Acta Cryst. (1984). C**40**, 211–214

$CeCu_{3.6}$, a Disordered Variant of $Gd_{14}Ag_{51}$ Type

By C. Allibert

Laboratoire de Thermodynamique et Physico-Chimie Métallurgiques, Institut National Polytechnique de Grenoble, BP 44, 38401 *Saint-Martin d'Hères, France*

and W. Wong-Ng* and S. C. Nyburg

Department of Chemistry, University of Toronto, Toronto, Canada M5S 1A1

(*Received* 9 *July* 1982; *accepted* 21 *September* 1983)

Abstract. $M_r = 371.59$, hexagonal, $P6/m$, $a = 11.858$ (4), $c = 9.107$ (3) Å, $U = 1109.0$ (6) Å^3, $Z = 14$ ($\equiv Ce_{14}Cu_{51}$ per unit cell), $D_x = 7.85$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 32.3$ mm^{-1}, $F(000) = 2291$, $T = 298$ K. Final $R = 0.074$ using 610 significant reflections out of 798 measured. The structure is of known $Gd_{14}Ag_{51}$ type but with disorder in the $z = 0$ plane. The disorder is such as to lengthen eight out of nine otherwise short Ce—Cu contacts from 2·62 to 2·91 Å. The ninth conflict could be avoided by leaving the Cu site vacant but there is no firm evidence for this.

Introduction. The phase diagram of the system Ce—Cu has been studied by Hanaman (1915), Byström, Kierkegaard & Knop (1952) and by Rhinehammer, Etter, Selle & Tucker (1964). In order to obtain a more accurate estimate of the temperature of peritectic formation of $CeCu_5$, Allibert & Girodin (1983) reinvestigated the phase diagram in the Cu-rich region. In this composition range, in addition to the four intermetallic compounds $CeCu_6$, $CeCu_5$, $CeCu_4$, and $CeCu_2$ mentioned by Rhinehammer, Etter, Selle & Tucker, a new phase was found with stoichiometric ratio $CeCu_{3.6}$. According to phase equilibrium results (Allibert & Girodin, 1983) this phase exists in a narrow temperature range; its formation can be easily delayed or even prevented during solidification at usual cooling rates (300 K h^{-1}). Moreover, due to the very small difference between the composition of $CeCu_{3.6}$ and $CeCu_4$, the two phases can be easily mistaken. These facts explain why $CeCu_{3.6}$ was not observed by previous authors. The crystal structures of the phases $CeCu_2$ and $CeCu_6$ were completely determined by Larson & Cromer (1961) and by Cromer, Larson & Roof (1960); that of $CeCu_5$ was established by Dwight (1961). For $CeCu_4$, the orthorhombic structure proposed by Rhinehammer, Etter, Selle & Tucker (1964) has not so far been confirmed.

The present investigation concerns the crystal structure of $CeCu_{3.6}$. In lanthanide–copper systems, compounds $AB_{3.6}$ are already known with A = Yb (Iandelli & Palenzona, 1971) and A = Th (Schiltz, Stevens & Carlson, 1971) [Buschow (1970) reports two compounds $ErCu_x$ both with x close to 4 but no structure analyses are available]. Compounds with A = Au (McMasters, Gschneider, Bruzzone & Palenzona, 1971) and with A = Ag (McMasters, Gschneider & Venteicher, 1970) have been identified by powder diffraction as belonging to the same structural type as $Gd_{14}Ag_{51}$. It seemed therefore highly likely that the present compound, $CeCu_{3.6}$, has stoichiometry $Ce_{14}Cu_{51}$.

Single-crystal analyses have been performed on $Gd_{14}Ag_{51}$ (Bailey & Kline, 1971), $Zr_{14}Cu_{51}$ and $Hf_{14}Cu_{51}$ (Gabathuler, White & Parthé, 1975). These are all of the same structural type (called '$GdAg_{3.6}$'). $Ce_{14}Ag_{51}$ has been shown to have the same structure by powder diffraction (McMasters, Gschneider & Venteicher, 1970).

