Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.
Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE*. Oak Ridge National Laboratory Report ORNL-TM-306.
Chieh, P. C. & Trotter, J. (1970). *J. Chem. Soc.* (*A*), pp. 911–914.
Churchill, M. R. & Kalra, K. L. (1974). *Inorg. Chem.* **13**, 1065–1071.
Churchill, M. R. & Veidis, M. V. (1972). *J. Chem. Soc. Dalton*, pp. 670–675.
Cromer, D. T. (1965). *Acta Cryst.* **18**, 17–23.
Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.
Ismailzade, I. G. & Zhdanov, G. S. (1953). *Zh. Fiz. Khim.* **27**, 550–553.
Johnson, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794 (revised, 1970).
Karipides, A., Forman, C., Thomas, R. H. P. & Reed, A. T. (1974). *Inorg. Chem.* **13**, 811–815.
Smith, D. L. (1962). *PLANET*. Ph.D. Thesis, Univ. of Wisconsin, Madison, Wisconsin.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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$Zr_{14}Cu_{51}$ and $Hf_{14}Cu_{51}$ with $GdAg_{3\cdot6}$ Structure Type

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Abstract. $Hf_{14}Cu_{51}$, hexagonal, $P6/m$ (No. 175), $a=11\cdot18$ (1), $c=8\cdot235$ (5) Å, $U=1782\cdot8$ Å^3, $Z=1$, F.W. 5739·4, $D_x=10\cdot69$ g cm^{-3}, $F(000)=2487$. Counter technique, absorption correction, direct methods, least-squares refinement. $R=0\cdot085$ for 568 reflexions. $Zr_{14}Cu_{51}$ ($a=11\cdot25$ (1), $c=8\cdot275$ (10) Å) and $Hf_{14}Cu_{51}$ are isotypic with $GdAg_{3\cdot6}$.

Introduction. In the Cu-rich part of the system Hf–Cu the phases $HfCu_4$ and $HfCu_5$ of unknown structure have been reported recently by Perry (1974). Phases of the same composition were found in the system Zr–Cu (Perry & Hugi, 1972).

Samples of composition $HfCu_4$ and $ZrCu_4$ were prepared by arc melting the component elements under purified argon atmosphere (Hf 99·9%, Zr 99·9%, Cu 99·999%). The alloying of Cu with Hf or Zr leads to an appreciable increase in hardness. It was possible to isolate small single crystals of $ZrCu_{\sim 4}$ and $HfCu_{\sim 4}$ ($\sim$40 μm diameter). Precession and Weissenberg photographs showed that the two compounds, later to be described by the formulae $Zr_{14}Cu_{51}$ and $Hf_{14}Cu_{51}$, were isotypic and that they crystallized with a hexagonal cell with $Zr_{14}Cu_{51}$: $a=11\cdot25$ (1), $c=8\cdot275$ (10) Å; $Hf_{14}Cu_{51}$: $a=11\cdot18$ (1), $c=8\cdot235$ (5) Å.

As there were no systematic extinctions and the crystals show low hexagonal Laue symmetry, the possible space groups were $P6$, $P\bar{6}$ and $P6/m$.

A structure analysis was performed on the $HfCu_{\sim 4}$ single crystal. 568 non-equivalent intensities were measured on a Philips four-circle automatic diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Correction for absorption [$\mu(Hf_{14}Cu_{51})=734$ cm^{-1}] was made (de Meulenaer & Tompa, 1965). The structure was solved by direct methods with the program *LSAM* (Main, Woolfson & Germain, 1972). The E map showed that the proper space group was $P6/m$, and it also allowed 14 Hf atoms and 48 Cu atoms to be located. A Fourier map showed three further Cu atoms distributed at random over six sites. The true composition of this compound is therefore $Hf_{14}Cu_{51}$ with a calculated density of 10·69 g cm^{-3}. The final positional parameters refined after applying anomalous dispersion corrections (*International Tables for X-ray Crystallography*, 1968) and using the least-squares program in the X-RAY system (1972) are given in Table 1.* The scattering factors have been generated with analytical

Table 1. *Positional parameters for* $Hf_{14}Cu_{51}$ *with* $GdAg_{3\cdot6}$ *structure type.*

Space group $P6/m$ (No. 175). The temperature factor is given by the equation $T=\exp\,[-2\pi^2\,.\,10^{-2}U\,(2\sin\theta/\lambda)^2]$.

