The Crystal Structure of Hf$_3$Cu$_8$ and Zr$_3$Cu$_8$

By Lars Bsenko

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

The crystal structure of the intermetallic phase Hf$_3$Cu$_8$ has been determined from three-dimensional single-crystal X-ray diffractometer data. The space group is *Pnma*, and the unit cell, of dimensions $a = 7.8113$ (5), $b = 8.1014$ (6), $c = 9.9470$ (7) Å, $V = 629.60$ Å^3, contains four formula units. Full-matrix least-squares refinement gave a conventional $R(F)$ value of 0.053. Two non-equivalent sets of Hf atoms occur in the structure, one with a coordination number of 13 and the other of 14. The six non-equivalent sets of Cu atoms have coordination numbers ranging from 11 to 13. X-ray powder diffraction data show that Zr$_3$Cu$_8$ is isostructural with Hf$_3$Cu$_8$.

Introduction

The first observation of a peritectic phase at about 70 at. % Cu in the Zr–Cu system was made by Lundin, McPherson & Hansen (1953). The phase was tentatively assigned the formula Zr$_2$Cu$_5$ and was thought to be formed by a reaction between the melt and a phase of composition ZrCu$_3$ or ZrCu$_4$. Using electron-probe microanalysis, Donachie (1963–1964) stated that the composition of the congruently melting phase is ZrCu$_4$. Perry & Hugi (1972) also found a phase at the composition ZrCu$_4$ and reported the formation of the peritectic phase Zr$_2$Cu$_5$. Later, Gabathuler, White & Parthé (1975) and Bsenko (1975), independently found that the phase denoted ZrCu$_4$ possessed the GdAg$_{3.6}$ type of structure determined by Bailey & Kline (1971), and hence had the ideal composition Zr$_{14}$Cu$_{51}$. Bsenko (1975) showed, by indexing the powder pattern, that the peritectic phase is orthorhombic. The Hf–Cu system was investigated by Markiv, Petkov, Storozhenko, Ivanchenko & Gorskii (1974), who found two intermediate phases in the region 70–75 at. % Cu, denoted Hf$_2$Cu$_5$ and HfCu$_3$. Hf$_2$Cu$_5$ was formed at 990°C by the reaction: liq.+HfCu$_3$ = Hf$_2$Cu$_5$. Perry (1974) found a phase denoted HfCu$_4$, which was later shown to be isostructural with GdAg$_{3.6}$ (Gabathuler, White & Parthé, 1975; Bsenko, 1975). It is probable that the phase denoted HfCu$_3$ by Markiv *et al.* is identical with Hf$_{14}$Cu$_{51}$. A phase with orthorhombic symmetry and forming peritectically was found by Bsenko (1975). The present investigation was undertaken in order to establish the structure of this peritectic phase.

Experimental

By arc-melting turnings of zirconium and hafnium metal (Koch-Light, Colnbrook, England; Zr of purity 99·9% containing less than 0·03% oxygen and zone-refined Hf containing 3% Zr) with copper (HCOKOF, certified grade copper, min. 99·99%), two alloys with the nominal compositions Hf$_{0.28}$Cu$_{0.72}$ and Zr$_{0.28}$Cu$_{0.72}$

were prepared. The melting was carried out on a water-cooled copper hearth under a purified argon atmosphere, with a non-consumable tungsten electrode. The alloy buttons were turned upside down and remelted to insure homogeneity. The weight loss was less than 0·5%.

The samples were wrapped in tantalum foil and annealed in sealed and evacuated silica tubes for 500 h at 850°C. After quenching in water the surfaces of the samples were wet-ground on a carborundum disc and polished with alumina. Etching with a mixture consisting of 10 parts of HF, 20 parts of HNO$_3$, and 70 parts of H$_2$O by volume, revealed the microstructure of the surface. Metallographic examination showed that the alloys were nearly single-phase.

The samples were crushed and small fragments were examined in a Weissenberg camera. All fragments turned out to be polycrystalline.

Assuming that the peritectically formed phase contained about 72 at.% copper, an alloy of nominal composition Hf$_{0.30}$Cu$_{0.70}$ was prepared and heat-treated as described earlier. This specimen was placed in a ZrO$_2$ crucible, inside an evacuated and sealed silica tube. The tube was held at a temperature of 1025°C for 24 h. After quenching in water, a metallographic examination of the polished and etched surface showed primary grown crystals, indicating that the annealing temperature was above the eutectic isotherm.

The alloy was crushed and a small fragment proved to be a single crystal when examined in a Weissenberg camera. The diffraction symmetry and the systematic absences of the reflexions indicated that the space group was *Pnma* or *Pn2$_1$a*. Diffractometric intensity data were collected on a four-circle Stoe–Philips X-ray diffractometer controlled by a PDP8/I computer. The $\omega/2\theta$ scan technique was employed and graphite-monochromatized Mo radiation was used ($\lambda = 0.71069$ Å). The 800, 040 and 006 reflexions were used as control reflexions, and during the data collection these were checked every 20th reflexion scanned. The differences in intensity of these reference reflexions were within the limits of the random statistical fluctuations.

F_o^2 and $\sigma_c(F_o^2)$ values were obtained from the integrated peak intensities by applying corrections for background, Lorentz and polarization effects and absorption, assuming the monochromator to be ideally imperfect. A linear absorption factor of 682 cm^{-1} was applied in computing absorption corrections. The crystal was of irregular shape, and was approximated with six boundary planes to a polyhedron with dimensions of the order of 0·06 × 0·03 × 0·01 mm for the purpose of making absorption corrections. The transmission factors were found to vary from 0·213 to 0·520. Data collection was carried out to $\sin\theta/\lambda = 0{\cdot}587$ Å^{-1}, and

Table 1. *Final structural parameters for* Hf_3Cu_8

E.s.d.'s are in units of the least significant digit. Positional parameters are × 10^5, thermal × 10^4. Anisotropic thermal parameters are in the form $\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)]$.

		x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hf(1)	8(*d*)	6255 (8)	44594 (7)	14022 (6)	21 (1)	22 (1)	11 (1)	−1 (1)	−1 (1)	−1 (1)
Hf(2)	4(*c*)	45964 (12)	¼	4670 (9)	25 (1)	29 (1)	12 (1)	0	2 (1)	0
Cu(1)	8(*d*)	37912 (25)	57601 (23)	16013 (18)	22 (2)	30 (2)	14 (1)	−3 (2)	−2 (1)	2 (1)
Cu(2)	8(*d*)	19893 (23)	49897 (21)	40644 (18)	26 (2)	19 (2)	16 (1)	1 (1)	−2 (1)	1 (1)
Cu(3)	4(*c*)	28548 (35)	¼	27349 (25)	24 (4)	32 (3)	8 (2)	0	−1 (1)	0
Cu(4)	4(*c*)	11655 (35)	¼	90329 (26)	18 (3)	23 (3)	16 (2)	0	−5 (2)	0
Cu(5)	4(*c*)	36932 (35)	¼	76548 (25)	23 (3)	20 (3)	9 (2)	0	−3 (2)	0
Cu(6)	4(*c*)	32283 (33)	¼	51676 (25)	16 (3)	20 (3)	9 (2)	0	−1 (2)	0

Table 2. *Observed and calculated X-ray structure factors for* Hf_3Cu_8

The four columns are, in order: k, l, F_o and F_c. Asterisks mark reflexions not included in the final refinement.

