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The Structure of the δ-Phase in the Cu—Sn System. A Phase of γ-Brass Type with an 18 Å Superstructure

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The gamma brass-like phase with the approximate composition $Cu_{41}Sn_{11}$ is face centered cubic, with a lattice parameter of ~17.96 Å. The space group is $F\bar{4}3m$. The structure may be described in terms of four different types of "cluster"; each cluster consisting of an inner tetrahedral, an outer tetrahedral, an octahedral and a cubo-octahedral position. The Sn atoms occupy one cubo-octahedral, one octahedral and one outer tetrahedral position of three different clusters, respectively. There are no Sn—Sn contacts in this idealized structure model. Some of the Sn atoms in the cubo-octahedral position of the model may, in the actual structure, be located at the inner tetrahedral position of the same cluster and at the octahedral position of the all-Cu cluster of the model.

The Cu—Sn system contains a γ-brass-like phase, called δ, with face-centered cubic superstructure. This phase, first described by Westgren and Phragmén,[1] has a very narrow homogeneity range around 20.5 atom % Sn. Knödler [2] investigated it by means of X-ray powder and Laue photographs and proposed a partially ordered structure with the nominal composition $Cu_{31}Sn_8$ (20.6 atom % Sn), having a valence electron concentration of 21 electrons/13 atoms. He based the model on a description of the related high-temperature γ-phase, in which all atoms were supposed to be situated at the lattice points of the body-centered cubic subcell ($a \sim 3$ Å). The shortest Sn—Sn contact, 4.2 Å, in the γ structure is the face diagonal of the subcell. The ideally ordered γ model has the stoichiometry Cu_3Sn, which lies within the homogeneity range of this phase.

In the δ phase, $Cu_{31}Sn_8$, some copper has been substituted for tin, and Knödler assumes this substitution to be completely random. Furthermore, the atomic arrangement described above is collapsed around the vacancies at 000 *etc.*, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ *etc.*, $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ *etc.*, and $\frac{3}{4}\frac{3}{4}\frac{3}{4}$ *etc.*, yielding a normal γ-phase structure, which may be expressed in terms of atomic clusters: A, B, C, D, centered at the sites mentioned. Each cluster is built up of an inner tetrahedral (IT), an outer tetrahedral (OT), an octahedral (OH) and a cubo-octahedral (CO) point complex.[3,4] In Knödler's model, then, the IT position in cluster C is occupied by Sn. Its position parameter ($x = \frac{1}{4} + 0.0515$), given by Knödler, implies an Sn—Sn distance of 2.6 Å within this cluster; to be compared with Schubert's [5] tabulated value: $2r_{Sn} = 3.16$ Å.

Since it is possible to redistribute the atoms in this model into a completely ordered arrangement without Sn—Sn contacts and with a stoichiometry approximating the experimental value, we decided to collect single-crystal X-ray data in order to compare the "improved" model with Knödler's original proposal. The investigation is part of an inventory of possible variations on the gamma brass structural theme.[4]

EXPERIMENTAL

Weighed amounts of copper (granular, Mallinckrodt Analytical Reagent) and tin (E. Merck, Darmstadt) were melted together in a sealed evacuated silica capsule at 1150 °C for 24 h to a homogeneous alloy containing 20.6 atom % Sn. After the heat treatment the capsule was quenched in water, reheated

at 550 °C for seven days and again quenched in water. The density of the alloy specimen was calculated from its weight in air and in benzene.

Guinier photographs were taken with Cu$K\alpha_1$ radiation ($\lambda = 1.54050$ Å) and with KCl ($a = 6.2919$ Å) as an internal standard.[6] Single crystal X-ray diffractometer data were collected with a PW 1100 (Philips Automatic Diffractometer) from an irregular crystal fragment measuring approximately 0.05³ mm³.

