ACTA CHEMICA SCANDINAVICA 6 (1952) 709—719

X-ray Investigation of Cu-Ce Alloys, Rich in Copper. With a Discussion of the Interatomic Distances in the A_5B Structure Type

ANDERS BYSTRÖM, PEDER KIERKEGAARD and OSWALD KNOP

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

The phase diagram of the system Cu-Ce has been determined by Hanamann[1]. He concluded from a thermal investigation of Cu-Ce alloys that four intermediate compounds exist, namely Cu_6Ce, Cu_4Ce, Cu_2Ce and CuCe. In the present paper, an X-ray investigation of alloys with cerium contents of 25 atomic percent will be reported.

The copper used in the investigation was obtained from Boliden Mining Co. and had a purity of 99.99 %. The cerium was less pure. A preliminary spectroscopic investigation showed that the chief impurities were Fe and Mg, and smaller amounts of Mn and Ca. The chemical analysis gave the following values: Fe: 0.9 %; Mg; 1.2 %; Ca, Mn < 0.1 %. Another sample of Ce used in the alloys from which single crystals of Cu_6Ce and Cu_4Ce were obtained, showed a considerably lower Mg content of 0.5 %.

The analysis of Ce was carried out in the following way: Ce was precipitated as oxalate, and re-precipitated twice. The Fe was precipitated with $NH_3 + NH_4Cl$, the precipitation dissolved and precipitated again, and determined as Fe_2O_3. Mg was determined as phosphate in the filtrate. 1.27 % Mg was obtained in this way. To avoid some of the reprecipitations, another method was also tried and with satisfactory results. With this latter method the solution containing Ce, Fe, and Mg was passed through an ion exchange column with Amberlite IR 120. Sufficient ion exchanger was used so that 95 % of Ce was absorbed. A qualitative analysis of the absorbed Ce showed no traces of Feand Mg. The remaining Ce was precipitated together with Fe with $NH_3 + NH_4Cl$, and Mg was determined in the filtrate as phosphate. 1.10 % Mg was found by this method, which was also used for the second sample of Ce.

The alloys were prepared by melting together Cu and Ce in evacuated silica tubes. The molten alloys were shaken vigourously. They were then rapidly quenched and the ingots annealed for 1—2 weeks. Filings were taken, avoiding the surface layer of the ingots, which contained some oxide. The filings were then annealed again.

The Cu Phase

The cube edge of the Cu used in the investigation was a = 3.615 ± 0.002 Å. (Cr-K radiation. $K_{\alpha_1} = 2.28962$ Å, powder photographs in focussing cameras) agreeing satisfactory with the precision value for pure Cu of $a = 3.6152$ Å [2]. Powder photographs of alloys in the two phase region Cu + Cu_6Ce, annealed at 770°, showed a Cu-phase with — within the limits of the errors in the determination — the same cell dimensions. Assuming Vegard's law to be valid, we can estimate that the solubility of Ce in solid Cu is < 0.5 atomic % at this temperature.

The Cu_6Ce Phase

It was found to be very difficult to attain equilibrium for alloys with 10—20 atomic % Ce. In spite of prolonged melting-time and prolonged annealing (several weeks sometimes proved insufficient), the x-ray examination showed for some alloys the presence of three phases: Cu and two intermediate phases. In other cases, different part of an ingot gave widely different powder photographs. Thus the composition of the first intermetallic phase in the system could not be deduced from the powder photographs. Single crystals of the phase could, however, be picked out under the microscope from an ingot with 17 atomic % Ce. Two samples of about 10 mg were analysed, and the following values obtained:

Observed weight %	Cu: 72.2	Ce: 27.1
Calculated for Cu_6Ce:	73.2	26.8

Cu was determined by electrolysis. As there was some indication in the literature[3] that Ce might disturb the Cu electrolysis, some control experiments were carried out. Samples with known amounts of Cu and 50 respectively 75 % Ce were electrolyzed. However, the added Cu amount was always completely recovered. Ce was precipitated after the electrolyses as oxalate and weighed as oxide.