0,K,L			
0	2	43	45
0	4	415	418
0	6	85	73
0	8	241	229
0	10	344	341
0	12	56	55
0	14	119	124
0	16	131	137
1	1	53	58
1	3	143	139
1	5	92	88
1	7	143	140
1	9	139	135
1	11	35	30*
1	13	246	250
1	15	76	82
2	0	59	56
2	2	180	191
2	4	649	772
2	6	271	264
2	8	184	179
2	10	38	40
2	12	89	85
2	14	194	202
2	16	33	22*
3	1	149	155
3	3	104	100
3	5	323	327
3	7	307	307
3	9	182	178
3	11	62	67
3	13	48	42
3	15	162	169
4	0	609	773
4	2	180	198
4	4	68	67
4	6	258	251
4	8	59	53
4	10	44	41
4	12	53	60
4	14	44	39
4	16	81	74
5	1	213	227
5	3	223	233
5	5	133	129
5	7	72	73
5	9	288	285
5	11	52	50
5	13	333	341
5	15	25	11*
6	0	518	596
6	2	18	28*
6	4	55	52
6	6	156	161
6	8	69	67
6	10	298	297
6	12	92	90
6	14	64	46
7	1	182	193
7	3	55	58
7	5	310	311
7	7	145	148
7	9	139	132
7	11	17	14*
7	13	37	23
8	0	95	101
8	2	195	207
8	4	337	349
8	6	337	348
8	8	156	149
8	10	176	179
8	12	25	21*
9	1	86	85
9	3	65	69
9	5	12	6*
9	7	146	143
9	9	59	59
9	11	70	74
10	0	378	402
10	2	16	3*
10	4	40	41
10	6	98	101
10	8	129	132
10	10	241	240
11	1	38	46
11	3	87	80
11	5	21	3*
11	7	54	52
11	9	100	100
12	0	180	189
12	2	79	80
12	4	113	114
12	6	113	115
12	8	84	79
13	1	120	116
13	3	38	38
13	5	185	183
1,K,L			
0	1	44	36
0	2	96	88
0	3	366	368
0	4	179	165
0	5	184	174
0	6	82	77
0	7	405	402
0	8	486	497
0	9	197	194
0	10	45	36
0	11	87	90
0	12	92	91
0	13	111	116
0	14	85	90
0	15	203	214
0	16	93	104
1	1	28	24
1	2	19	18*
1	3	40	33
1	4	397	401
1	5	187	174
1	6	269	257
1	7	48	45
1	8	6	24*
1	9	50	33
1	10	31	31*
1	11	55	45
1	12	113	115
1	13	43	45
1	14	87	85
1	15	34	12
1	16	106	100
2	1	242	262
2	2	91	93
2	3	104	96
2	4	338	336
2	5	11	4*
2	6	96	86
2	7	151	145
2	8	38	30
2	9	152	149
2	10	87	88
2	11	386	392
2	12	202	200
2	13	34	27*
2	14	30	16*
2	15	114	118
2	16	27	7*
3	1	16	10*
3	2	544	647
3	3	23	27
3	4	58	58
3	5	61	58
3	6	149	140
3	7	113	110
3	8	380	387
3	9	113	113
3	10	93	90
3	11	80	79
3	12	166	167
3	13	30	30*
3	14	68	70
3	15	99	101
3	16	72	72
4	1	75	83
4	2	177	186
4	3	191	196
4	4	23	16
4	5	30	24
4	6	45	51
4	7	195	193
4	8	272	268
4	9	90	101
4	10	17	35*
4	11	95	97
4	12	20	9*
4	13	88	89
4	14	119	121
4	15	53	53
4	16	55	64
5	1	71	70
5	2	252	267
5	3	89	89
5	4	388	403
5	5	159	158
5	6	379	383
5	7	34	33
5	8	121	119
5	9	12	22*
5	10	118	110
5	11	105	99
5	12	229	227
5	13	43	23
5	14	63	56
5	15	44	52
6	1	21	14*
6	2	210	217
6	3	133	132
6	4	80	81
6	5	143	142
6	6	80	76
6	7	133	131
6	8	155	151
6	9	185	178
6	10	47	51
6	11	82	74
6	12	52	46
6	13	88	64
6	14	17	22*
6	15	77	88
7	1	41	45
7	2	292	300
7	3	61	64
7	4	122	123
7	5	70	68
7	6	47	50
7	7	116	120
7	8	198	197
7	9	17	25*
7	10	88	91
7	11	53	45
7	12	86	87
7	13	62	54
7	14	86	93
8	1	222	232
8	2	238	252
8	3	96	97
8	4	75	72
8	5	66	72
8	6	133	133
8	7	96	95
8	8	102	97
8	9	70	72
8	10	28	15*
8	11	262	263
8	12	83	84
8	13	41	5*
9	1	41	39
9	2	112	119
9	3	70	70
9	4	114	114
9	5	51	46
9	6	69	84
9	7	12	3*
9	8	113	106
9	9	72	70
9	10	22	29*
9	11	25	13*
9	12	19	19*
10	1	88	91
10	2	127	132
10	3	233	237
10	4	70	70
10	5	102	103
10	6	77	73
10	7	216	217
10	8	90	85
10	9	87	77
10	10	20	10*
10	11	20	21*
11	1	12	23*
11	2	65	69
11	3	11	19*
11	4	176	177
11	5	75	74
11	6	144	152
11	7	24	13*
11	8	28	27*
11	9	21	2*
11	10	10	29*
12	1	146	145
12	2	79	77
12	3	85	80
12	4	21	8*
12	5	26	15*
12	6	64	58
12	7	56	57
12	8	114	121
13	1	39	34
13	2	197	197
13	3	29	40*
13	4	37	34*
13	5	23	16*
2,K,L			
0	0	241	280
0	1	145	146
0	2	86	85
0	3	45	39
0	4	206	256
0	5	153	144
0	6	246	239
0	7	212	209
0	8	22	21*
0	9	197	197
0	10	360	369
0	11	43	43
0	12	208	209
0	13	94	94
0	14	89	94
0	15	114	116
0	16	53	57
1	0	41	34
1	1	72	68
1	2	69	65
1	3	298	287
1	4	427	431
1	5	68	67
1	6	112	103
1	7	192	190
1	8	34	27
1	9	163	159
1	10	29	33*
1	11	6	8*
1	12	52	59
1	13	77	78
1	14	57	57
1	15	46	49
1	16	26	29*
2	0	46	50
2	1	192	201
2	2	303	314
2	3	398	408
2	4	91	61
2	5	90	80
2	6	257	249
2	7	119	115
2	8	285	277
2	9	27	33*
2	10	71	75
2	11	33	20*
2	12	33	4*
2	13	133	135
2	14	180	194
2	15	7	15*
2	16	32	23*
3	0	567	674
3	1	205	216
3	2	115	117
3	3	89	93
3	4	73	74
3	5	358	361
3	6	256	254
3	7	215	211
3	8	146	137
3	9	99	95
