30$	$y=-0.30$	$z=-0.06$

For the refinement of these rhombohedral models the 26 non-zero structure factors with unambiguous indices, derived from the Guinier photographs, were used. Consequently, it was not possible to refine all the 27 structural parameters (*i.e.* one scale factor, 17 positional and 9 isotropic thermal parameters). In addition it had already been observed, during the refinement of the "average" structure, that the coordinates of the copper atoms had very large standard deviations and that their final values yielded unreasonably short Cu—Cu distances. However, in the copper-containing gamma phase structures so far refined,⁶ the sizes of the copper tetrahedra and octahedra have been observed to be reasonably constant.

Thus, the copper framework of the Cu₇Hg₆ structure models was constructed so as to yield the same Cu—Cu distances as those existing in Cu₅Zn₈, Cu₅Cd₈, and Cu₉Al₄. Subsequently, the seven positional parameters of the Hg atoms were refined for each model and, last of all, the nine thermal parameters.

The following final results were obtained in the four runs:

Model A: $R=7.5\%$. All $B_{\text{Hg}}=1$. Range of $B_{\text{Cu}}=-4$ to $+2 \text{ \AA}^2$. Largest standard deviation of $B_{\text{Cu}}=\pm 7$.

Model B: $R=15.4\%$. $B_{\text{HgOH}(3)}=4$, $B_{\text{HgCO}(3')}=1$, $B_{\text{HgCO}(6)}=2$. Range of $B_{\text{Cu}}=-3$ to $+6 \text{ \AA}^2$. Largest standard deviation of $B_{\text{Cu}}=\pm 15$.

Model C: $R=31.4\%$. $B_{\text{HgOH}(3)}=0$, $B_{\text{HgCO}(3)}=2$, $B_{\text{HgCO}(6)}=0$. Range of $B_{\text{Cu}}=-7$ to $+12 \text{ \AA}^2$. Largest standard deviation of $B_{\text{Cu}}=\pm 42$.

Model D: $R=25.3\%$. $B_{\text{HgOH}(3')}=0$, $B_{\text{HgCO}(3)}=2$, $B_{\text{HgCO}(6)}=1$. Range of $B_{\text{Cu}}=-5$ to $+9 \text{ \AA}^2$. Largest standard deviation of $B_{\text{Cu}}=\pm 21$.

In all refined models, except A, Hg—Hg distances of approximately 2.50 Å occur, whereas in model A the shortest Hg—Hg distance is 2.80 Å.

As was pointed out above, it is possible to devise other ordering schemes in the lower space group, *R3* (No. 146), in which position CO(6) is further broken down into two threefold positions (CO(6a) and CO(6b)), one of which might contain mercury and the other copper. Subject to the same conditions as before as regards the Cu/Hg ratio in the CO and OH groups of positions the following two structure models are possible:

Model	IT(1)	IT(3)	OT(1)	OT(3)	OH(3)	OH(3')	CO(3)	CO(3')	CO(6a)	CO(6b)
E	Cu	Cu	Cu	Cu	Cu	Hg	Hg	Hg	Hg	Cu
F	Cu	Cu	Cu	Cu	Hg	Cu	Hg	Hg	Hg	Cu

It should be noted that positions CO(6a) and CO(6b) are entirely equivalent, so that no new structures result from an interchange of Cu and Hg between them.

It is not possible to refine these models using powder data, since $F(hkl)$ and $F(khl)$ cannot be independently measured. Therefore, one must be content with a calculation of powder intensities based upon Cu and Hg position parameters directly borrowed from models A—D. In so doing, one has to reintroduce the short Hg—Hg distances which make models B—D less believable than A.