This paper concerns a single-crystal analysis of $Ce_{14}Cu_{51}$ which proves to be based on $GdAg_{3.6}$ type but which has a somewhat disordered form of those previously proposed. This disorder allows certain interatomic distances, which would otherwise be quite short, to be avoided.

Experimental. A Cu–Ce alloy containing about 26 at.% Ce was prepared by induction melting of pure Cu (99·9%) and pure Ce (99·9%) in a water-cooled copper crucible under argon at atmospheric pressure. The liquid alloy was maintained in levitation for some minutes then cast in a copper mold. The ingot obtained was placed in a tantalum boat located in a silica vessel sealed under vacuum. The encapsulated alloy was heated in a resistance furnace providing a thermal gradient 20 K cm^{-1}. The sample was maintained for 70 h in the thermal gradient 873–1053 K then quickly cooled by water-quenching. A few large single crystals

---

[*] Present address: JCPDS-International Center for Diffraction Data, 1601 Park Lane, Swarthmore, PA 19081, USA.

0108-2701/84/020211-04$01.50

were formed in the hottest part of the tantalum boat from which they could be easily extracted. In the coldest part of the boat, the ingot kept its starting shape; after mechanical polishing, its micrography showed two phases. Electron microprobe analysis of several parts of the sample indicated the single crystals to be $CeCu_{3.6}$, while the two-phase region consisted of a mixture of $CeCu_2$ and $CeCu_{3.6}$. The structure analysis reported here was carried out on one of the single crystals. Powder diffraction patterns were obtained from the $CeCu_2$–$CeCu_{3.6}$ mixture using Cu *Kα* radiation. Some samples gave very poor patterns possibly due to rapid surface oxidation. Better results were obtained on mechanically-polished bulk samples. However, in these cases strong preferred-orientation effects were observed and patterns had to be recorded for several different orientations of the same sample.

Specimen used for structure analysis: irregularly shaped flake without any straight edges, ~0·03 mm thick and 0·11 × 0·91 mm in area. Preliminary photographic examination showed Laue symmetry to be $6/m$ without systematic absences. Cell dimensions from diffractometer settings of 13 reflections using Zr-filtered Mo *Kα* radiation (also used for data collection). Space group $P6$, $P\bar{6}$ or $P6/m$ (confirmed). Intensity data collected in θ–2θ mode at 2° min^{-1} to $\theta = 57°$ on an automated Picker four-circle diffractometer. A twelfth part of reciprocal space was scanned bounded by $h,k = 0$ to 13, $l = 0$ to 11. A φ-sweep absorption correction was made. (This improved the residual by about 1% but had no significant effect on any atomic parameters.) Merging consistency for $0kl$, $k0l$, 0·10. Of 798 independent reflections recorded, 610 considered significant on criterion $F_o > 2\sigma(F_o)$, $\sigma(F_o)$ being $\{[\sigma(I)\mathrm{Lp}]^2 + 0{\cdot}02F_o^4\}^{1/2}/2F_o$, Lp the Lorentz–polarization correction.

The structure was assumed to be of $GdAg_{3.6}$ type and trial coordinates for Ce and Cu corresponding to those for Gd and Ag were used to initiate anisotropic least-squares refinement using *ORXFLS* (Busing, Martin & Levy, 1971). Wyckoff positions and initial occupancies are given in Table 1. Scattering factors (including f' and f'') were taken from *International Tables for X-ray Crystallography* (1974).