Because of the difficulty in obtaining homogeneous samples, it was difficult to obtain a reliable value for the density. However, determinations on several samples indicated a value of 8.0. Preliminary cell dimensions from rotation and Weissenberg photographs were refined from powder photographs (Cr-K). The following orthorhombic unit cell was obtained:

$$a = 8.08_5 \text{ Å} \qquad b = 5.09_7 \text{ Å} \qquad c = 10.17_2 \text{ Å}$$

The reflexions in the range $\sin^2\Theta = 0.07-0.50$ are listed in Table 1.

Table 1. Powder photographs of Cu$_6$Ce Comparison between observed and calculated $\sin^2\Theta$ *values. Cr-*K *radiation, β-reflexions omitted.*

hkl	$10^4\sin^2\Theta_{\mathrm{calc}}$	$10^4\sin^2\Theta_{\mathrm{obs}}$	I_{obs}
202	1310	1304	w
211	1435	1430	vvw
013	1646	1647	v st
113	1850	1851	st
020	2020	2016	vvst
104	2230	2236	vvst
302	2314	2305	m
121	2348	2353	m
311	2438	2439	vvst
022	2527	2530	st
122	2728	2739	w
114	2735		
312	2819	2827	st
220	2823		
204	2832		
221	2948	2941	m
303	2950		
401	3338	3326	vst
105	3371	3372	vst
015	3675	3687	vw
304	3835	3823	vw
321	3953	3963	w
223	3964		
205	3973		
124	4250	4251	w
322	4334	4324	vw
314	4340		
106	4766	4772	vvw
224	4852	4837	vvw
413	4857		
421	5358	5368	w
206	5368		

Assuming 4 formula units Cu$_6$Ce in the unit cell, a density of 8.27 would be expected, in plausible agreement with the observed value of 8.0.

The reflexions in the Weissenberg photographs (Cu$-K$) registering $hk0$, $hk1$, $h0l$, and $h1l$ reflexions indicated that the space group is $D_{2h}^{16}-Pnma$, provided that the structure is centro-symmetric. With this space group the four Ce atoms must be placed in $4(c){:}x\frac{1}{4}z$, because in the other four-fold positions the atoms are placed only $\frac{b}{2} = 2.55$ Å.

apart, which is improbably short for a Ce—Ce distance (r_{Ce} = 1.8 Å). Because of the mirror-plane perpendicular to *b*, the atoms in the general positions will be $\frac{b}{2}$ = 2.55 Å, this implies that the *y* parameter must be close to 0 for atoms in the general position. For the atoms with $y = 0$ (thus for those in the general position and in 4(*a*) and 4(*b*)) the structure factor of the reflexions *hk*0 is equal to zero, when *k* is odd. The Weissenberg photograph *hk*0 shows, however, that some of the reflexions *h*10 are in fact stronger than those with *k* even. This indicates that not only the Ce atoms but also some of the Cu atoms must be placed in 4(*c*). Consideration of the intensities of the reflexions 0*k*0 indicates that eight Cu atoms are placed either in 4(*a*) + 4(*b*), or in 8(*d*) with $y \sim 0$, and four Ce atoms + sixteen Cu atoms in the position 4(*c*) with $y = \frac{1}{4}$. The structure determination thus involves the determination of five or six *x* parameters and an equal number of *z* parameters, but attempts to solve the problem have so far been unsuccessful.

The Cu_4Ce Phase

Single crystals of this phase were easily obtained from alloys with 20—25 atomic % Ce. The hexagonal unit cell determined from powder photographs (Cr-*K* radiation) has the dimensions $a = 5.150 \pm 0.002$ and $c = 4.102 \pm 0.002$ Å. There were no systematic extinctions in the Weissenberg photographs.

It was easily found that the observed intensities corresponded to a structure of the same type as Zn_5Ca[4], and it was therefore inferred that the formula of this Cu-Ce phase was Cu_5Ce. However, at this stage of the investigation a paper appeared by Heumann [5] on the composition of this phase. Heumann concludes from a microscopical investigation of alloys that the composition of the phase is Cu_4Ce and he assumes that the unit cell, for which he gives the dimensions $a = 5.131$ kX $c = 4.124$ kX, contains 1.2 formula units, thus six atoms. This indicates that 0.2 Ce atoms are placed in one or both of the Cu positions (see below) together with 4.8 Cu atoms. Because of the large difference in atomic radii ($r_{Cu} = 1.25$, $r_{Ce} = 1.8$ Å) this seemed rather improbable but further investigation confirmed Heumann's results.

