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A Redetermination of the Distribution of Atoms in Cu_5Zn_8, Cu_5Cd_8, and Cu_9Al_4

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The atomic distribution in gamma brass, Cu_5Zn_8, has been established by neutron powder diffraction. It is of the Au_5Zn_8 type. The structures of Cu_5Cd_8 and Cu_9Al_4 have been refined from single-crystal diffractometer data and the distribution of atoms in these structures reconfirmed.

Cu_5Zn_8 is the prototype of the gamma-brass structure ($D8_{1-3}$), and was characterized as such by Westgren and Phragmén[1] at this Institute in 1925. The structure was investigated by Bradley and Thewlis,[2] and refined by Bradley and Gregory[3] who determined the position parameters of the atoms, but could only infer the ordering scheme ($D8_2$) by analogy with the ordering in Au_5Zn_8 since, with X-rays, it was not possible to tell the difference between Cu and Zn. Furthermore, the atomic distribution assumed in Cu_5Zn_8 differs from that in Cu_5Cd_8.[3] Thus, it was concluded that a redetermination of the atomic distribution in both these phases was well warranted.

A refinement of the Cu_9Al_4 structure[4] based upon single crystal diffractometer data was carried out and published by one of the present authors.[5] Some peculiarities remained, however, at the end of the refinement, especially in the temperature factors of the aluminum atoms. Since the least-squares calculations were carried out with a program which could only handle orthorhombic and lower symmetries, it was deemed to be of value to repeat the refinement, using the old data, with a program suited to the treatment of cubic symmetry.

EXPERIMENTAL

The starting materials copper (elektrolytkoppar, granular, $\geq$ 99.9 % Cu, Kebo AB), zinc (granular, Mallinckrodt Analytical Reagent) and cadmium (sticks, specially pure, the British Drug Houses, 99.9 % Cd) were weighed out to match the compositions Cu_5Zn_8 and Cu_5Cd_8. The components were heated together at ~1000°C in sealed, evacuated silica capsules until reaction was complete. This was checked by quenching of the capsules

in water, extraction and crushing, in a steel mortar, of the solidified alloy pellets to make sure that they were homogeneous, and brittle.

Subsequently, the specimens were again sealed into evacuated silica tubes, re-heated at 950°C (Cu_5Zn_8) and 530°C (Cu_5Cd_8) for 1—3 days and then cooled to room temperature.

Many such preparations had to be made of the Cu_5Zn_8 phase to produce enough material, ~10 g, for neutron powder diffraction. A mixture of these several specimens was analyzed for copper electrolytically and for zinc by phosphate precipitation according to standard practice,[6] and was found to have the desired composition to within 0.5 mole %.

The density measurements reported were carried out by weighing of the samples in air and in chloroform.

Guinier photographs were taken, with Cu$K\alpha_1$ radiation (λ = 1.54050 Å) and potassium chloride (a = 6.2919 Å) as an internal standard, of all individual alloy preparations. The γ-(Cu,Zn) specimens all had the same lattice parameter to within ± 0.002 Å. This was taken as evidence for their being identical in composition.

Single crystal X-ray intensity measurements were carried out, on a crystal of Cu_5Cd_8, with a General Electric Diffractometer equipped with a full circle Single Crystal Orienter and a scintillation counter, using Ni-filtered Cu$K\alpha$ radiation and pulse height discrimination. Pulses were counted for 400 sec during a θ-2θ scan across each diffraction peak.

The crystal was a fairly irregular prism, ~50 × 50 × 100 μ. 200 intensities were collected, with the crystal oriented so that absorption effects were likely to be minimized, corrected for absorption by approximate numerical integration and, applying the appropriate Lp-factors, converted to 80 independent structure factors.

For Cu_9Al_4 the number of independent F's was 164.