3	10	320	320
3	11	44	46
3	12	45	46
3	13	93	91
3	14	107	111
3	15	138	138
3	16	25	30*
4	0	13	15*
4	1	122	125
4	2	114	116
4	3	48	48
4	4	15	12*
4	5	109	104
4	6	95	92
4	7	54	55
4	8	100	99
4	9	65	62
4	10	207	205
4	11	15	27*
4	12	143	143
4	13	53	60
4	14	27	18*
4	15	74	85
4	16	32	53*
5	0	184	190
5	1	186	191
5	2	94	97
5	3	295	295
5	4	478	499
5	5	97	95
5	6	191	184
5	7	140	138
5	8	122	120
5	9	257	259
5	10	87	81
5	11	47	35
5	12	4	20*
5	13	153	153
5	14	137	135
5	15	21	5*
6	0	259	277
6	1	76	73
6	2	155	158
6	3	165	172
6	4	195	193
6	5	43	39
6	6	37	41
6	7	50	43
6	8	54	54
6	9	139	142
6	10	106	110
6	11	45	35
6	12	69	68
6	13	77	75
6	14	12	16*
6	15	26	31*
7	0	263	279
7	1	122	121
7	2	15	9*
7	3	71	74
7	4	37	42
7	5	238	240
7	6	63	59
7	7	148	146
7	8	110	104
7	9	59	54
7	10	168	163
7	11	32	33*
7	12	89	88
7	13	53	58
7	14	69	72
8	0	206	217
8	1	62	63
8	2	119	119
8	3	129	130
8	4	140	193
8	5	93	89
8	6	54	50
8	7	21	2*
8	8	191	197
8	9	116	113
8	10	32	20*
8	11	10	5*
8	12	68	54
8	13	165	172
9	0	158	164
9	1	24	12*
9	2	16	19*
9	3	114	114
9	4	98	103
9	5	76	70
9	6	61	60
9	7	118	111
9	8	2	13*
9	9	61	66
9	10	99	105
9	11	25	1*
9	12	20	9*
10	0	246	259
10	1	89	90
10	2	87	80
10	3	46	55
10	4	191	192
10	5	164	166
10	6	33	13*
10	7	24	5*
10	8	9	17*
10	9	176	181
10	10	130	126
10	11	46	36
11	0	44	43
11	1	63	63
11	2	52	46
11	3	127	125
11	4	191	199
11	5	10	0*
11	6	81	80
11	7	77	74
11	8	32	34*
11	9	106	101
11	10	33	22*
12	0	90	89
12	1	82	81
12	2	60	61
12	3	76	73
12	4	84	88
12	5	93	98
12	6	26	11*
12	7	53	52
12	8	108	106
13	0	179	175
13	1	87	84
13	2	19	15*
13	3	25	10*
13	4	28	21*
13	5	155	150
3,K,L			
0	1	8	6*
0	2	568	666
0	3	434	457
0	4	113	108
0	5	182	174
0	6	198	185
0	7	173	168
0	8	328	330
0	9	28	17*
0	10	126	122
0	11	31	24*
0	12	264	269
0	13	141	146
0	14	44	46
0	15	44	18*
0	16	86	90
1	1	296	308
1	2	46	44
1	3	22	10*
1	4	9	11*
1	5	26	24
1	6	210	203
1	7	58	60
1	8	27	12*
1	9	24	38*
1	10	25	8*
1	11	189	191
1	12	123	121
1	13	21	2*
1	14	45	40
1	15	36	17
1	16	138	144
2	1	461	528
2	2	434	448
2	3	38	38
2	4	176	166
2	5	105	94
2	6	413	422
2	7	52	46
2	8	53	46
2	9	47	43
2	10	51	43
2	11	57	57
2	12	76	74
2	13	34	5*
2	14	95	97
2	15	20	32*
2	16	153	166
3	1	72	76
3	2	92	92
3	3	217	215
3	4	53	50
3	5	152	149
3	6	86	82
3	7	325	319
3	8	19	14*
3	9	43	41
3	10	126	123
3	11	77	84
3	12	184	178
3	13	53	43
3	14	99	108
3	15	202	217
3	16	48	48
4	1	134	141
4	2	137	141
4	3	155	158
4	4	116	115
4	5	154	152
4	6	71	67
4	7	33	12
4	8	52	49
4	9	101	97
4	10	56	52
4	11	78	82
4	12	68	67
4	13	59	61
4	14	70	66
4	15	32	12*
5	1	350	367
5	2	51	44
5	3	182	177
5	4	30	32
5	5	93	87
5	6	230	226
5	7	129	121
5	8	30	24*
5	9	36	30
5	10	38	34
5	11	298	295
5	12	67	61
5	13	51	47
5	14	7	19*
5	15	57	71
6	1	202	209
6	2	164	167
6	3	211	215
6	4	98	99
6	5	60	61
6	6	23	23*
6	7	149	151
6	8	255	257
6	9	40	44
6	10	65	63
6	11	34	42*
6	12	176	173
6	13	107	82
6	14	74	70
7	1	21	17*
7	2	132	131
7	3	215	215
7	4	17	14*
7	5	67	70
7	6	54	52
7	7	257	255
7	8	57	60
7	9	28	21*
7	10	55	57
7	11	38	37
7	12	150	149
7	13	59	62
7	14	55	50
8	1	171	179
8	2	199	206
8	3	15	16*
8	4	146	199
8	5	74	74
8	6	257	262
8	7	119	119
8	8	145	141
8	9	91	95
8	10	74	70
8	11	135	138
8	12	124	123
8	13	6	5*
9	1	152	161
9	2	41	24
9	3	33	37
9	4	58	54
9	5	13	20*
9	6	110	110
9	7	23	26*
9	8	18	28*
9	9	36	31
9	10	50	40
9	11	69	77
9	12	78	73
10	1	118	123
10	2	166	167
10	3	131	129
10	4	62	58
10	5	28	11*
10	6	54	60
10	7	111	112
10	8	202	196
10	9	19	3*
10	10	117	113
10	11	70	68
11	1	137	135
11	2	38	13
11	3	37	28
11	4	25	13*
11	5	17	24*
11	6	101	94
11	7	7	11*
11	8	20	3*
11	9	22	19*
12	1	73	68*
12	2	30	27*
12	3	58	57
12	4	67	62
12	5	43	35
12	6	121	116
12	7	44	30
13	1	38	14
13	2	73	68
13	3	135	134
13	4	36	10*
4,K,L			
0	0	134	144
0	1	200	213
0	2	155	160
0	3	174	170
0	4	115	111
0	5	503	531
0	6	102	104
0	7	128	123
0	8	81	80
0	9	276	271
0	10	24	5*
0	11	99	99
0	12	137	161
0	13	237	248
0	14	28	5*
0	15	126	135
0	16	38	39*
1	0	141	145
1	1	261	279
1	2	169	167
1	3	53	54
1	4	89	79
1	5	155	140
1	6	100	97
1	7	37	9
1	8	230	223
1	9	71	64
1	10	53	54
1	11	42	37