Table 1. Observed and calculated X-ray Guinier powder diffraction intensities. For models E and F (in space group $R\bar{3}$) the sum of $I_c(hkl)$ and $I_c(khl)$ is given. Overall $B=1 \text{ \AA}^2$. $R_I = \sum |I_o - I_c| / \sum I_o$.

hkl	I_o	I_c					
		A	B	C	D	E	F
$\bar{1}10$	126	115	155	103	43	203	203
110	23	76	46	278	27	278	380
220	154	133	81	39	103	109	97
$\bar{3}10$	250	219	159	94	93	109	94
310	188	174	99	89	59	203	193
$\bar{2}22$	91	85	53	139	154	236	145
222	113	98	93	71	107	60	67
321	68	85	77	94	85	109	115
400	43	42	36	62	36	24	30
332	4	2	4	21	19	30	33
422	18	16	42	60	49	3	31
431	24	51	4	24	4	51	6
$52\bar{1}$	8	12	40	12	64	30	33
521	38	64	26	27	53	133	67
530	13	24	49	41	16	20	30
433	13	15	21	15	13	24	36
440	4	2	6	21	15	6	19
440	5	5	9	1	1	7	7
442	71	61	81	22	26	49	46
$\bar{6}20$	19	23	19	18	12	47	15
620	19	19	13	4	24	17	18
622	8	6	8	2	2	16	33
$\bar{4}44$	122	108	135	118	98	151	169
444	10	15	1	1	5	36	24
$\bar{6}40$	8	10	13	15	4	5	4
640	43	50	44	14	41	67	67
$\bar{2}20$	0	2	1	19	8	31	31
200	0	1	61	236	95	0	54
420	0	8	25	34	7	22	37
420	0	5	18	86	3	60	54
442	0	6	20	56	25	15	48
$\bar{2}11$							
$2\bar{1}1$	13	16	241	31	314	308	290
211							
$\bar{3}21$							
$3\bar{2}1$	440	423	216	197	267	515	446
$32\bar{1}$							
411							
330	764	568	556	608	595	1140	1060
$\bar{3}32$							
$33\bar{2}$	140	169	162	176	203	181	169
$\bar{4}22$							
$4\bar{2}2$	28	44	57	42	104	121	145
$\bar{4}31$							
$4\bar{3}1$	5	25	63	92	79	133	200
510							

Table 1. Continued.

hkl	I_o	I_c					
		A	B	C	D	E	F
$4\bar{3}\bar{1}$ $5\bar{1}0$	24	25	25	42	59	55	60
$\bar{5}\bar{2}1$ $5\bar{2}1$	16	28	33	77	66	103	60
$\bar{4}\bar{3}3$ $\bar{4}\bar{3}3$ $\bar{5}30$	62	73	80	122	78	301	84
600 $44\bar{2}$	87	103	75	86	60	224	203
$\bar{6}11$ $5\bar{3}2$ $\bar{5}32$	121	109	68	18	81	118	121
611 $6\bar{1}1$ $5\bar{3}2$ $5\bar{3}\bar{2}$	143	141	139	53	103	97	103
$\bar{5}41$ $5\bar{4}1$	43	57	76	51	64	67	89
$54\bar{1}$ 541	30	24	6	31	62	45	21
$\bar{6}22$ $6\bar{2}2$	93	97	43	34	56	84	67
$\bar{6}31$ $6\bar{3}1$	107	138	72	36	101	193	139
$63\bar{1}$ 631 $\bar{5}50$ $\bar{5}43$ $5\bar{4}3$ $\bar{5}43$ $\bar{7}10$	6	20	51	94	37	45	103
543 543 543 $\bar{7}10$	136	95	144	95	111	132	121
550 710 543	8	38	29	51	56	42	54
$R_I =$		0.20	0.44	0.59	0.54	0.78	0.69

In Table 1 are listed Guinier powder pattern intensities calculated for all the six models described above, assuming in each case an overall temperature factor of $B=1$. The scaling against observed intensities has been done using the uniquely indexable non-zero reflexions.

It is clearly seen, especially by inspection of the calculated I values for the reflexions with $I_{\text{obs}}=0$, that model A is the correct one. The refined struc-

Table 2. Atomic distribution and structural parameters of Cu_7Hg_6 , model A. $R=7.5\%$.