Because of the difficulty in reaching equilibrium for alloys containing this phase, too, the analysis was carried out in microscale on selected single crystals by the same method as for Cu_6Ce. The following values were obtained:

Observed weight %:	Cu: 64.2	Ce: 35.5
Calculated for Cu_4Ce:	64.47	35.53

As for Cu_6Ce, a reliable determination of the density was difficult, but determinations on different samples placed the value at about 8.0. With 1.2 Cu_4Ce in the unit cell the calculated density would be 8.36 and with 1 Cu_4Ce in the cell 6.95. Obviously the six atomic positions in the cell are completely or very near completely filled with atoms. The arrangement of the atoms is:

Table 2. Weissenberg photographs of Cu_4Ce*. Comparison between* $|F_{obs}|$ *and* $|F_{calc}|$*. Cu-K radiation.*

$h\,k\,l$	$\|F_{obs}\|$	$\|F_{calc}\|$	$h\,k\,l$	$\|F_{obs}\|$	$\|F_{calc}\|$
001	25	26	111	83	109
002	182	147	112	50	58
003	33	20	113	116	80
004	166	102	114	83	43
005	30	15	115	91	61
100	7	1	220	66	114
200	75	88	221	17	19
300	45	55	222	66	105
400	50	62	223	17	16
500	13	2	224	116	86
101	43	49	330	17	41
102	0	2	331	33	65
103	66	35	332	33	38
104	7	3	210	0	3
105	35	27	211	18	39
201	31	39	212	0	3
202	70	83	213	17	31
203	36	27	214	15	2
204	75	57	310	0	4
301	106	87	311	0	33
302	45	49	312	0	3
303	99	73	313	13	29
304	73	41	314	8	3
401	15	26	410	26	44
402	35	57	411	55	70
403	13	23	412	20	41
501	18	28	413	83	61
502	10	3	510	0	3
110	50	70	511	31	26

Space group D^1_{6h}

Ce in 1 (a): 000 0.2 Ce + 4.8 Cu in 2 (c): $\frac{1}{3}\frac{2}{3}0$; $\frac{2}{3}\frac{1}{3}0$ + 3 (g): $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

The Ce atoms may obviously be placed either in 2(c) with only Cu atoms in 3(g), or in 3(g) with only Cu atoms in 2(c), or in both positions. The effect on the intensities is however too slight to enable a conclusion to be drawn as to which of these three arrangements is correct. Table 2 gives the observed and calculated F-values, assuming the Ce atoms to be statistically distributed among the Cu atoms.

The interatomic distances are:

(Cu_1 denotes an atom in 2 (c), Cu_2 an atom in 3 (g).)

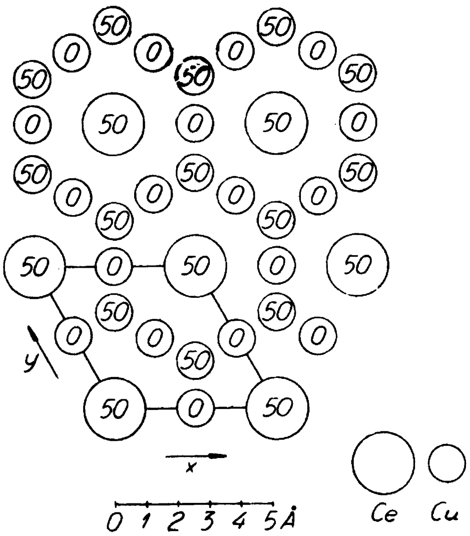

Fig. 1. Cu_4Ce. *Projection on the xy plane of the structure. The figures denote the height of the atoms in percentages of c.*

Ce— 6 Cu_1 = 2.973 Å ± 0.002;
Ce—12 Cu_2 = 3.292 » »
Ce— 2 Ce = 4.102 » »

Cu_1—3 Ce = 2.973 Å ± 0.002;
Cu_1—3 Cu_1 = 2.973 » »
Cu_1—6 Cu_2 = 2.533 » »

Cu_2—4 Ce = 3.292 ± 0.002 Å
Cu_2—4 Cu_1 = 2.575 Å
Cu_2—4 Cu_2 = 2.533 »

As will be seen, the coordination number of the Ce atoms is twenty (Fig. 1).