1	12	71	71
1	13	20	21*
1	14	113	119
1	15	26	8*
1	16	22	18*
2	0	57	28
2	1	186	176
2	2	17	18*
2	3	233	215
2	4	7	21*
2	5	143	132
2	6	156	145
2	7	225	215
2	8	104	107
2	9	371	375
2	10	152	149
2	11	27	30*
2	12	66	72
2	13	198	206
2	14	27	13*
2	15	16	2*
2	16	25	0*
3	0	354	361
3	1	68	70
3	2	55	56
3	3	34	26
3	4	340	336
3	5	311	304
3	6	148	140
3	7	106	98
3	8	40	37
3	9	33	17
3	10	309	311
3	11	71	71
3	12	164	166
3	13	5	25*
3	14	104	106
3	15	45	50
4	0	70	71
4	1	29	28
4	2	62	59
4	3	272	268
4	4	36	12
4	5	237	231
4	6	50	49
4	7	78	75
4	8	94	96
4	9	49	44
4	10	83	83
4	11	54	50
4	12	55	55
4	13	75	87
4	14	6	3*
4	15	44	48
5	0	327	337
5	1	236	232
5	2	174	177
5	3	53	49
5	4	270	266
5	5	97	95
5	6	191	191
5	7	26	22*
5	8	309	312
5	9	60	61
5	10	86	84
5	11	36	47
5	12	26	7*
5	13	22	24*
5	14	208	218
5	15	18	3*
6	0	141	147
6	1	145	144
6	2	83	87
6	3	17	12*
6	4	115	114
6	5	213	216
6	6	30	23
6	7	214	210
6	8	74	64
6	9	41	26
6	10	41	40
6	11	28	32*
6	12	134	132
6	13	17	23*
6	14	4	8*
7	0	202	212
7	1	138	143
7	2	45	53
7	3	29	33*
7	4	193	196
7	5	127	120
7	6	77	77
7	7	21	5*
7	8	14	9*
7	9	50	39
7	10	207	215
7	11	27	11*
7	12	125	124
7	13	21	11*
8	0	75	84
8	1	227	240
8	2	6	29*
8	3	307	310
8	4	35	30
8	5	91	88
8	6	58	61
8	7	18	23*
8	8	83	70
8	9	189	189
8	10	72	80
8	11	13	11*
8	12	17	27*
9	0	19	8*
9	1	38	46
9	2	72	73
9	3	34	22
9	4	11	8*
9	5	154	161
9	6	3	24*
9	7	28	50*
9	8	100	99
9	9	12	14*
9	10	73	70
9	11	36	40*
10	0	33	20
10	1	178	181
10	2	27	28*
10	3	63	63
10	4	24	31*
10	5	242	250
10	6	13	43*
10	7	151	151
10	8	66	57
10	9	73	73
10	10	68	65
11	0	97	104
11	1	116	113
11	2	75	76
11	3	25	25*
11	4	74	88
11	5	47	46
11	6	73	69
11	7	43	19*
11	8	133	134
12	0	17	29*
12	1	122	121
12	2	44	53
12	3	168	172
12	4	42	28
12	5	28	20*
12	6	35	29*
13	0	165	162
13	1	48	58
13	2	31	14*
5,K,L			
0	1	180	194
0	2	375	403
0	3	36	37
0	4	104	99
0	5	334	339
0	6	126	116
0	7	26	14*
0	8	168	168
0	9	6	16*
0	10	169	166
0	11	21	17*
0	12	215	225
0	13	68	72
0	14	136	137
0	15	52	58
1	1	259	283
1	2	70	71
1	3	55	53
1	4	20	2*
1	5	29	22*
1	6	31	30*
1	7	140	135
1	8	178	177
1	9	185	184
1	10	25	26*
1	11	139	139
1	12	53	37
1	13	68	66
1	14	71	12*
1	15	48	48
2	1	114	117
2	2	107	103
2	3	68	66
2	4	219	209
2	5	33	22
2	6	311	302
2	7	32	11
2	8	81	67
2	9	172	166
2	10	115	111
2	11	44	36
2	12	73	74
2	13	81	85
2	14	28	20*
2	15	22	11*
3	1	58	52
3	2	244	233
3	3	484	495
3	4	166	158
3	5	100	93
3	6	185	179
3	7	262	252
3	8	26	18*
3	9	86	83
3	10	14	8*
3	11	97	98
3	12	92	84
3	13	193	202
3	14	49	49
3	15	51	62
4	1	172	169
4	2	207	200
4	3	68	68
4	4	99	99
4	5	230	226
4	6	66	56
4	7	19	24*
4	8	95	87
4	9	59	58
4	10	38	19
4	11	85	81
4	12	94	93
4	13	45	39
4	14	57	57
4	15	43	26
5	1	353	360
5	2	155	158
5	3	145	137
5	4	46	40
5	5	30	33*
5	6	38	41
5	7	282	279
5	8	204	201
5	9	177	175
5	10	47	49
5	11	243	243
5	12	78	81
5	13	37	3*
5	14	37	12*
6	1	65	63
6	2	157	157
6	3	53	50
6	4	111	113
6	5	54	53
6	6	10	17*
6	7	51	35
6	8	58	63
6	9	57	62
6	10	73	78
6	11	59	64
6	12	93	104
6	13	83	90
7	1	22	20*
7	2	78	76
7	3	264	264
7	4	53	47
7	5	84	81
7	6	100	108
7	7	134	128
7	8	65	56
7	9	114	111
7	10	36	19
7	11	66	61
7	12	35	35*
7	13	121	124
8	1	60	61
8	2	92	93
8	3	26	19*
8	4	147	148
8	5	167	117
8	6	229	227
8	7	88	91
8	8	67	66
8	9	59	55
8	10	101	98
8	11	138	132
8	12	73	72
9	1	91	92
9	2	36	43
9	3	121	124
9	4	54	63
9	5	14	6*
9	6	59	48*
9	7	20	3*
9	8	33	30*
9	9	68	67
9	10	6	38*
9	11	66	61
10	1	11	15*
10	2	223	238
10	3	49	50*
10	4	3	8*
10	5	33	30*
10	6	71	72
10	7	87	87
10	8	128	131
10	9	84	79
11	1	150	153
11	2	58	60
11	3	28	25*
11	4	33	23*
11	5	21	1*
11	6	10	1*
11	7	108	105
11	8	114	110
12	1	21	19*
12	2	60	60
12	3	47	51
12	4	110	112
12	5	97	98
6,K,L			
0	0	161	181
0	1	213	232
0	2	123	131
0	3	281	286
0	4	267	271
0	5	496	523
0	6	117	116
0	7	131	120
0	8	119	119
0	9	49	37
0	10	160	164
0	11	45	50
0	12	78	79
0	13	44	54
0	14	120	125
0	15	190	201
1	0	212	236
1	1	79	77
1	2	184	181
1	3	22	5*
1	4	88	75
1	5	27	26*
1	6	31	37*
1	7	7	13*
1	8	145	142
1	9	110	106
1	10	28	35*
1	11	30	15*
1	12	42	48
1	13	25	16*
1	14	79	82
1	15	49	51