	a	$9.4024 \pm 4 \text{ \AA}$			
	α	$90.425 \pm 5^\circ$			
IT(1)	Atom	Cu	OH(3)	Atom	Cu
	x	0.097		x	0.005
	B	$2 \pm 7 \text{ \AA}^2$		z	0.345
				B	$-4 \pm 4 \text{ \AA}^2$
IT(3)	Atom	Cu	OH(3')	Atom	Hg
	x	-0.097		x	-0.003
	z	0.097		z	-0.352
	B	$0 \pm 5 \text{ \AA}^2$		B	$1 \pm 1 \text{ \AA}^2$
OT(1)	Atom	Cu	CO(3)	Atom	Cu
	x	-0.163		x	0.295
	B	$0 \pm 5 \text{ \AA}^2$		z	0.068
				B	$2 \pm 5 \text{ \AA}^2$
OT(3)	Atom	Cu	CO(3')	Atom	Hg
	x	0.163		x	-0.307
	z	-0.163		z	0.040
	B	$-2 \pm 4 \text{ \AA}^2$		B	$1 \pm 1 \text{ \AA}^2$
			CO(6)	Atom	Hg
				x	-0.060
				y	0.337
				z	-0.284
				B	$1 \pm 1 \text{ \AA}^2$

tural parameters of that model are listed in Table 2. It is related to Schosberger's⁸ conjectural cubic structure by an interchange of Cu and Hg between positions CO(3) and OH(3').

DISCUSSION

Table 3 gives a survey of interatomic distances shorter than 3.3 Å in the structure. No standard deviations are given in the table since, in most cases, they are impossible to ascertain. However, it may be estimated that the uncertainty in the Hg—Hg distance values is of the order of 0.15 Å. Thus, although one of these distances is calculated to be 2.80 Å, it cannot be said to be unreasonably short. The interatomic distance in pure mercury is 3.0 Å, and in the cubic gamma-brass like Ag_2Hg_3 phase Cohen and Farnhurst⁷ have found the shortest Hg—Hg distances to be 2.92 Å. In this connexion it should

Table 3. Coordinations, number of contacts, and interatomic distances (Å) in Cu_7Hg_6 .

A:	CO(6) Hg	CO(3') Hg	CO(3) Cu	OH(3) Cu	OH(3') Hg	OT(3) Cu	OT(1) Cu	IT(3) Cu	IT(1) Cu
A: CO(6) Hg				2.78 × 2		2.90 × 2		2.89 × 2	
CO(3') Hg					2.92 × 2		2.71 × 3	2.83	
CO(3) Cu			3.03 × 2	2.83 × 2		2.77			2.64 × 3
OH(3) Cu	2.78		2.83 × 2		2.85	2.77 × 2		2.68	2.64 × 3
OH(3') Hg		2.92 × 2		2.85		2.82	2.78 × 3	2.73 × 2	
OT(3) Cu	2.90		2.77	2.77 × 2	2.82			2.60 × 2	2.61 × 3
OT(1) Cu		2.71			2.78			2.59	
IT(3) Cu	2.89	2.83		2.68	2.73 × 2	2.60 × 2	2.59 × 3	2.58 × 2	2.56 × 3
IT(1) Cu			2.64	2.64		2.61		2.56	
	2.99								
B: CO(6) Hg	2.98 × 2	3.21 × 2	2.68 × 2	2.70 × 2	3.23 × 2	2.65 × 2			
CO(3') Hg	3.21		2.76 × 2	3.08	2.80	2.82			
CO(3) Cu	2.68	2.76 × 2			2.78		2.59 × 3		
OH(3) Cu	2.70	3.08							
OH(3') Hg	3.23	2.80	2.78						
OT(3) Cu	2.65	2.82							
OT(1) Cu			2.59						
Total no. of con- tacts:	11	11	12	12	11	12	12	12	12

be pointed out that the mercury atoms in Cu_7Hg_6 are all 11-coordinated, whereas the copper atoms have a coordination number of 12, which can be seen by inspection of Table 3.

If one counts all the distances listed in the table as contacts, one obtains, within one cluster:

45 Cu—Cu contacts
6 Hg—Hg »
36 Cu—Hg »

Between one cluster and adjacent clusters:

6 Cu—Cu contacts
48 Hg—Hg »
72 Cu—Hg »

Although the mercury atoms in a cluster appear to be aggregated within one half of that cluster (lower left front part of Fig. 1), there is actually a remarkably low number of Hg—Hg contacts within the cluster.

The available data do not allow one to say much about possible solid solubility mechanisms. It might be hypothesized that the negative B value of the Cu atom in OH(3) indicates the presence of some Hg in that position. The large standard deviations of B_{Cu} make this a mere conjecture, however.

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