The Relation between Bond Number and Atomic Radii for the A/B Structure Type

It is of some interest to discuss the relation between bond number and radius recently put forward by Pauling[6] for the A_5B structure type, partly because of the high coordination number of the B atoms and the large contraction in A_1—B distances, and partly because of the astonishing deviation from the ideal formula for some phases belonging to this structure type.

The equation used by Pauling is: $R(1)-R(n) = 0.300 \log n$. $R(1)$ and $R(n)$ are the radii corresponding to the bond numbers 1 and n, respectively. The bond number n is defined as the number of shared electron pairs in the bond.

The following table gives the cell dimensions of all hitherto investigated A/B phases. The original values are probably all expressed in kX units and have been transformed into Å units.

	a	c	
Co_5Ce	4.955 Å	4.055 Å	Heumann [5]
Co_5Th	4.950	4.039	»
Ni_5Ca	4.960	3.948	Nowotny [7]
Ni_5La	4.962	4.008	»
Ni_5Ce	4.874	4.004	»
Ni_5Pr	4.948	3.973	Fülling [8]
Ni_5Cd	4.91	3.99	Endter, Klemm [9]
Ni_5Th	4.921	3.990	Heumann [5]
Cu_5Ca	5.107	4.073	Nowotny [7]
$(Cu_{4.8}La_{0.2})La$	5.169	4.116	»
$(Cu_{4.8}Ce_{0.2})Ce$	5.150	4.102	this paper
Zn_5Ca	5.382	4.250	Nowotny[7]
Zn_5La	5.427	4.225	»
$Zn_5(Th_{0.6}Zn_{0.4})$	5.247	4.451	» [10]

Somewhat different values have been given for Cu_5Ca and Zn_5Ca by Haucke [4] with $a = 5.092$ Å, $c = 4.086$ Å, and $a = 5.416$ Å, $c = 4.191$ Å, respectively.

From the values in the above table, the interatomic distances in the A_5B phases have been calculated. These distances have been compared with distances calculated from Pauling's equation assuming the values of the metallic valency V, which are shown in Table 3. The radii of the metals used in the calculations are taken from Pauling [6] and transformed into Å units.

The following table gives the B—6 A distances in the A_5B phases compared with those calculated in this way. As will be seen, differences ranging from 0.5 to 0.1 Å are obtained.

The small differences in electronegativity for the A and B metal — of the order 0—1.2 units — makes it rather improbable that there is an appreciable amount of ionic character in the bonds, as was assumed by Dehlinger, Nowotny *et. al.* (see (13) and (14)) in several alloys, especially those containing alkali atoms. In fact, the direction of the electron transfer, which probably takes place in these phases (from the A atoms to the B atoms, see below) will decrease these differences in electronegativity and thus the amount of ionic character in the bonds still more.

The effect of an electron gain or loss on the two kinds of atoms was now considered. Pauling assumed that the gain of an electron for a calcium atom results in an decrease in radius (because of dsp hybridization) slightly less than the difference r(1)Ca—r(1)Sc[6]. If we follow this suggestion, the following radii would be expected:

Table 3.