2	0	201	207
2	1	417	401
2	2	8	2*
2	3	172	159
2	4	100	81
2	5	29	18*
2	6	187	173
2	7	61	38
2	8	136	128
2	9	203	200
2	10	137	136
2	11	110	106
2	12	55	50
2	13	119	123
2	14	97	102
2	15	30	16*
3	0	342	330
3	1	135	121
3	2	201	188
3	3	123	120
3	4	86	74
3	5	200	192
3	6	45	38
3	7	58	52
3	8	30	42*
3	9	87	95
3	10	104	108
3	11	50	45
3	12	183	184
3	13	121	128
3	14	60	56
4	0	41	37
4	1	61	54
4	2	72	72
4	3	158	149
4	4	77	73
4	5	198	193
4	6	32	6
4	7	174	170
4	8	9	10*
4	9	134	126
4	10	37	39*
4	11	70	67
4	12	37	37*
4	13	103	101
4	14	40	24
5	0	68	67
5	1	168	165
5	2	171	167
5	3	71	68
5	4	177	174
5	5	147	139
5	6	85	79
5	7	20	6*
5	8	204	202
5	9	193	192
5	10	41	37
5	11	20	7*
5	12	27	2*
5	13	86	88
6	0	101	98
6	1	6	8*
6	2	47	52
6	3	9	6*
6	4	159	155
6	5	329	332
6	6	5	8*
6	7	45	24
6	8	38	32
6	9	53	47
6	10	31	37*
6	11	45	37
6	12	32	11*
6	13	29	15*
7	0	302	320
7	1	80	82
7	2	100	102
7	3	78	78
7	4	105	96
7	5	137	133
7	6	42	42
7	7	16	31*
7	8	18	3*
7	9	48	60
7	10	126	120
7	11	43	39
7	12	92	92
8	0	201	216
8	1	192	201
8	2	23	13*
8	3	20	14*
8	4	120	115
8	5	68	48
8	6	89	88
8	7	131	125
8	8	104	102
8	9	245	247
8	10	78	84
8	11	104	107
9	0	66	66
9	1	5	24*
9	2	131	133
9	3	10	11*
9	4	70	69
9	5	16	4*
9	6	71	75
9	7	24	18*
9	8	60	56
9	9	48	42
9	10	23	6*
10	0	121	130
10	1	8	6*
10	2	49	44
10	3	30	22*
10	4	156	164
10	5	239	239
10	6	24	24*
10	7	25	27*
10	8	56	66
11	0	92	88
11	1	64	56
11	2	82	85
11	3	25	19*
11	4	44	47
11	5	24	39*
11	6	14	20*
12	0	96	96
12	1	31	45*
12	2	18	19*
12	3	17	29*
7,K,L			
0	1	97	111
0	2	121	124
0	3	328	350
0	4	148	149
0	5	73	73
0	6	109	103
0	7	270	268
0	8	109	116
0	9	29	16*
0	10	158	159
0	11	261	276
0	12	63	65
0	13	150	154
0	14	76	85
1	1	86	91
1	2	75	80
1	3	19	12*
1	4	51	36
1	5	35	4*
1	6	95	84
1	7	15	5*
1	8	22	14*
1	9	186	188
1	10	47	51
1	11	139	144
1	12	31	40*
1	13	58	55
1	14	19	2*
2	1	132	132
2	2	177	161
2	3	171	154
2	4	231	209
2	5	35	44*
2	6	190	183
2	7	287	279
2	8	23	2*
2	9	131	131
2	10	23	8*
2	11	129	135
2	12	61	64
2	13	36	3*
2	14	52	51
3	1	72	63
3	2	184	167
3	3	236	220
3	4	25	21*
3	5	22	5*
3	6	150	144
3	7	193	185
3	8	135	134
3	9	95	91
3	10	124	119
3	11	60	57
3	12	124	128
3	13	136	143
3	14	81	78
4	1	83	72
4	2	133	124
4	3	69	62
4	4	95	88
4	5	103	97
4	6	134	130
4	7	27	29*
4	8	131	133
4	9	39	45*
4	10	77	73
4	11	129	125
4	12	46	38
4	13	54	57
5	1	136	130
5	2	225	218
5	3	84	82
5	4	82	84
5	5	31	10*
5	6	199	193
5	7	72	64
5	8	81	76
5	9	176	179
5	10	120	116
5	11	168	172
5	12	121	128
5	13	21	20*
6	1	109	113
6	2	140	144
6	3	189	186
6	4	197	198
6	5	29	24*
6	6	83	86
6	7	90	54
6	8	31	11*
6	9	50	44
6	10	78	78
6	11	71	69
6	12	28	15*
7	1	21	4*
7	2	144	144
7	3	91	89
7	4	49	46
7	5	21	20*
7	6	98	97
7	7	94	94
7	8	130	127
7	9	123	121
7	10	52	61
7	11	64	48
8	1	198	200
8	2	9	22*
8	3	158	158
8	4	75	81
8	5	179	129
8	6	156	159
8	7	175	176
8	8	64	66
8	9	59	55
8	10	15	11*
9	1	11	11*
9	2	39	44
9	3	72	72
9	4	31	42*
9	5	28	12*
9	6	30	29*
9	7	56	56
9	8	37	7
9	9	64	73
10	1	113	115
10	2	174	174
10	3	167	169
10	4	88	89
10	5	49	55
10	6	38	23
10	7	85	95
11	1	61	65
11	2	69	71
11	3	22	31*
11	4	5	23*
11	5	34	1
8,K,L			
0	0	257	297
0	1	48	26
0	2	123	129
0	3	156	168
0	4	182	186
0	5	90	85
0	6	83	81
0	7	71	75
0	8	144	141
0	9	38	12
0	10	109	113
0	11	15	3*
0	12	138	142
0	13	51	45
1	0	131	147
1	1	190	204
1	2	150	160
1	3	63	72
1	4	33	20*
1	5	47	36
1	6	36	3*
1	7	10	26*
1	8	68	58
1	9	84	81
1	10	73	73
1	11	68	71
1	12	42	50
1	13	25	54*
2	0	202	219
2	1	48	54
2	2	100	99
2	3	71	72
2	4	273	268
2	5	37	41*
2	6	79	78
2	7	162	160
2	8	171	166
2	9	52	53
2	10	16	19*
2	11	13	42*
2	12	24	2*
2	13	78	86
3	0	126	109
3	1	185	164
3	2	175	159
3	3	112	96
3	4	36	39*
3	5	362	353
3	6	29	16*
3	7	69	63
3	8	62	57
3	9	204	197
3	10	54	57
3	11	60	65
3	12	53	55
3	13	85	85
4	0	186	175
4	1	22	5*
4	2	112	105
4	3	161	150
4	4	51	55
4	5	64	60
4	6	88	67
4	7	88	83
4	8	13	7*
4	9	12	6*
4	10	42	40*
4	11	31	19*
4	12	3	21*
5	0	182	131
5	1	318	311
5	3	144	142
5	4	23	14*
5	5	188	188
5	6	15	4*
5	7	47	31
5	8	53	49
5	9	203	201
5	10	61	64
5	11	101	102
5	12	45	43
6	0	5	11*
6	1	57	59
6	2	77	73