202 independent intensities (out of 260 measured), with $\sigma(I)/I < 0.4$, were used in the final refinement. The measured intensities have been corrected for absorption, with the crystal assumed to be a sphere of diameter 0.05 mm ($\mu r = 4.3$). Atomic scattering factors were taken from Cromer and Waber [7] and corrected for dispersion according to Cromer.[8] Least squares structure refinements were carried out with the program LALS on the IBM 360/75 computer at the Stockholm Data Center.

In the final stages of refinement Cruickhank's weighting scheme [11] with $w = (1000 + 0.0002 |F_o|^2)^{-1}$ was employed. The extinction proved to be negligible; an attempt to correct for it resulted in extinction factors ranging between 0.98 and 1.00.

REFINEMENT AND RESULTS

The Guinier record could be completely indexed on the basis of a face-centered cubic lattice with $a = 17.9646(6)$ Å at 20.6 % Sn (*cf.* Knödler's[2] value, $a = 17.9550(3)$ Å at 20.51 % Sn). The density and composition values yield 416 ± 1 atoms per unit cell; almost exactly $= 8 \times 52$. This is, thus, a gamma phase structure without "extra" vacancies.

Both Knödler's structure model and our own proposal are formulated in space group $F\bar{4}3m$ (No. 216), but we started the structure refinement with models of the "ordinary gamma brass cell", *i.e.* a subcell with $a = 8.9823$ Å. When we refined such a model in space group $I\bar{4}3m$ ($h+k+l=4n$), with all atoms assumed to be Cu, very low values for B_{OT} and B_{OH} strongly indicated a preferred concentration of Sn at the OT and OH sites. The value of $R = 100 \sum||F_o| - |F_c|| / \sum|F_o|$ was 10 %.

On the basis of this first result we tested several models with a stoichiometry approximating the experimental one. Eventually we obtained fairly uniform values of the thermal parameters, and a value of $R = 9.7$ %, for the IT position containing only Cu; the OT, OH and CO positions all containing Cu and Sn in the proportion 3:1. We tested the atomic distribution further, using subcell diffraction data pertaining to space group $P\bar{4}3m$ (h, k and l all even). The best refinement ($R = 13.8$ %) produced a model containing Sn at the OH and CO positions around the origin of the subcell (averaging the A and B clusters), and at the OT position around $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ (averaging clusters C and D). This corresponds to our proposed modification of Knödler's structure.

Finally, we refined the following complete models ($a = 17.9646$ Å) in space group $F\bar{4}3m$:

Table 1. Atomic distributions and parameters of the refined structure. Standard deviations in parentheses.

		a/Å	17.9646 (6)		
		Cluster A	Cluster B	Cluster C	Cluster D
IT	Atom	Cu(Sn)	Cu	Cu	Cu
16(*e*)	x	0.0508(8)	0.5540(11)	0.3001(10)	0.8079(8)
	B/Å²	1.9(4)	2.3(5)	1.9(5)	1.7(4)
OT	Atom	Cu	Cu	Cu	Sn
16(*e*)	x	−0.0836(12)	0.4142(10)	0.1664(9)	0.6609(5)
	B/Å²	2.5(7)	1.3(4)	0.9(5)	1.6(2)
OH	Atom	Cu	Sn	Cu(Sn)	Cu
24(*f*)	x	0.1751(14)	0.6809(6)	0.4272(11)	0.9264(18)
24(*g*)	B/Å²	2.7(4)	1.3(2)	0.8(4)	2.7(6)
CO	Atom	Sn(Cu)	Cu	Cu	Cu
48(*h*)	x	0.1580(4)	0.6592(6)	0.3945(9)	0.9062(6)
	z	0.0186(4)	0.5121(7)	0.2779(10)	0.7706(8)
	B/Å²	2.1(2)	1.5(3)	2.9(4)	1.2(3)

I. Our model, described in the introduction, in which the clusters A, C, B, D, situated along the body diagonal of the cell in the order mentioned, contain Sn at the CO(A), OH(B) and OT(D) positions. The R value obtained was 9.9 %.