The atomic coordinates obtained by preliminary least-squares refinement (on F) gave distances Cu(1)–Cu(2), 2·38 Å, and Ce(2)–Cu(7), 2·62 Å. If the effective atomic radii of Cu and of Ce are taken as 1·28 and 1·83 Å respectively, these distances are clearly quite short. In addition, the β_{11} and β_{22} anisotropic temperature factors for Cu(1) and Ce(2) were much larger than their β_{33} factors. This strongly implied disorder in the xy plane. Moreover the ΔF map around Ce(2) showed another peak *ca* 3·5 e Å^{-3} and around Cu(1) there were three trigonally related peaks *ca* 6·3 e Å^{-3}.

An analogous somewhat short distance between Gd(2) and Ag(1) in $Gd_{14}Ag_{51}$ was noted by Bailey & Kline (1971). They comment that a shift of Gd(2) away from Ag(7) would relieve this conflict when the Ag(7) site was occupied.* However, no attempt appears to have been made to determine whether this alternative site was genuinely occupied. In our case we found that two positions for the original Ce(2), Ce(2′) and Ce(2″) could be refined with respect to position, occupancy and anisotropic temperature factors. These latter had now more reasonable values. The occupancies refined to 0·504 in both cases and were reset to 0·5. If the appropriate site for Ce(2) is chosen when Cu(7) is occupied, the previously short Ce(2)–Cu(7) distance of 2·62 Å increased to 2·91 (1) Å.

We examined Cu(1) in a similar way and found that instead of lying on Wyckoff positions 2(*c*), the atoms appear to lie in positions 6(*j*) around the trigonal axes. These positions refined satisfactorily also and led to a slight lengthening of the distance to Cu(2) (which lies on the trigonal axis), from 2·38 to 2·434 (6) Å.

Final $R = 0{\cdot}074$, $wR = 0{\cdot}09$, $w \propto 1/\sigma_F^2$, $(\Delta/\sigma)_{\max} = 0{\cdot}03$. The right-hand side of Table 1 gives the Wyckoff positions and occupancies for the revised structure. [For the occupancy of Cu(7), see *Discussion*.] Fractional atomic coordinates and $B_{\rm eq}$ values are given in Table 2,† interatomic distances in Table 3.

Due to preferred orientation, indexing powder diffraction patterns of bulk samples is difficult; however, most of the intense reflections calculated from the single-crystal data are present in the powder patterns recorded from the eutectic mixture $CeCu_{3.6}$–$CeCu_2$.

Discussion. Diagrams of the $GdAg_{3.6}$ structure have been given elsewhere (Bailey & Kline, 1971; Gabathuler, White & Parthé, 1975). The structure proposed here differs only in the $z = 0$ plane. Fig. 1 shows the potential sites for all the atoms in this plane and Fig. 2 shows one (of the many) possible arrangements in which sites occupied are such as to avoid particularly short interatomic distances.

In the example of Fig. 2 one Cu(1) has been placed arbitrarily at position 1′. Accordingly, Ce(2) is not occupied at 6′ but at 6. It will be seen that, encircling the origin, Cu(7) and Ce(2) are accordingly staggered, Ce(2) being in Ce(2′) positions when Cu(7) is occupied and in Ce(2″) positions otherwise. The other Cu(1) atom has been placed arbitrarily at 3″.

---

* Bailey & Kline (1971) call Ag(7), Ag(*).

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Dviision as Supplementary Publication No. SUP 38884 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

There are three possible positions for each of the two Cu(1) atoms, giving nine combinations in all. One combination, Cu(1) at 1′ and at 1″, is of particular interest. One or other of these atoms would lie close to a Ce(2′) atom and this could only be avoided by Ce(2) moving to Ce(2″) which, in turn, would cause conflict with Cu(7). One possible way in which this could be overcome would be for the Cu(7) to be left vacant in this situation. Statistically this could be expected once in every nine cases, reducing the Cu(7) site occupancy to $\frac{8}{9}\times\frac{1}{2}=0{\cdot}444$. In fact, least-squares refinement yields an occupancy 0·49 (2) which implies no significant deviation from $\frac{1}{2}$. If the Cu(7) occupancy were nevertheless 0·444 the Cu content of this intermetallic compound would be 77·95 at. % rather than 78·46 at. %. Unfortunately this could not be checked by analysis. The precision of electron microprobe analysis is low for rare-earth compounds because it is not possible to use as standards rare-earth metals which rapidly oxidize. Better precision could be expected from chemical analysis but no single-phase samples were obtained large enough for this. The same problem arose with $GdAg_{3.6}$ (Bailey & Kline, 1971).