In the 10-cycle, full matrix refinements of Cu_5Cd_8, and also of Cu_9Al_4, the atomic scattering factors of Cromer and Waber [7] and dispersion correction terms published by Cromer [8] were employed, and Cruickshank's weighting function, $w = (|F_o|_{min} + |F_o| + 2|F_o|_{max}^{-1} \cdot |F_o|^2)^{-1}$ was used.

Versions modified for the Uppsala CDC 3600 computer of *World list* [9] programs No:s 6031 (Goniostat settings), 384 (Least-squares refinement) and an absorption program (not in the list), originally written by Coppens, Leiserowitz and Rabinovich, were used.

The Cu_5Zn_8 neutron powder diffraction record was prepared for us, as a chart recorder trace, by the Neutron Diffraction Group at the Swedish Research Councils' Laboratory, Studsvik. The sample holder was a cylindrical aluminum container, ø = 10 mm. The neutron wavelength was 1.07 Å. Experimental intensities were derived by graphical integration of the areas under the diffractometer chart peaks.

In the derivation of calculated intensities for various atomic distributions the neutron scattering factors and diffracted intensity expression listed by Bacon [10] were used. Thus, $b_{Zn} = 0.59 \times 10^{-12}$ cm and $b_{Cu} = 0.79 \times 10^{-12}$ cm. These calculations were performed on the computer TRASK, using a modified version of a program [11] written for the FACIT computer (not in the *World list*).

GENERAL DESCRIPTION OF THE STRUCTURES

Cu_5Zn_8 and Cu_5Cd_8 have been reported to belong to space group No. 217, $I\bar{4}3m$ [2,3] and Cu_9Al_4 to space group No. 215, $P\bar{4}3m$.[4] No indications to the contrary have been found in the present investigation.

The structure type may be described in terms of two clusters, each comprising 26 atoms. One cluster, A, has its center at the origin 0,0,0; the other, B, is centered on $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. In space group $I\bar{4}3m$, the clusters are identical, in space group $P\bar{4}3m$, the atomic distributions in A and B are different, and the correspondence between position parameters in the two clusters is only approximate.

The clusters are built up of an Inner Tetrahedral position (IT), an Outer Tetrahedral position (OT), an Octahedral (OH), and a somewhat distorted Cubo-Octahedral (CO) position, with the following approximate parameters:

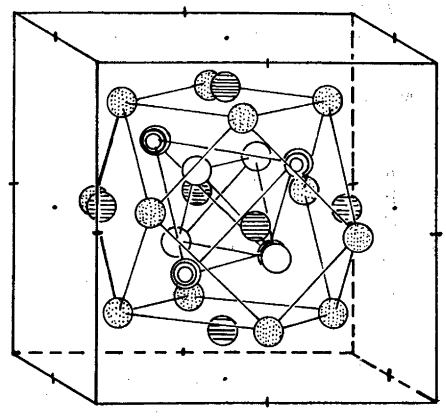

Fig. 1. Atomic sites in cluster A. IT = inner tetrahedral, OT = outer tetrahedral, OH = octahedral, and CO = cubo-octahedral position.

	$P\bar{4}3m$	$I\bar{4}3m$		Cluster A	Cluster B
IT	4(*e*)	8(*c*)	*x*,*x*,*x*; etc.	$x = 0.10$	
OT	4(*e*)	8(*c*)	*x*,*x*,*x*; »	$x = -0.17$	$+(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$ in $I\bar{4}3m$
OH	6(*g*)	12(*e*)	*x*,0,0; »	$x = 0.35$	
CO	12(*i*)	24(*g*)	*x*,*x*,*z*; »	$x = 0.30$, $z = 0.05$	$+(\sim 0.50, \sim 0.50, \sim 0.50)$ in $P\bar{4}3m$.

Fig. 1 shows the full complement of atomic sites in a cluster (A).

Final atomic distributions and refined parameters for the three structures are given in Table 5. Coordination and interatomic distances appear in Table 6.