II. A rearrangement of that model, containing Sn at CO(A), OH(B) and OT(C). Model II refined to $R = 12.4$ % and yielded $B_{OT(D)} = -1.7$ Å² (*cf.* Table 1). All other rearrangements of Sn_{OT}, Sn_{OH} and Sn_{CO} over three different clusters are identical with either I or II.

III. Knödler's model, *i.e.* Sn at CO(A), OH(B), IT(C) and OT(D), which refined to $R = 10.1$ %. The thermal parameter of the Sn atom at IT(C), $B = 5.0$ Å², became very high in relation to the others (1.0 – 2.6 Å²).

We then tested model I by means of F_o and difference Fourier syntheses in the ($\bar{1}10$) plane. The difference map was essentially featureless; the most prominent maxima had a height of 10 % of those in the F_o synthesis.

Nevertheless, the scatter of thermal parameter values was still considerable (0.4 – 2.8 Å²); this seemed to warrant a special investigation of whether some Sn might be located, *e.g.*, at OH(C), with $B = 0.4$. The following strategy proved to be effective: First, we refined isotropic extinction correction, over-all temperature factor and over-all scale factor separately, whereupon, having found extinction to be negligible, we refined the over-all scale and temperature factors together. Then we calculated and refined the occupancy parameters and, finally, occupancies and over-all temperature factors jointly. The fact that none of these changed in the last run supports the correctness of the result. Moreover, a similar refinement of Knödler's structure proposal converged to exactly the same final model.

The resulting structural parameters closely approximate those of our proposed model I. The difference between the refined structure and the idealized model is a redistribution of 6.8 Sn atoms per unit cell from the CO(A) type sites (= 14 % of the atoms) to the IT(A) (2.7 atoms/cell = 17 % substitution) and OH(C) (4.6 atoms/cell = 19 % substitution) sites. The Sn content of the refined model is 21.3 atom %, with an uncertainty of around ± 4 % estimated from the standard deviations of the occupancy parameters; this is indistinguishable from the experimental value of the synthetic composition: 20.6 % Sn.

Table 2. Structure factors for the refined $Cu_{41}Sn_{11}$ model. $R = 8.2$ %.