V_A → V_B ↓	Co_5 5.78	Ni_5 5.78	Cu_5 5.44	Zn_5 4.44
Ca 2		2.864 Å 3.349 − 0.485	2.949 3.352 − 0.403	3.107 3.411 − 0.304
La 3		2.866 3.160 − 0.295	2.984 3.181 * − 0.197	3.133 3.258 − 0.125
Ce 3.2	2.860 3.095 − 0.234	2.814 3.087 − 0.273	2.973 3.116 * − 0.143	
Pr 3.1		2.857 3.108 − 0.251		
Gd 3		2.835 3.076 − 0.241		
Th 4	2.858 3.043 − 0.185	2.841 3.039 − 0.198		3.039 3.104 * − 0.075

		+ 1 electron	+ 2 electrons
r(1)Ca:	1.739 Å	1.46 Å	1.34 Å
r(1)La:	1.693 »	1.44 »	
r(1)Th:	1.655 »	1.50 »	

The effect of the electron loss on the A metals is small and — as it probably amounts only to 0.02—0.04 Å — has been neglected (see below).

A—B distances corresponding to the addition of one and two electrons to the B metals were now calculated from these radii and the new values for valencies and bond numbers. Thus we obtain for Ni_5Ca:

+ 1 electron $n_1 = 0.305$; Ca—6 $Ni_1 = 1.46 + 1.15 - 0.6 \log n_1 = 2.94$Å
+ 2 » $n_1 = 0.410$; Ca—6 $Ni_1 = 1.34 + 1.15 - 0.6 \log n_1 = 2.74$ Å

---

* Calculated for the ideal composition A_5B. See p. 715.

As will be seen from Table 3, the actual value observed is 2.863 Å. Interpolation between the values for + 1 and + 2 electrons gives a gain of 1.4 electrons.

The electron gain were calculated in the same manner for the Ca, La, and Th phases. The results are collected in the table p. 12.

Attempts were made to find whether a relation exists between the differences in electronegativity and the contractions. As the electronegativity for Cu is probably higher than both that for Ni and that for Zn [11, 12] whereas the contractions steadily decrease in the series Ni—Cu—Zn (with the same B partner), there seems to be at least no simple relation between the electronegativities and the contractions (see the table below). It must, however, be remembered that the electronegativity values are very approximate.

It seemed possible that the relative size of the atoms $\frac{r_B}{r_A}$ was of importance for the magnitude of the electron gain of the B atoms. The quotients $\frac{r_B}{r_A}$, calculated with the radii for 18 coordination for the B atom and 12 coordination for the A atom, and also the differences in electronegativity $n_A - n_B$ have been collected in the table below together with the values of the electron gain g of the B atoms:

		Ni	Cu	Zn
Ca	g	1.4	1	0.7
	r_B/r_A	1.625	1.584	1.466
	$n_A - n_B$	0.8	1.2	0.2
La	g	0.9	0.6	0.4
	r_B/r_A	1.589	1.549	1.433
	$n_A - n_B$	0.6	1.0	0
Th	g	0.9		0
	r_B/r_A	1.558	1.519	1.406
	$n_A - n_B$	0.6	1.0	0

As will be seen, the values of the electron gains and those of the relative size of the atoms decrease in the same way for the listed compounds. Thus it seems, that the relative size of the atoms in the A_5B alloy is the dominating factor in determining the amount of electron transfer, though of course the difference in electronegativity may also be of importance. An investigation of the contractions of the interatomic distances in the Laves' phases of the C 15 structure type shows, that for them this latter factor (the difference in electronegativity) is the most important, though the influence of the relative size is obvious also in that case (Byström and Kierkegaard to be published).

It was first assumed that this electron gain was proportional to the difference in valency. We can then calculate the gains from the value in Ni_5Ca from the formula $g = 1.4 \dfrac{V_A - V_B}{V_{Ni} - V_{Ca}}$. The following values are obtained:

	Ni	Cu	Zn
Ca	1.4	1.3	0.9
La	1.0	0.9	0.5
Th	0.7		

As will be seen, the agreement between the two sets of values may indicate a relation, s suggested. However, the further study of the Laves' phases indicated no such relation, and the agreement between the two sets of g values is probably accidental.