THE Cu_5Zn_8 STRUCTURE

The average value of the lattice parameter obtained in this investigation is:

$$a = 8.869 \pm 2 \text{ Å}$$

For the composition Cu_5Zn_8, with 52 atoms per unit cell, a comparison of measured and calculated densities yields:

$$d_{obs} = 7.99 \text{ g cm}^{-3}, \qquad d_{calc} = 8.01 \text{ g cm}^{-3}$$

The atomic positional parameters were fairly accurately determined by Bradley and Gregory [3] and are reproduced, with estimated standard deviations, in Table 5 alongside the refined parameters of the two other structures.

Table 1. Atomic distribution models for Cu_5Zn_8. For each model, the symbol Cu,Zn signifies a random distribution of Cu and Zn over all sites so designated.

Model	IT	OT	OH	CO	Type
A	Zn	Cu	Cu	Zn	Au_5Zn_8
B	Cu,Zn	Cu,Zn	Cu	Zn	
C	Zn	Cu	Cu,Zn	Cu,Zn	
D	Cu	Cu	Zn	Cu,Zn	
E	Cu	Cu	Cu,Zn	Cu,Zn	Cu_5Cd_8
F	Cu,Zn	Cu,Zn	Cu,Zn	Cu,Zn	Random

Table 1 summarizes the atomic distribution models tested and Table 2 gives their fit with the observed neutron diffraction intensities. The completely ordered Au_5Zn_8 type distribution, model A, is seen to give the best agreement with the observations. The somewhat randomized versions, B and C, of the distribution type might conceivably be considered to give an acceptable fit, so that a certain measure of substitution of Cu for Zn and *vice versa*, can not be completely ruled out. The Cu_5Cd_8 type distribution model, E, a slightly more ordered version thereof, D, and the completely random distribution, model F, are definitely poorer and can be eliminated.

Table 2. Observed and calculated neutron diffraction intensities for Cu_5Zn_8. Distribution models as in Table 1.

h k l	I_{obs}	I_{calc} A	B	C	D	E	F
211	11	15	8	8	7	4	2
220	—	0	0	0	0	0	0
310	—	0	0	0	0	1	0
222	10	9	14	13	14	17	16
321	12	9	13	12	12	14	14
400	—	0	0	0	0	1	0
420	—	2	3	3	3	3	3
332	18	17	22	19	26	26	19
422	20	19	18	15	19	19	11
510, 431	8	7	11	10	9	16	12
521	—	1	2	4	2	3	5
440	—	1	2	2	3	4	2
433, 530	—	2	2	4	1	2	2
600, 442	54	62	57	60	52	49	44
611, 532	14	11	11	9	11	9	8
620	—	0	0	0	0	0	0
541	—	3	2	2	2	4	1
622	—	0	1	1	1	1	1
631; 444; 710, 550, 543; 640	80	76	87	79	83	86	73
633, 721, 552	147	148	147	144	138	133	116
642	—	5	6	6	6	6	6
730	—	3	3	2	2	2	2
732, 651	11	11	15	13	15	17	13

Table 3. Structure factors for final refined model of Cu_5Cd_8. $R = 11$ %.

hkl	$\|F_o\|$	$\|F_c\|$	*hkl*	$\|F_o\|$	$\|F_c\|$
011	0	6	266	261	252
002	47	30	466	94	81
112	28	42	666	287	274
022	48	47	017	81	84
222	311	362	127	359	386
013	194	185	037	83	93
123	233	202	237	170	172
033	776	891	147	237	222
233	313	363	347	99	81
004	145	170	057	46	36
114	663	671	257	229	230
024	46	48	457	137	126
224	344	301	167	71	66
134	94	82	367	58	66
334	121	114	077	96	77
044	85	93	277	86	75
244	237	218	008	216	238
444	574	633	118	32	21
015	161	174	028	204	214
125	80	61	228	182	202
035	156	125	138	32	30
235	154	122	338	151	165
145	190	177	048	59	50
345	112	99	248	34	34
055	625	473	448	129	137
255	141	113	158	115	130
455	106	116	358	208	228
006	291	270	068	102	96
116	113	123	268	40	38
026	133	140	019	60	62
226	190	200	129	92	96
136	298	255	039	41	42
336	352	349	239	95	109
046	79	73	149	142	166
246	159	136	349	47	63
446	188	188	059	202	187
156	203	164	00.10	170	193
356	160	137	11.10	146	158
556	80	67	02.10	112	102
066	397	301	22.10	244	276