H	K	L	|FO|	|FC|
6	0	0	1983	1709
12	0	0	3237	3448
16	0	0	609	666
18	0	0	704	795
20	0	0	714	847
6	2	0	340	280
8	2	0	415	405
10	2	0	986	863
18	2	0	491	462
8	4	0	699	576
16	4	0	982	953
20	4	0	363	331
6	6	0	6552	6714
10	6	0	391	331
12	6	0	1256	1157
14	6	0	580	556
16	6	0	248	261
18	6	0	1241	1191
20	6	0	131	153
8	8	0	425	467
12	8	0	703	641
16	8	0	298	195
10	10	0	2173	1940
12	10	0	261	237
14	10	0	197	173
12	12	0	2714	2339
14	12	0	168	173
16	12	0	316	300
14	14	0	329	214
5	1	1	472	482
9	1	1	327	325
11	1	1	646	592
15	1	1	264	282
17	1	1	233	224
21	1	1	132	134
5	3	1	244	231
9	3	1	271	261
11	3	1	511	503
19	3	1	398	365
5	5	1	597	602
7	5	1	228	189
9	5	1	334	287
11	5	1	615	517
15	5	1	215	179
17	5	1	384	392
7	7	1	353	338
19	7	1	159	152
13	9	1	347	369
11	11	1	423	397
15	11	1	175	209
17	11	1	483	430
13	13	1	242	229
17	13	1	164	174
4	2	2	402	470
6	2	2	318	309
8	2	2	3621	3589
12	2	2	904	929
14	2	2	443	441
16	2	2	313	277
18	2	2	233	237
20	2	2	1043	1017
8	4	2	694	723
16	4	2	332	302
10	4	2	429	394
12	4	2	215	282
14	4	2	1953	1832
16	4	2	321	306
18	4	2	408	391
20	4	2	208	218
8	6	2	628	355
12	6	2	1068	1033
14	6	2	243	156
16	6	2	334	382
20	6	2	130	81
8	8	2	456	455
12	8	2	256	209
14	8	2	1996	1958
18	8	2	630	678
10	10	2	353	406
12	10	2	467	475
16	10	2	265	252
18	10	2	182	169
14	12	2	214	178
16	12	2	148	109
14	14	2	654	553
16	14	2	405	395
3	3	3	1599	1487
7	3	3	275	226
9	3	3	799	801
13	3	3	215	255
15	3	3	540	570
17	3	3	249	238
19	3	3	334	321
21	3	3	209	219
5	5	3	365	326
7	5	3	209	52
11	5	3	245	212
19	5	3	186	167
13	5	3	180	195
7	7	3	390	360
13	7	3	608	569
19	7	3	383	372
9	9	3	898	820
11	9	3	188	170
13	9	3	199	212
15	9	3	270	268
11	11	3	221	252
17	11	3	147	138
13	13	3	249	241
15	13	3	149	127
15	15	3	180	146
4	4	4	1775	1799
8	4	4	1232	1335
10	4	4	330	368
12	4	4	403	367
14	4	4	205	254
16	4	4	668	666
18	4	4	195	188
20	4	4	968	914
6	6	4	1526	1478
8	6	4	511	527
10	6	4	476	527
12	6	4	227	136
14	6	4	554	556
18	6	4	250	276
20	6	4	109	62
8	8	4	1711	1599
12	8	4	491	550
14	8	4	426	431
16	8	4	186	173
10	10	4	897	900
14	10	4	679	678
16	10	4	343	325
18	10	4	343	344
12	12	4	987	953
16	12	4	402	409
14	14	4	767	646
5	5	5	946	987
9	5	5	206	223
11	5	5	712	670
15	5	5	387	413
17	5	5	428	468
7	7	5	213	184
11	7	5	516	553
13	7	5	240	230
17	7	5	268	319
9	9	5	197	202
11	9	5	335	322
13	9	5	180	176
17	9	5	150	105
11	11	5	665	717
15	11	5	230	227
17	11	5	211	229
13	13	5	149	117
6	6	6	1191	1414
8	6	6	402	467
12	6	6	2669	2810
16	6	6	528	554
18	6	6	452	443
10	8	6	485	544
14	8	6	411	367
18	8	6	274	261
12	10	6	461	579
16	10	6	1089	1096
12	12	6	533	532
16	12	6	226	269
9	7	7	526	358
13	7	7	177	229
15	7	7	175	167
17	7	7	134	143
19	7	7	128	156
17	9	7	152	92
11	11	7	343	352
17	11	7	116	194
13	13	7	167	220
15	13	7	164	187
8	8	8	2918	3385
10	8	8	273	299
12	8	8	701	773
14	8	8	596	630
16	8	8	175	198
18	8	8	126	116
10	10	8	337	427
14	10	8	657	695
16	10	8	292	377
12	12	8	321	308
14	14	8	1668	1667
9	9	9	193	184
15	9	9	296	315
17	9	9	125	129
11	11	9	292	255
15	11	9	280	268
13	13	9	396	423
10	10	10	331	377
12	10	10	159	207
16	10	10	412	430
14	12	10	220	264
11	11	11	157	217
13	13	11	149	161
12	12	12	1036	1100

DISCUSSION

The idealized structure model arrived at has the stoichiometry $Cu_{41}Sn_{11}$. It is a modification, without Sn – Sn contacts, of Knödler's proposal.[2] Table 3 shows that the IT(C) – IT(C) distance, 2.55 Å, represents a Cu – Cu contact

Table 3. Coordination, number and type of contacts, interatomic distances (Å) with standard deviations.