The gain of 0.5 — 1.4 electrons by the B atoms corresponds to a mean loss of 0.1 — 0.3 electrons by the A atoms. As is apparent from a comparison between the radii of the transition metals, this loss has a comparatively small influence on the interatomic distances: an increase in the A — A distances of some few hundredths of an Å unit would be expected. The increase actually found varied between — 0.02 and 0.10 Å with a mean value of 0.05 Å, the smallest increase being found for the Zn alloys with also the least amount of electron transition. It must, however, be observed that the cell dimension of the A_5B phases may not have the four figure accuracy assumed in the calculations of the distances. A comparison of Nowotny's and Haucke's values (see p. 1000) shows differences as large as 0.06 Å. A detailed discussion of the differences in observed and calculated A — A distances is therefore hardly possible without a careful re-determination of the cell dimensions.

The suggested electron transfer in the A_5B phases may offer an explanation of the deviation from the ideal formula observed for three of the alloys. As we have seen, the electron gain of the B atoms leads to a partial equalisation of the metal valencies, and also of the metal radii. Thus the difference between the "normal" metal radii of Cu and Ce is about 0.55 Å but the electron transfer diminishes this difference to about 0.2 Å. The increase in the A radii, which probably results from the occurence of Ce (and La) atoms in Cu positions, was not taken into account in the calculations of the A—B and A—A distances. Assuming Vegard's law to be valid, it amounts to about 0.02 Å and may be an explanation of the relatively large differences between observed and calculated A—A distances for these two alloys (0.08—0.09 Å).

For the Zn—Th phase a solution of A atoms in the B atoms is found (Nowotny [10]), leading to the formula $Zn_5(Th_{0.6}Zn_{0.4})$. This gives an almost complete equilization of the metal valencies of the A and B atoms, the values being 4.44 and 4.17 respectively. The quotient $R(18)_A{}'R(12)_B$ has a low value and hence no or a very small contraction of the A—B distances is to be expected. The apparent $R(1)$ radius for the B atoms, derived from the observed A—B distances, is 1.59 Å. The value expected from Vegard's law ($0.6\, R_{Th} + 0.4\, R_{Zn}$) is 1.49, but this deviation is by no means unacceptable.

The assumption of an electron transfer from the A atoms to the B atoms seems to lead to an explanation of the contraction of the A—B distances and elongation of the A—A distances in the A_5B phases. It is, of course, of interest to investigate whether contractions found in alloys of other structural types can be explained in a similar way. In a following paper the contractions on the Laves' phases of the C 15 structure type will be discussed.

SUMMARY

The cell dimensions and symmetry of two intermediate Cu—Ce phases, Cu_6Ce and Cu_4Ce, have been determined. Cu_4Ce belongs to the A_5B structure type with a cell content of 1.2 Cu_4Ce.

The interatomic distances in the A_5B structure type are discussed. It is shown that the amount of the contractions of the A—B distances is due to the relative size of the atoms and probably also to the difference in electronegativity. An electron transfer from the A toms to the B atoms is shown to agree with the observed distances.

This investigation was supported financially by the Swedish Natural Science Research Council.

REFERENCES

1. Hanamann, F. *Intern. Z. Metallog.* **7** (1915) 174.
2. Neuburger, M. C. *Z. Krist.* **93** (1936) 10.
3. Treadwell, F. P. *Elektroanalytische Methoden.* (1915) 162.
4. Haucke, W. *Z. anorg. u. allgem. Chem.* **244** (1940) 17.
5. Heymann, T. *Nachr. Akad. Wiss. Göttingen, Math.-Physik.-Chem. Abt.* **1** (1948) 21.
6. Pauling, L. *J. Am. Chem. Soc.* **69** (1947) 542.
7. Nowotny, H. *Z. Metallkunde* **34** (1942) 247.
8. Vogel, R. *Z. Metallkunde* **38** (1947) 97; *Metallforschung* **2** (1947) 97.
9. Endter, F. and Klemm, W. *Z. anorg. Chem.* **252** (1943) 64.
10. Nowotny, H. *Z. Metallkunde* **37** (1946) 31; *Metallforschung* **1** (1946) 31.
11. Pauling, L. *Nature of the Chemical Bond.* (1945).
12. Gordy, W. *J. Chem. Phys.* **15** (1947) 81.
13. Nowotny, H. *Z. Metallkunde* **34** (1942) 237.
14. Dehlinger, U., and Nowotny, H. *Z. Metallkunde* **34** (1942) 200.

Received May 17, 1951.