A few other models, with inverted distributions of Cu and Zn have also been tried. The calculated neutron diffraction intensities for all these models were completely at variance with the observed data.

THE Cu_5Cd_8 STRUCTURE

The lattice parameter of the investigated sample is:

$$a = 9.5888 \pm 3 \text{ Å}.$$

Table 4. Structure factors for refined model of Cu_9Al_4. $R = 14.5$ %.

hkl	$\|F_o\|$	$\|F_c\|$	*hkl*	$\|F_o\|$	$\|F_c\|$	*hkl*	$\|F_o\|$	$\|F_c\|$
001	38	33	006	321	401	077	25	22
011	29	22	016	43	42	177	31	32
111	33	21	116	99	93	277	123	99
002	31	24	026	18	7	377	28	30
012	71	54	126	25	19	477	245	242
112	105	80	226	33	26	008	47	46
022	10	9	036	59	44	018	14	16
122	84	67	136	114	108	118	41	38
222	147	124	236	33	32	028	106	109
003	163	151	336	318	336	128	21	23
013	21	19	046	91	87	228	94	94
113	37	26	146	40	37	038	47	53
023	13	14	246	65	61	138	49	54
123	74	55	346	32	27	238	32	36
223	50	38	446	96	89	338	60	58
033	427	672	056	47	52	048	38	30
133	49	39	156	47	49	148	31	36
233	149	129	256	37	31	248	24	28
333	122	93	356	71	54	348	11	15
004	11	6	456	16	13	448	20	20
014	10	8	556	34	30	058	18	25
114	276	345	066	276	292	158	29	28
024	67	51	166	20	22	258	27	33
124	50	40	266	134	124	358	151	148
224	164	144	366	42	29	458	25	24
430	27	22	466	47	41	558	93	90
134	43	37	566	12	16	068	49	48
234	51	43	666	205	155	168	20	21
334	57	47	007	44	49	268	68	70
044	58	48	017	11	4	368	28	30
144	69	56	117	54	52	468	28	29
244	213	184	027	7	6	078	8	2
344	19	17	127	203	215	178	52	67
444	330	372	227	30	27	278	34	43
005	14	13	037	70	70	009	23	4
015	84	72	137	24	21	019	63	72
115	72	65	237	83	84	119	32	33
025	11	2	337	35	37	029	10	3
125	28	21	047	23	18	129	42	50
225	64	59	147	222	232	229	40	40
035	13	9	247	12	7	039	166	162
135	44	35	347	51	47	139	14	16
235	68	59	447	69	75	239	40	36
335	37	35	057	12	9	339	25	25
045	55	51	157	12	13	049	28	31
145	59	41	257	98	91	149	81	92
245	25	23	357	11	5	249	9	8
345	70	56	457	112	98	349	47	46
445	34	28	557	25	24	449	19	21
055	203	208	067	16	14	059	32	35
155	32	29	167	31	30	159	17	15
255	123	109	267	19	18	259	35	46
355	17	18	367	37	30	359	6	10
455	75	68	467	16	20	069	25	23
555	62	63	567	42	38			

The positional parameters of Ref. 3 were used as a starting point for refinements of four different distribution models, *viz.*

A) a Cu_5Zn_8 (Au_5Zn_8) type distribution
B) model A with Cu and Cd interchanged between IT and OT
C) the Cu_5Cd_8 type reported in Ref. 3.
D) a completely random distribution of Cu and Cd over all sites.