3	IT(A)–IT(A)	Cu(Sn)–Cu(Sn) 2.582(33)
3	–OT(A)	–Cu 2.554(31)
3	–OH(A)	–Cu 2.579(23)
3	–CO(A)	–Sn(Cu) 2.785(20)
3	OT(A)–IT(A)	Cu–Cu(Sn) 2.554(31)
3	–OH(A)	–Cu 2.686(19)
3	–CO(A)	–Sn(Cu) 2.636(11)
[1	–IT(D)	–Cu 3.375(45)]
3	–CO(D)	–Cu 2.632(29)
2	OH(A)–IT(A)	Cu–Cu(Sn) 2.579(23)
2	–OT(A)	–Cu 2.686(19)
4	–CO(A)	–Sn(Cu) 2.875(6)
1	–OH(B)	–Sn 2.587(28)
[2	–CO(C)	–Cu 3.256(26)]
2	–CO(D)	–Cu 2.576(18)
1	CO(A)–IT(A)	Sn(Cu)–Cu(Sn) 2.785(20)
1	–OT(A)	–Cu 2.636(11)
2	–OH(A)	–Cu 2.875(6)
[2	–CO(B)	–Cu 3.328(12)]
1	–OT(C)	–Cu 2.665(19)
1	–OH(C)	–Cu(Sn) 2.531(12)
2	–CO(C)	–Cu 2.823(15)
1	–OH(D)	–Cu 2.863(21)
2	–CO(D)	–Cu 2.655(10)
3	IT(B)–IT(B)	Cu–Cu 2.743(45)
3	–OT(B)	–Cu 2.638(26)
3	–OH(B)	–Sn 2.661(9)
3	–CO(B)	–Cu 2.778(26)
[1	–OT(D)	–Sn 3.329(38)]
3	OT(B)–IT(B)	Cu–Cu 2.638(26)
3	–OH(B)	–Sn 2.769(11)
3	–CO(B)	–Cu 2.564(15)
3	–CO(C)	–Cu 2.499(29)
1	OH(B)–OH(A)	Sn–Cu 2.587(28)
2	–IT(B)	–Cu 2.661(9)
2	–OT(B)	–Cu 2.769(11)
4	–CO(B)	–Cu 2.895(9)
2	–CO(C)	–Cu 2.781(22)
2	–CO(D)	–Cu 2.878(17)
[2	CO(B)–CO(A)	Cu–Sn(Cu) 3.328(12)]
1	–IT(B)	–Cu 2.778(26)
1	–OT(B)	–Cu 2.546(15)
2	–OH(B)	–Sn 2.895(9)
1	–OH(C)	–Cu(Sn) 2.764(18)
2	–CO(C)	–Cu 2.582(15)
1	–OT(D)	–Sn 2.676(16)
1	–OH(D)	–Cu 2.557(20)
2	–CO(D)	–Cu 2.746(14)
3	IT(C)–IT(C)	Cu–Cu 2.547(24)
3	–OT(C)	–Cu 2.547(24)
3	–OH(C)	–Cu(Sn) 2.614(17)
3	–CO(C)	–Cu 2.430(31)
3	OT(C)–CO(A)	Cu–Sn(Cu) 2.665(19)
3	–IT(C)	–Cu 2.547(24)
3	–OH(C)	–Cu(Sn) 2.708(14)
3	–CO(C)	–Cu 2.531(20)

Table 3. Continued.