Table 1. *Wyckoff positions and initial occupancies*

Columns *a* and *c* are the Wyckoff notations, columns *b* and *d* the occupancies for the $GdAg_{3.6}$-type structure and modified structure respectively.

	'$GdAg_{3.6}$ structure type'		Modified structure		
	a	*b*		*c*	*d*
Ce(1)	2(*e*)	1		same	
Ce(2)	6(*j*)	1	Ce(2′) Ce(2″)	6(*j*) 6(*j*)	$\frac{1}{2}$ $\frac{1}{2}$
Ce(3)	6(*k*)	1		same	
Cu(1)	2(*c*)	1	Cu(1)	6(*j*)	$\frac{1}{3}$
Cu(2)	4(*h*)	1			
Cu(3)	6(*k*)	1		same	
Cu(4), Cu(5), Cu(6)	12(*l*)	1		same	
Cu(7)	6(*j*)	$\frac{1}{2}$	Cu(7)	6(*j*)	0·49 (2)

Table 2. *Fractional atomic coordinates* (×10⁴) *with e.s.d.'s in parentheses and equivalent isotropic temperature factors* (Å²)

$$[\mathrm{T.F.} = \exp(-\textstyle\sum_i\sum_j\beta_{ij}h_ih_j).\ B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.]$$

	x	*y*	*z*	B_{eq}
Ce(1)	0	0	2974 (4)	1·3 (1)
Ce(2′)	1309 (6)	4193 (5)	0	1·2 (2)
Ce(2″)	1056 (6)	3585 (7)	0	1·7 (2)
Ce(3)	4712 (1)	1412 (2)	5000	0·9 (1)
Cu(1)	6202 (12)	3202 (26)	0	2·1 (7)
Cu(2)	6667	3334	2618 (6)	1·4 (1)
Cu(3)	593 (3)	2376 (4)	5000	1·1 (1)
Cu(4)	1959 (3)	2693 (3)	2509 (3)	1·7 (1)
Cu(5)	4939 (3)	1117 (3)	1693 (4)	2·2 (1)
Cu(6)	1079 (3)	4285 (3)	3064 (3)	1·4 (1)
Cu(7)	1405 (8)	1027 (8)	0	2·1 (3)

Table 3. *Interatomic distances less than* 3·3 Å

Distances in square brackets can be avoided by choice of site occupancy.

Ce(1)–Cu(3)	3·139 (4)	Ce(3)–Cu(2)	3·161 (4)
Cu(4)	2·890 (3)	Cu(3)	3·014 (4)
Cu(7)	3·093 (6)	Cu(4)	3·098 (3)
Ce(2′)–Cu(1)	2·940 (2)	Cu(6)	2·995 (4)
[Cu(1)	2·22 (2)]	Cu(1)–Cu(2)	2·434 (6)
Cu(4)	3·217 (6)	Cu(5)	2·65 (2)
Cu(5)	2·917 (7)	Cu(2)–Cu(5)	2·536 (4)
Cu(6)	2·811 (3)	Cu(6)	2·781 (3)
Cu(7)	2·915 (12)	Cu(3)–Cu(3)	2·540 (6)
Ce(2″)–Cu(1)	2·79 (2)	Cu(4)	2·702 (4)
Cu(4)	2·935 (6)	Cu(6)	2·695 (5)
Cu(5)	3·134 (7)	Cu(4)–Cu(6)	2·560 (4)
Cu(6)	2·907 (4)	Cu(7)	2·864 (7)
[Cu(7)	2·29 (1)]	Cu(5)–Cu(6)	2·549 (4)
		Cu(7)–Cu(7)	2·59 (1)