		x	y	z	U[Å^2]
2Hf(1)	2(*e*)	0	0	0·3114 (7)	0·2 (1)
6Hf(2)	6(*j*)	0·1138 (4)	0·3893 (4)	0	0·7 (1)
6Hf(3)	6(*k*)	0·4712 (3)	0·1417 (3)	$\frac{1}{2}$	0·4 (1)
2Cu(1)	2(*c*)	$\frac{1}{3}$	$\frac{2}{3}$	0	0·7 (4)
4Cu(2)	4(*h*)	$\frac{1}{3}$	$\frac{2}{3}$	0·2931 (14)	0·3 (2)
6Cu(3)	6(*k*)	0·0611 (10)	0·2403 (9)	$\frac{1}{2}$	0·2 (2)
12Cu(4)	12(*l*)	0·1914 (7)	0·2651 (7)	0·2365 (8)	0·7 (2)
12Cu(5)	12(*l*)	0·4942 (7)	0·1163 (7)	0·1520 (8)	0·5 (1)
12Cu(6)	12(*l*)	0·1044 (6)	0·4373 (6)	0·3296 (8)	0·4 (1)
3Cu(7)	6(*i*)	0·1146 (26)	0·1352 (26)	0	1·9 (5)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30719 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

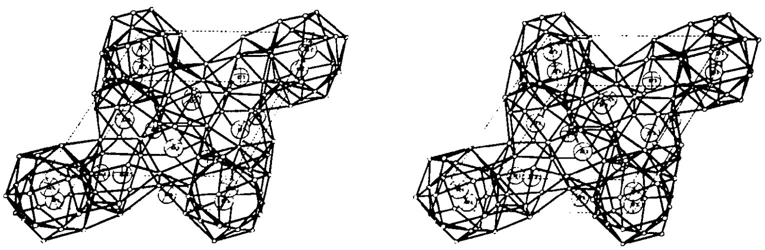

Fig. 1. Stereo drawing of copper polyhedra around Hf(3) ($z=\frac{1}{2}$) and Hf(1) ($z\simeq\frac{1}{3},\frac{2}{3}$).

Table 2. *Calculated and observed powder pattern for* $Hf_{14}Cu_{51}$ *with* $GdAg_{3\cdot6}$ *structure type*

Cu $K\alpha$ radiation ($\lambda=1\cdot5418$ Å), Guinier–Nonius camera, SiO_2 monochromator.

$I_{hkl}=\mathrm{Lp}mF^2_{hkl}$ where $\mathrm{Lp}=(1+0\cdot7987\cos^2 2\theta)/[\sin\theta\,.\,\cos^2(2\theta-30°)\,.\,\sin 2\theta]$

h	k	i	l	$10^3\,.\,\sin^2\theta_c$	$10^3\,.\,\sin^2\theta_o$	I_c	I_o
1	0	$\bar{1}$	0	6·3		2·6	
0	0	0	1	8·7		9·6	
1	0	$\bar{1}$	1	15·1		0·0	
1	1	$\bar{2}$	0	19·0		0·4	
2	0	$\bar{2}$	0	25·4		3·3	
1	1	$\bar{2}$	1	27·8	27·6	21·1	*w*
2	0	$\bar{2}$	1	34·1		13·7	
0	0	0	2	35·0	34·9	74·9	*m*
1	0	$\bar{1}$	2	41·3	41·3	59·7	*mw*
2	1	$\bar{3}$	0	44·4	44·1	56·5	*m*
1	2	$\bar{3}$	0	44·4		59·7	
2	1	$\bar{3}$	1	53·1	53·1	197·1	*s*
1	2	$\bar{3}$	1	53·1		198·7	
1	1	$\bar{2}$	2	54·0	53·9	55·5	*mw*
3	0	$\bar{3}$	0	57·1		9·0	
2	0	$\bar{2}$	2	60·4	60·0	30·1	*w*
3	0	$\bar{3}$	1	65·8	65·7	14·7	*vvw*
2	2	$\bar{4}$	0	76·1		3·2	
0	0	0	3	78·8		3·2	
1	2	$\bar{3}$	2	79·4	79·3	35·1	*mw*
2	1	$\bar{3}$	2	79·4		31·2	
1	3	$\bar{4}$	0	82·4	82·6	15·2	*ms*
3	1	$\bar{4}$	0	82·4		140·3	
2	2	$\bar{4}$	1	84·8	85·0	38·9	*mw*
1	0	$\bar{1}$	3	85·1		22·9	
1	3	$\bar{4}$	1	91·2		8·9	
3	1	$\bar{4}$	1	91·2		0·8	
3	0	$\bar{3}$	2	92·1	92·2	34·0	*w*
1	1	$\bar{2}$	3	97·8	97·8	33·1	*w*
4	0	$\bar{4}$	0	101·4	101·7	64·9	*mw*
2	0	$\bar{2}$	3	104·1		0·8	
4	0	$\bar{4}$	1	110·2		32·5	
2	2	$\bar{4}$	2	111·1	110·8	102·7	*ms*
1	3	$\bar{4}$	2	117·4	117·6	493·9	*vs*
3	1	$\bar{4}$	2	117·4		97·8	
2	3	$\bar{5}$	0	120·5	120·6	73·0	*m*
3	2	$\bar{5}$	0	120·5		10·2	
2	1	$\bar{3}$	3	123·2	123·2	1000·0	*vvs*
1	2	$\bar{3}$	3	123·2		302·7	
3	2	$\bar{5}$	1	129·2	129·3	83·1	*ms*
2	3	$\bar{5}$	1	129·2		57·2	
4	1	$\bar{5}$	0	133·1	133·2	104·4	*vs*
1	4	$\bar{5}$	0	133·1		772·5	
3	0	$\bar{3}$	3	135·8	136·0	244·8	*s*
4	0	$\bar{4}$	2	136·5		56·4	
0	0	0	4	140·0	140·0	145·7	*ms*
4	1	$\bar{5}$	1	141·9	141·5	363·7	*s*
1	4	$\bar{5}$	1	141·9		26·4	
1	0	$\bar{1}$	4	146·4		30·4	
2	2	$\bar{4}$	3	154·9	155·2	98·6	*m*, diff.
3	2	$\bar{5}$	2	155·5		8·0	
2	3	$\bar{5}$	2	155·5		119·3	
5	0	$\bar{5}$	0	158·5	158·6	67·9	*m*