2	OH(C)–CO(A)	Cu(Sn)–Sn(Cu) 2.531(12)
2	–CO(B)	–Cu 2.764(18)
2	–IT(C)	–Cu 2.614(17)
2	–OT(C)	–Cu 2.708(14)
4	–CO(C)	–Cu 2.708(13)
1	–OH(D)	–Cu 2.629(38)
[1	CO(C)–OH(A)	Cu–Cu 3.256(26)]
2	–CO(A)	–Sn(Cu) 2.823(15)
1	–OT(B)	–Cu 2.499(29)
1	–OH(B)	–Sn 2.781(22)
2	–CO(B)	–Cu 2.582(15)
1	–IT(C)	–Cu 2.430(31)
1	–OT(C)	–Cu 2.531(20)
2	–OH(C)	–Cu(Sn) 2.708(13)
2	–CO(C)	–Cu 2.961(35)
[1	IT(D)–OT(A)	Cu–Cu 3.375(45)]
3	–IT(D)	–Cu 2.944(34)
3	–OT(D)	–Sn 2.755(14)
3	–OH(D)	–Cu 2.588(27)
3	–CO(D)	–Cu 2.584(23)
[1	OT(D)–OT(A)	Sn–Cu 3.329(38)]
3	–CO(B)	–Cu 2.676(16)
3	–IT(D)	–Cu 2.755(14)
3	–OH(D)	–Cu 2.753(19)
3	–CO(D)	–Cu 2.606(16)
2	OH(D)–CO(A)	Cu–Sn(Cu) 2.863(21)
2	–CO(B)	–Cu 2.557(20)
1	–OH(C)	–Cu(Sn) 2.629(38)
2	–IT(D)	–Cu 2.588(27)
2	–OT(D)	–Sn 2.753(19)
4	–CO(D)	–Cu 2.853(11)
1	CO(D)–OT(A)	Cu–Cu 2.632(29)
1	–OH(A)	–Cu 2.576(18)
2	–CO(A)	–Sn(Cu) 2.655(10)
1	–OH(B)	–Sn 2.878(17)
2	–CO(B)	–Cu 2.746(14)
1	–IT(D)	–Cu 2.584(23)
1	–OT(D)	–Sn 2.606(16)
2	–OH(D)	–Cu 2.853(11)
[2	–CO(D)	–Cu 3.444(27)]

in our model ($2r_{Cu} = 2.56$ Å) and an Sn–Sn contact in Knödler's ($2r_{Sn} = 3.16$ Å). The shortest Cu–Cu distance in the structure, *viz.* IT(C)–CO(C), is 2.43 Å, which is not remarkable; such a distance, 2.48 (1) Å, occurs, *e.g.*, in the Cu_9Al_4 structure.[9] The IT(A)–IT(A) and CO(A)–OH(C) distances, which might contain some element of Sn–Sn contact in the real structure (defect model I), are longer: 2.58 and 2.53 Å, respectively.

The sum of the copper and tin radii is 2.86 Å, according to Schubert,[5] but the copper-tin distance observed [10] in the high temperature γ phase (Cu_3Sn composition) is only 2.65 Å. In the δ structure the Sn–Cu contacts range from 2.90 (OH(B)–CO(B)) down to 2.53 Å (CO(A)–OH(C)), which is shorter than the Cu_3Sn value. All the other distances from the Sn atoms in CO(A) to the surrounding Cu atoms are ≥2.64 Å, however. From Sn at OT(D) there are three fairly short contacts to Cu at CO(D) and one short distance from Sn at OH(B) to Cu at OH(A), but the remaining contacts are all longer than 2.65 Å.

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REFERENCES

1. Westgren, A. and Phragmén, G. *Z. Anorg. Allg. Chem. 175* (1928) 80.
2. Knödler, H. *Metall 18* (1964) 1172.
3. Johansson, A. and Westman, S. *Acta Chem. Scand. 24* (1970) 3471.
4. Westman, S. *Chem. Commun. Univ. Stockholm* (1972) No. 4.
5. Schubert, K. *Kristallstrukturen Zweikomponentiger Phasen*, Springer Verlag, Berlin 1964.
6. Hambling, P. G. *Acta Crystallogr. 6* (1953) 98.
7. Cromer, D. T. and Waber, J. T. *Acta Crystallogr. 18* (1965) 104.
8. Cromer, D. T. *Acta Crystallogr. 18* (1965) 17.
9. Heidenstam, O. von, Johansson, A. and Westman, S. *Acta Chem. Scand. 22* (1968) 653.
10. Hendus, H. and Knödler, K. *Acta Crystallogr. 9* (1956) 1036.
11. Cruickshank, D. W. I. Lecture at the Summer School of Modern Methods of X-Ray Crystallography, Manchester 1960.

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