6	3	54	56
6	4	30	35*
6	5	58	54
6	6	113	108
6	7	112	116
6	8	47	44
6	9	39	38
6	10	98	95
6	11	25	17*
7	0	102	101
7	1	48	39
7	2	115	115
7	3	57	54
7	4	22	22*
7	5	182	181
7	6	13	1*
7	7	29	5*
7	8	45	45
7	9	115	114
7	10	60	56
8	0	70	69
8	1	18	6*
8	2	107	110
8	3	119	110
8	4	130	139
8	5	43	39
8	6	39	38
8	7	67	67
8	8	147	141
8	9	18	3*
9	0	75	76
9	1	18	28*
9	2	93	100
9	3	17	19*
9	4	32	35*
9	5	79	79
9	6	21	14*
9	7	54	59
10	0	126	136
10	1	38	34
10	2	29	13*
10	3	38	38
10	4	82	84
10	5	34	33*
11	0	77	78
11	1	134	138
9,K,L			
0	1	115	127
0	2	48	47
0	3	254	273
0	4	113	121
0	5	9	23*
0	6	114	110
0	7	307	317
0	8	43	24
0	9	25	20*
0	10	92	92
0	11	86	87
0	12	53	43
1	1	90	99
1	2	22	20*
1	3	105	108
1	4	43	38
1	5	5	44*
1	6	194	192
1	7	99	100
1	8	16	41*
1	9	14	4*
1	10	13	34*
1	11	56	60
1	12	22	12*
2	1	220	229
2	2	16	17*
2	3	203	199
2	4	10	9*
2	5	97	97
2	6	42	37
2	7	94	90
2	8	121	134
2	9	62	61
2	10	65	56
2	11	154	161
2	12	90	100
3	1	207	192
3	2	177	154
3	3	60	50
3	4	35	10*
3	5	29	28*
3	6	17	7*
3	7	31	34*
3	8	122	118
3	9	39	46*
3	10	184	181
3	11	135	129
3	12	138	142
4	1	48	37
4	2	67	64
4	3	18	23*
4	4	130	125
4	5	23	3*
4	6	52	54
4	7	101	95
4	8	36	24*
4	9	45	50*
4	10	15	29*
4	11	36	29*
5	1	55	46
5	3	128	146
5	4	88	72
5	5	39	52*
5	6	272	265
5	7	145	139
5	8	38	31*
5	9	34	8*
5	10	39	34*
6	1	18	7*
6	2	19	38*
6	3	175	119
6	4	35	6*
6	5	42	39
6	6	91	97
6	7	251	178
6	8	95	98
6	9	36	23*
6	10	42	22*
7	1	121	122
7	2	152	157
7	3	29	11*
7	4	20	26*
7	5	33	14*
7	6	38	9*
7	7	13	6*
7	8	135	127
7	9	32	8*
8	1	153	158
8	2	108	116
8	3	158	164
8	4	71	76
8	5	44	49
8	6	33	18*
8	7	106	105
9	1	84	94
9	2	14	30*
9	3	30	17*
9	4	49	53
9	5	35	32*
10	1	29	34*
10	2	82	81
10,K,L			
0	0	121	131
0	1	204	223
0	2	27	22*
0	3	174	185
0	4	43	47
0	5	128	130
0	6	123	118
0	7	84	74
0	8	48	40
0	9	152	158
0	10	204	216
0	11	56	39
1	0	78	76
1	1	44	51
1	2	35	52*
1	3	140	142
1	4	35	33*
1	5	39	6*
1	6	58	56
1	7	63	75
1	8	33	5*
1	9	62	63
1	10	111	110
1	11	27	5*
2	0	39	11*
2	1	80	96
2	2	113	115
2	3	5	26*
2	4	92	94
2	5	208	210
2	6	111	107
2	7	28	47*
2	8	126	128
2	9	92	88
2	10	16	29*
2	11	69	84
3	0	23	17*
3	1	117	111
3	2	67	56
3	3	39	49*
3	4	147	138
3	5	204	188
3	6	63	60
3	7	72	73
3	8	127	122
3	9	84	91
3	10	43	49*
4	0	21	26*
4	1	63	39
4	2	43	34*
4	3	117	104
4	4	53	45
4	5	65	58
4	6	81	68
4	7	31	31*
4	8	35	32*
4	9	21	50*
4	10	132	141
5	0	153	147
5	1	126	121
5	3	176	165
5	4	58	48
5	5	80	84
5	6	9	15*
5	7	70	62
5	8	67	65
5	9	134	133
6	0	148	149
6	1	120	118
6	2	81	73
6	3	108	110
6	4	45	50
6	5	55	46
6	6	29	29*
6	7	66	72
6	8	27	10*
7	0	49	58
7	1	58	63
7	2	25	22*
7	3	61	49
7	4	128	130
7	5	126	124
7	6	92	93
7	7	66	64
8	0	104	104
8	1	88	88
8	2	33	46*
8	3	17	16*
8	4	140	147
8	5	172	178
9	0	86	79
9	1	18	2*
9	2	40	54
11,K,L			
0	1	51	62
0	2	184	207
0	3	121	129
0	4	24	15*
0	5	82	90
0	6	157	164
0	7	49	44
0	8	26	43*
0	9	72	69
1	1	64	13*
1	2	25	2*
1	3	93	106
1	4	107	113
1	5	26	17*
1	6	62	56
1	7	64	80
1	8	31	34*
1	9	34	9*
2	1	141	158
2	2	132	139
2	3	16	47*
2	4	43	32*
2	5	39	0*
2	6	114	107
2	7	54	19
2	8	75	75
2	9	37	33*
3	1	184	190
3	2	124	122
3	3	166	156
3	4	33	43*
3	5	47	58*
3	6	25	19*
3	7	158	155
3	8	111	118
4	1	74	70
4	2	130	117
4	3	101	108
4	4	14	12*
4	5	52	57
4	6	48	61*
4	7	17	20*
4	8	78	66
5	1	77	66
5	2	49	48
5	3	206	198
5	4	172	118
5	5	13	16*
5	6	78	84
5	7	179	174
6	1	106	104
6	2	25	9*
6	3	89	70
6	4	26	45*
6	5	36	32*
6	6	40	41*
7	1	116	115
7	2	72	66
7	3	78	60
7	4	64	60
12,K,L			
0	0	203	228
0	1	130	146
0	2	29	5*
0	3	60	72
0	4	20	20*
0	5	184	184
0	6	51	65
0	7	13	11*
1	0	36	42*
1	1	11	8*
1	2	23	36*
1	3	40	46*
1	4	50	35
1	5	103	103
1	6	64	64
1	7	90	87
2	0	67	65
2	1	81	87
2	2	40	11*
2	3	15	19*
2	4	77	80
2	5	139	139
2	6	60	75
2	7	50	38
3	0	135	142
3	1	28	54*
3	2	47	64*
3	3	60	54
3	4	144	134
3	5	21	34*
3	6	22	22*
4	0	144	146
4	1	25	16*
4	2	27	31*
4	3	18	2*
4	4	14	18*
4	5	31	35*
5	0	141	139
5	1	26	15*
5	2	47	13*
5	3	70	40
5	4	126	122
6	0	130	119
6	1	98	88
13,K,L			
0	1	121	138
0	2	119	129
0	3	51	63
1	1	54	63
1	2	65	69
1	3	30	4*
2	1	31	34*
2	2	114	112
2	3	104	109
3	1	25	30*