functions (Cromer & Mann, 1968). The weighting scheme was unity and the number of parameters refined was 30. The residual $R=\sum|F_o-|F_c||/\sum F_o$ for 470 reflexions with $F_o>2\sigma$ is 8·5%. A refinement of the occupation parameter of Cu(7) on site 6(*j*) gave a value of 47 ± 3%. From simple geometric considerations this sixfold site cannot be occupied by more than three atoms. A comparison between the observed powder reflexions for $Hf_{14}Cu_{51}$ and those calculated (Yvon, Jeitschko & Parthé, 1969) is given in Table 2.

Discussion. In Figs. 1 and 2 are shown two stereo drawings of the $Hf_{14}Cu_{51}$ structure projected along **c** (*ORTEP*, Johnson, 1970). The first represents the Cu polyhedra around Hf(3) ($z=\frac{1}{2}$) and Hf(1) ($z\simeq\frac{1}{3},\frac{2}{3}$), the second the polyhedra around Hf(2) ($z=1$) and Hf(1) ($z\simeq\frac{2}{3},\frac{4}{3}$). Hf(2) and Hf(3) have 14-coordination, Hf(1) 16-coordination. There is only one Hf–Hf bond of 3·1 Å between two Hf(1) atoms.

$Hf_{14}Cu_{51}$ reveals a striking resemblance to the structure of $GdAg_{3\cdot6}$ recently determined by Bailey & Kline (1971). Within the limits of error the two are identical and isotypic. The compounds $T_{14}B_{51}$ already known to have this structure type are rare-earth–silver alloys (T = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er and Y) studied by McMasters, Gschneidner & Venteicher (1970) and rare-earth–gold alloys (T = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy and Ho) investigated by McMasters, Gschneidner, Bruzzone & Palenzona (1971). If all the known compounds with this structure type are plotted according to the value of the radius ratio $r_T/r_{\mathrm{Cu,Ag,Au}}$ (Fig. 3) it can be seen that they lie within a narrow radius-ratio range from 1·22 to 1·31. With smaller radius-ratio values the $MoNi_4$ or the $ZrAu_4$ types occur which have smaller coordination polyhedra compared with $GdAu_{3\cdot6}$ [see for example the survey by Steeb, Gebhardt & Reule (1972)].

The reasons for the random occupations of site 6(*j*) by 3 Cu(7) atoms are not obvious. In an attempt to check that ordering does not occur ar 0*kl* precession photograph of $Hf_{14}Cu_{51}$ was exposed for 2 weeks. Very weak superstructure reflexions appeared, indicating that the dimension of the crystallographic cell has to be doubled along **c**. A study of this superstructure is in progress.