According to the results of Gabathuler, White & Parthé (1975), known compounds of $A_{14}B_{51}$ type correspond to atomic-radius ratios r_A/r_B in the range 1·22 to 1·31. In the case of $Ce_{14}Cu_{51}$, such a ratio would correspond to a Ce atomic radius in the range 1·56–1·68 [estimated as 1·67 Å for fully tetravalent Ce by Zachariasen & Ellinger (1977)]. This would be consistent with the Ce—Cu interatomic distances found in the present study.

In summary, the structure of $Ce_{14}Cu_{51}$ is of $GdAg_{3.6}$ type but there is evidence of disorder which prevents the occurrence of some otherwise short interatomic distances. Whether such disorder is also present in other alloys of $GdAg_{3.6}$ type is not at present known.

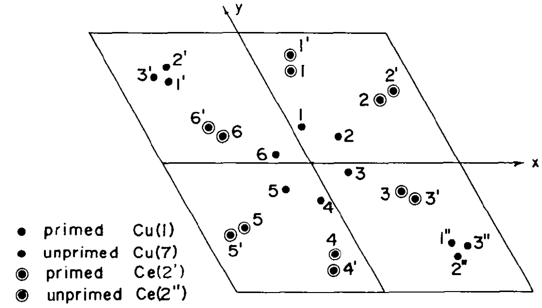

Fig. 1. Proposed structure showing all possible atomic sites in the $z = 0$ plane.

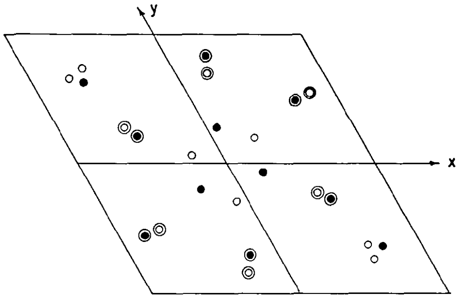

Fig. 2. One (of many) possible site occupancies in which short Ce···Cu and Cu···Cu distances are avoided.

We thank Professor U. Franklin, Department of Materials Science, University of Toronto, for helpful comments concerning the interpretation of certain powder patterns. Financial assistance (to SCN and WW-N), from the Natural Sciences and Engineering Research Council of Canada, is gratefully acknowledged.

References

ALLIBERT, C. H. & GIRODIN, D. (1983). To be published.
BAILEY, D. M. & KLINE, G. R. (1971). *Acta Cryst.* **B27**, 650–653.
BUSCHOW, K. H. J. (1970). *Philips Res. Rep.* **25**, 227–230.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1971). *ORXFLS*3, an extensively modified version of the 1962 *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
BYSTRÖM, A., KIERKEGAARD, P. & KNOP, O. (1952). *Acta Chem. Scand.* **6**, 709–719.
CROMER, D. T., LARSON, A. C. & ROOF, R. B. JR (1960). *Acta Cryst.* **13**, 913–918.
DWIGHT, A. E. (1961). *Trans. Am. Soc. Met.* **53**, 479–500.
GABATHULER, J.-P., WHITE, P. & PARTHÉ, E. (1975). *Acta Cryst.* **B31**, 608–610.
HANAMAN, F. (1915). *Int. Z. Metallogr.* **7**, 174–212.
IANDELLI, A. & PALENZONA, A. (1971). *J. Less-Common Met.* **25**, 333–335.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72 *et seq.* Birmingham: Kynoch Press.
LARSON, A. C. & CROMER, D. T. (1961). *Acta Cryst.* **14**, 73–74.
MCMASTERS, O. D., GSCHNEIDER, K. A. JR, BRUZZONE, G. & PALENZONA, A. (1971). *J. Less-Common Met.* **25**, 135–160.
MCMASTERS, O. D., GSCHNEIDER, K. A. JR & VENTEICHER, R. F. (1970). *Acta Cryst.* **B26**, 1224–1229.
RHINEHAMMER, T. B., ETTER, D. E., SELLE, J. E. & TUCKER, P. A. (1964). *Trans. Am. Inst. Min. Metall. Pet. Eng.* **230**, 1193–1198.
SCHILTZ, R. J. JR, STEVENS, E. R. & CARLSON, O. N. (1971). *J. Less-Common Met.* **25**, 175–185.
ZACHARIASEN, W. H. & ELLINGER, F. H. (1977). *Acta Cryst.* **A33**, 155–160.