The residual, $R = \sum||F_o|-|F_c||/\sum|F_o|$, at the end of each refinement was

$$R_A = 0.25,\ R_B = 0.24,\ R_C = 0.11 \text{ and } R_D = 0.16$$

Thus, of the models tested, C is obviously the best one. This is also substantiated by the fact that the refinement of C yielded the lowest standard deviations in all parameters. The result is listed in Table 5. A comparison of observed and calculated structure factors is given in Table 3.

It was not considered necessary to test any further models, since the final individual thermal parameters in each of the cases A, B, and D showed what was amiss with the model. An excess of Cd with respect to model C, at any site, showed up as a very high B value and an excess of Cu, naturally, as a very low (negative) B.

The average temperature factor value for model C is $\bar{B} = 1.6$ Å^2, which is within two standard deviations of all individual B's.

The weight analyses, both according to $|F_o|$ and according to $\sin^2\theta$, were without significant trend and remarkable excursions, except as regards the three of four strongest reflections.

Table 5. Atomic distributions, positional and thermal parameters in the refined structures. Cu_5Zn_8 parameters from Bradley and Gregory.[3] The symbol, Cd,Cu signifies a random occupation of the site by Cd and Cu in the ratio 8:1.

		Cu_5Zn_8	Cu_5Cd_8	Cu_9Al_4 Cluster A	Cu_9Al_4 Cluster B
	$a \pm \sigma$ Å	8.869 ± 2	9.5888 ± 3	8.7023 ± 5	
IT	Atom	Zn	Cu	Al	Cu
	$x \pm \sigma$	0.110 ± 3	0.0939 ± 11	0.1144 ± 17	0.6046 ± 7
	$B \pm \sigma$ Å^2	1	1.1 ± 4	−0.1 ± 3	−0.3 ± 2
OT	Atom	Cu	Cu	Cu	Cu
	$x \pm \sigma$	−0.172 ± 3	−0.1617 ± 12	−0.1690 ± 9	0.3248 ± 9
	$B \pm \sigma$ Å^2	1	1.2 ± 4	0.3 ± 3	0.3 ± 2
OH	Atom	Cu	Cd,Cu	Cu	Cu
	$x \pm \sigma$	0.355 ± 3	0.3506 ± 9	0.3565 ± 10	0.8554 ± 10
	$B \pm \sigma$ Å^2	1	2.0 ± 2	0.0 ± 2	0.0 ± 2
CO	Atom	Zn	Cd,Cu	Cu	Al
	$x \pm \sigma$	0.313 ± 3	0.2980 ± 5	0.3142 ± 6	0.8108 ± 12
	$z \pm \sigma$	0.036 ± 3	0.0577 ± 7	0.0337 ± 7	0.5367 ± 16
	$B \pm \sigma$ Å^2	1	1.6 ± 2	0.1 ± 2	0.4 ± 3

Table 6. Coordination, number and type of contacts, and interatomic distances (Å), with standard deviations, in the γ-phases.