a total number of 1734 independent reflexions were recorded. Of these, 1323 were in excess of $2\sigma_c(F_o^2)$ and were used in the final refinement.

From the Weissenberg photographs preliminary cell dimensions were obtained, and these were used in indexing the X-ray powder patterns for $Hf_{0.28}Cu_{02.7}$

and $Zr_{0.28}Cu_{0.28}$. The X-ray powder photographs were taken with a Guinier–Hägg type focusing camera (Philips XDC 700), using zone-refined silicon ($a = 5.43088$ Å) as internal calibration standard and Cr $K\alpha_1$ radiation ($\lambda = 2.28975$ Å). A least-squares refinement using the local program *CELNE* (Lundgren, 1974)

Table 3. *Comparison of calculated and observed Q values and intensities for* Zr_3Cu_8

$Q = 1/d^2$, d is the interplanar spacing in Å. Calculated intensities less than 1.0 are omitted.

| hkl	Q_c (×10⁵)	Q_o (×10⁵)	I_c	I_o	hkl	Q_c (×10⁵)	Q_o (×10⁵)	I_c	I_o
011	2506	2497	2·1	0·5	133	24165	–	3·0	–
121	8629	8615	2·9	3·9	322	24555	24553	38·9	45·3
022	10022	–	1·6	–	400	25836	25819	3·0	15·2
103	10639	10634	4·7	7·1	105	26681	–	1·9	–
122	11637	–	1·1	–	401	26839	–	1·3	–
221	13473	13466	4·6	4·2	410	27339	27354	4·0	–
004	16043	16038	7·6	10·5	042	28057	–	2·5	–
222	16481	16476	19·1	20·0	115	28184	28190	9·0	11·0
213	16986	16989	15·4 }	} 56·5	411	28342	28345	22·5	22·6
311	17038	17049	15·7 }		233	29009 }	} 29039	2·4 }	} 5·3
104	17657	17658	4·9	4·2	331	29061 }		3·7 }	
302	18543	18542	36·8	41·7	142	29671	29668	14·6	17·7
132	19151 }	} 19145	70·4 }	} 100·0	402	29847	–	2·4	–
114	19160 }		29·6 }		240	30505 }	} 30548	2·2 }	} 4·7
230	19985	19980	45·4	50·5	304	30575 }		1·6 }	
231	20988	20983	7·7	8·0	412	31350	–	2·6	–
223	21494 }	} 21521	34·7 }	} 86·6	241	31508	31515	4·5	3·9
321	21547 }		60·5 }		314	32078	–	1·3	–
024	22054	22049	58·3	62·9	242	34515	–	1·2	–
204	22502	22498	4·0	8·6	143	34685	34698	4·4	4·4
033	22560	–	1·5	–	403	34860	34855	7·1	4·8
303	23557	23561	19·3 }	} 71·9	324	36587	–	1·3	–
124	23669	23678	27·3 }						
232	23996 }		5·8 }						
214	24004 }	} 24008	43·9 }	} 85·7					
040	24046 }		33·0 }						
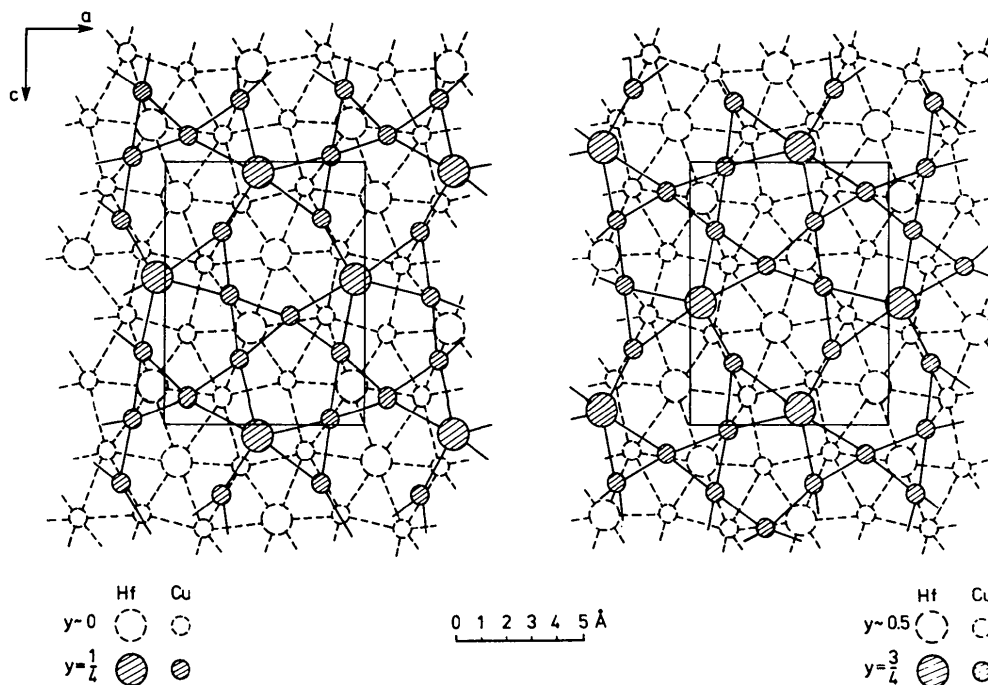
Fig. 1. The two sections of the structure of Hf_3Cu_8 projected on (010).