Acta Cryst. (1984). C**40**, 214–217

Synthetic Phosphorus-Substituted Analcime, $Na_{13}Al_{24}Si_{13}P_{11}O_{96}.16H_2O$, with Ordered Al and Si/P

BY G. ARTIOLI, J. J. PLUTH AND J. V. SMITH

Department of Geophysical Sciences, The University of Chicago, Chicago, Illinois 60637, *USA*

(*Received* 28 *February* 1983; *accepted* 13 *October* 1983)

Abstract. $M_r = 3476\cdot5$, cubic, $I4_132$, $a = 13\cdot7290\,(7)$ Å, $V = 2587\cdot7$ Å^3, $D_x = 2\cdot23$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 72$ cm^{-1}, $F(000) = 1730$, $T \simeq 295$ K, $R = 0\cdot042$ for 242 reflections. The structure has the analcime framework with alternation of 24 Al and (13 Si + 11 P) over tetrahedral sites. No evidence was found for ordering of Si and P.

Introduction. Ordering of Al and Si on tetrahedral nodes of framework structures has been studied extensively, particularly in feldspars (Smith, 1974) and zeolite molecular sieves (Breck, 1974; Rabo, 1976; many recent papers). Alternation of Al and P over tetrahedral nodes was found for the fifth member of a new series of $AlPO_4$ molecular sieves (Bennett, Cohen, Flanigen, Pluth & Smith, 1983). We now return to the problem of ordering of Al, P and Si in the aluminosilicophosphate zeolites synthesized by Flanigen & Grose (1971). X-ray data were collected in 1965 by J. D. Birle, C. R. Knowles, J. V. Smith and L. G. Dowell for an 80 μm cube of zeolite P–C depicted in plate 1 of Flanigen & Grose (1971) and satisfactory refinement was obtained for an average structure of analcime type with space group $Ia3d$. Alternation of (7P + 17Si) and (23Al + 1Si) over the tetrahedral sites was considered, but the X-ray data were inadequate for a valid test. We now report a structural refinement of a trapezohedron of zeolite P–C (Flanigen & Grose, 1971) in space group $I4_132$ which allows ordering between (Si,P) and Al over adjacent tetrahedral nodes.

Refinements of the crystal structure of analcime minerals were made by Calleri & Ferraris (1964), Knowles, Rinaldi & Smith (1965) and Ferraris, Jones & Yerkess (1972). Optical and X-ray anomalies were reported by Coombs (1955), and Mazzi & Galli (1978) showed that tetragonal and orthorhombic varieties resulted from partial Si,Al order over the tetrahedral sites. The ideal topological symmetry of analcime is cubic ($Ia3d$), and a review of known phases related to analcime or leucite is given by Galli, Gottardi & Mazzi (1978).

Experimental. Trapezohedra about 50 μm across, synthesized from gel at 483 K for 160 h, supplied by E. M. Flanigen. Electron-microprobe analyses (ARL-EMX-SM instrument, 15 kV, 1 nA beam current, 10 μm beam diameter, wavelength-dispersive system, Chicago 1976 correction procedure) show less than 0·1 wt%

0108-2701/84/020214-04$01.50