		Cu_5Zn_8	Cu_5Cd_8	Cu_9Al_4(A)	Cu_9Al_4(B)
3 IT(A)	—IT(A)	Zn—Zn 2.75	Cu—Cu 2.574 ± 24	Al—Al 2.815 ± 33	Cu—Cu 2.574 ± 14
3	—OT(A)	—Cu 2.61	—Cu 2.618 ± 17	—Cu 2.556 ± 14	—Cu 2.585 ± 11
3	—OH(A)	—Cu 2.57	—Cd 2.771 ± 8	—Cu [2.534 ± 7	—Cu 2.534 ± 8
3	—CO(A)	—Zn 2.62	—Cd 2.789 ± 15	—Cu 2.557 ± 18	—Al 2.605 ± 11
3 OT(A)	—IT(A)	Cu—Zn 2.61	Cu—Cu 2.618 ± 17	Cu—Al 2.556 ± 14	Cu—Cu 2.585 ± 11
3	—OH(A)	—Cu 2.69	—Cd 2.844 ± 8	—Cu 2.643 ± 7	—Cu 2.666 ± 7
3	—CO(A)	—Zn 2.55	—Cd 2.800 ± 7	—Cu 2.511 ± 7	—Al 2.487 ± 14
3	—CO(B)	—Zn 2.59	—Cd 2.746 ± 16	—Al 2.573 ± 17	—Cu 2.536 ± 10
2 OH(A)	—IT(A)	Cu—Zn 2.57	Cd—Cu 2.771 ± 8	Cu—Al 2.534 ± 7	Cu—Cu 2.534 ± 8
2	—OT(A)	—Cu 2.69	—Cu 2.844 ± 8	—Cu 2.643 ± 7	—Cu 2.666 ± 7
1	—OH(A)	—Cu 2.56	—Cd 2.865 ± 17	—Cu 2.497 ± 17	—Cu 2.517 ± 17
4	—CO(A)	—Zn 2.81	—Cd 2.954 ± 4	—Cu 2.774 ± 5	—Al 2.751 ± 9
2	—CO(B)	—Zn 2.53	—Cd 2.877 ± 7	—Al 2.507 ± 15	—Cu 2.482 ± 8
2	—CO(B)′	—Zn 2.83	—Cd 3.383 ± 8	—Al 2.808 ± 15	—Cu 2.764 ± 9
1 CO(A)	—IT(A)	Zn—Zn 2.62	Cd—Cu 2.789 ± 15	Cu—Al 2.557 ± 18	Al—Cu 2.605 ± 16
1	—OT(A)	—Cu 2.55	—Cu 2.800 ± 7	—Cu 2.511 ± 7	—Cu 2.487 ± 14
2	—OH(A)	—Cu 2.81	—Cd 2.954 ± 4	—Cu 2.774 ± 5	—Cu 2.751 ± 9
1	—OT(B)	—Cu 2.59	—Cu 2.746 ± 16	—Cu 2.536 ± 10	—Cu 2.573 ± 17
1	—OH(B)	—Cu 2.53	—Cd 2.877 ± 7	—Cu 2.482 ± 8	—Cu 2.507 ± 15
1	—OH(B)′	—Cu 2.83	—Cd 3.383 ± 8	—Cu 2.764 ± 9	—Cu 2.808 ± 15
4	—CO(B)	—Zn 2.63	—Cd 2.994 ± 4	—Al 2.575 ± 9	—Cu 2.575 ± 9
2	—CO(B)′	—Zn 2.63	—Cd 3.259 ± 12	—Al 2.601 ± 11	—Cu 2.601 ± 11

The differences between the refined position parameters and those of Bradley and Gregory [3] are of the order of 0.002 units. It is to be expected that the accuracy of their Cu_5Zn_8 parameters is as good, or better.

THE Cu_9Al_4 STRUCTURE

The observed lattice parameter:

$$a = 8.7023 \pm 5 \text{ Å}.$$

and atomic positional and thermal parameters taken from Ref. 5 were used as a starting point for the computations. The shifts obtained in the atomic positions were within the standard deviations of the present refinement (which are a little larger than those of Ref. 5) except for the shift in the CO(B) parameter x_{Al}, which was approximately 1.5 standard deviations.

The significant changes occurred in the individual thermal parameter values which now lie mostly within one standard deviation (2 s.d.'s for $Cu_{IT(B)}$) from their average value, $\overline{B} = 0.1$ Å^2. This is taken as evidence that the atomic distribution is the correct one. (That the value of $\overline{B}$ is so small may indicate an insufficiently large correction for absorption). The standard deviations of the B's had obviously also been quite erroneously calculated by the program available in the previous investigation.[5] The present ones are about five times larger.

Structure factors are listed in Table 4, refined parameters and interatomic distances in Tables 5 and 6, respectively.

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