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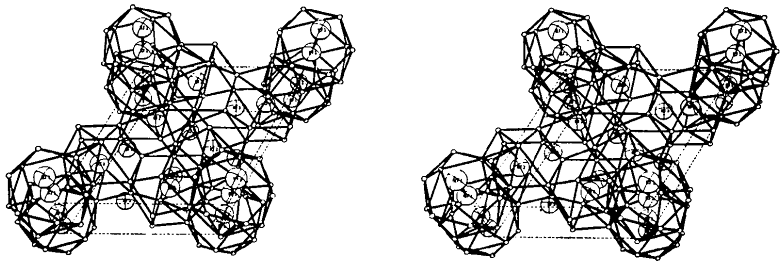

Fig. 2. Stereo drawing of copper polyhedra around Hf(2) ($z=1$) and Hf(1) ($z\simeq\frac{2}{3},\frac{4}{3}$).

References

Bailey, D. M. & Kline, G. R. (1971). *Acta Cryst.* **B27**, 650–653.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

International Tables for X-ray Crystallography (1968). Vol. III. Birmingham: Kynoch Press.

Johnson, C. K. (1970). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.

McMasters, O. D., Gschneidner, K. A. Jr, Bruzzone, G. & Palenzona, A. (1971). *J. Less-Common Met.* **25**, 135–160.

McMasters, O. D., Gschneidner, K. A. Jr & Venteicher, R. F. (1970). *Acta Cryst.* **B26**, 1224–1229.

Main, P., Woolfson, M. M. & Germain, G. (1972). *LSAM: A System of Computer Programs for the Automatic Solution of Centrosymmetric Crystal Structures.* Dept. of Physics, Univ. of York, York, England and Laboratoire de Chimie Physique, Université de Louvain, 39 Schapenstraat, Leuven, Belgium.

Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.

Perry, A. J. (1974). *Mater. Sci. Eng.* **13**, 57–62.

Perry, A. J. & Hugi, W. (1972). *J. Inst. Met.* **100**, 378–380.

Steeb, S., Gebhardt, E. & Reule, H. (1972). *Mh. Chem.* **103**, 716–735.

X-RAY system (1972). Tech. Rep. TR-192 of the Computer Science Center, Univ. of Maryland.

Yvon, K., Jeitschko, W. & Parthé, E. (1969). *A Fortran IV Program for the Intensity Calculation of Powder Patterns.* Univ. de Genève, Laboratoire de Cristallographie aux Rayons X.

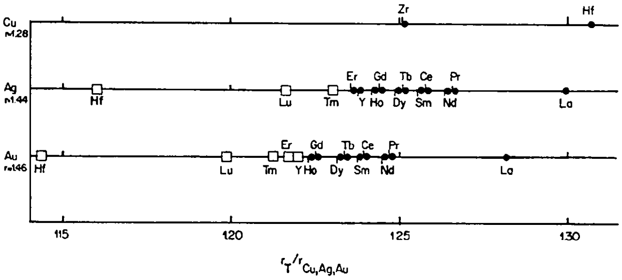

Fig. 3. Radius-ratio values for compounds with $GdAg_{3.6}$ (circles) and $MoNi_4$ or $ZrAu_4$ structure types (squares). Metallic radii for coordination number 12 according to the periodic table of elements of Sargent–Welch.

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1,2,3,4,4aα,5,11aα-Heptahydroacetoxy-11β*H*-dibenz[*b*,*e*]azepine-6-one

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Abstract. $C_{16}H_{19}NO_3$, monoclinic, $P2_1/c$, $a=9{\cdot}462$ (4), $b=16{\cdot}082$ (6), $c=10{\cdot}280$ (6) Å, $\beta=110{\cdot}9$ (1)°, $Z=4$, $D_{\text{calc}}=1{\cdot}24$ g cm^{-3}. The structure was solved by the symbolic addition procedure and refined by full-matrix least-squares calculations to a final R value of 4·8%. The molecule has a *cis* junction between the seven-membered ring and the saturated six-membered ring and the peptide group which is part of the seven-membered ring is planar.

Experimental. One method of preparing benzazepinones is by carrying out a Norrish type II photoreaction (Wagner, 1971) on *N*-alkylated phthalimides (Kanaoka, Migita, Koyama, Sata, Nakai & Mizoguchi, 1973). The benzazepinone to be discussed here was obtained as one of the products in such a reaction (Kanaoka, Koyama, Flippen, Karle & Witkop, 1974). Crystals used in the X-ray analysis were provided by Dr B. Witkop of the National Institutes of Health. An automatic computer-controlled diffractometer was used to collect 2346 independent reflections from a colorless crystal (~0·40 × 0·45 × 0·16 mm) with Cu $K\alpha$ radiation ($\lambda=1{\cdot}54178$ Å, Ni filter). Data were collected by the θ–2θ scanning technique (max $\sin\theta/\lambda=0{\cdot}521$) over a scan width of 1·75° and at a scanning speed of 2° min^{-1}.