gave the cell parameters. The X-ray powder photograph of the sample $Zr_{0.28}Cu_{0.72}$ was measured in an automatic film scanner SAAB model 2, and integrated intensities were obtained following the procedure of Malmros & Werner (1973). Some of the reflexions could not be resolved and for these the sums of the integrated intensities were obtained.

Determination and refinement of the Hf₃Cu₈ structure

At the start of the structure determination, the unit-cell content of the crystal was estimated in the following manner. From a plot of X-ray densities against composition, based on crystallographic data for Hf from Russell (1953), for Hf_2Cu from Nevitt & Downey (1962), for Hf_7Cu_{10} and $Hf_{14}Cu_{51}$ from Bsenko (1975) and for Cu from Frohnmeyer & Glocker (1953), theoretical densities were obtained for alloys containing 71–73 at.% Cu. This range should include the composition of the crystal concerned. An examination of the various possibilities yielded a cell content of 12 Hf atoms and 32 Cu atoms as the only alternative compatible with a structure of $Pn2_1a$ or $Pnma$ symmetry without disorder or vacancies. A three-dimensional Patterson synthesis was computed, and the largest maxima could be interpreted in terms of 12 Hf atoms situated in one 8(d) and one 4(c) position in space group $Pnma$. From this starting point, a series of Fourier difference syntheses successively revealed the positions of the Cu atoms.

The full-matrix least-squares program *UPALS* (Lundgren, 1974) was used for refining the structure. The function minimized in the least-squares program was $w(|F_o|-|F_c|)^2$ where $w^{-1}=\sigma_c^2(F_o)+(0.04|F_o|)^2$, with $\sigma_c(F_o)$ based on counting statistics. Atomic scattering factors for Cu were taken from Hanson, Herman, Lea & Skillman (1964) and for Hf from Cromer & Waber (1965). Dispersion correction factors were taken from Cromer & Liberman (1970). No extinction correction was made. The parameters varied were: one scale factor, 19 atomic positional parameters and 38 anisotropic temperature factors. In the last cycle the changes in parameters were all smaller than 0.01σ. The conventional agreement index $R(F)$ was 0·053 for 1323 reflexions with F_o^2 larger than $2\sigma_c(F_o^2)$, and including zero-weight data an $R(F)$ value of 0·076 was obtained for all 1734 reflexions. The positional and the anisotropic thermal parameters are given in Table 1. The anisotropies in the thermal parameters result from the difficulty in applying a proper absorption correction to the irregular crystal. The calculated structure factors are compared with the observed structure factors in Table 2.

The structure of Zr₃Cu₈

With the positional and thermal parameters obtained for Hf₃Cu₈, the powder intensities of the reflexions for Zr₃Cu₈ were calculated. Atomic scattering factors

for Zr were taken from Cromer & Waber (1965). The intensities were obtained with the formula $I_c = g\,Lp\,|F^2|A$ in which g, Lp, F and A represent the multiplicity factor, the Lorentz–polarization factor, the structure factor and the absorption factor for the film respectively. The calculated and observed intensities on a relative scale from 0–100 are given in Table 3. The reliability index $R=\sum|I_o-I_c|/\sum I_c$ is 0·22.

Description of the structure

The structure of Hf₃Cu₈ can be described in terms of layers of atoms parallel to (010) and stacked in a

Table 4. *Interatomic distances shorter than 3·5 Å in* Hf₃Cu₈

E.s.d.'s are in units of the least significant digit.

Hf(1)–Hf(1)	1	3·083 (1) Å	Cu(3)–Hf(1)	2	2·703 (2) Å
Hf(1)	1	3·175 (1)	Hf(1)	2	2·819 (2)
Cu(1)	1	2·666 (2)	Hf(2)	1	2·633 (3)
Cu(1)	1	2·697 (2)	Hf(2)	1	3·112 (3)
Cu(2)	1	2·886 (2)	Cu(1)	2	2·964 (2)
Cu(2)	1	2·910 (2)	Cu(2)	2	2·506 (2)
Cu(2)	1	3·014 (2)	Cu(6)	1	2·438 (3)
Cu(3)	1	2·703 (2)			
Cu(3)	1	2·819 (2)	Cu(4)–Hf(1)	2	2·866 (1)
Cu(4)	1	2·866 (1)	Hf(1)	2	2·875 (2)
Cu(4)	1	2·875 (2)	Hf(2)	1	3·036 (3)
Cu(5)	1	2·811 (1)	Cu(1)	2	2·798 (3)
Cu(6)	1	2·895 (1)	Cu(2)	2	2·492 (2)
Cu(6)	1	2·909 (2)	Cu(5)	1	2·403 (4)
			Cu(5)	1	2·558 (4)
Hf(2)–Cu(1)	2	2·941 (2)	Cu(6)	1	2·430 (4)
Cu(1)	2	2·793 (2)			
Cu(2)	2	2·760 (2)	Cu(5)–Hf(1)	2	2·811 (1)
Cu(2)	2	2·789 (2)	Hf(2)	1	2·886 (3)
Cu(3)	1	2·633 (3)	Cu(1)	2	2·528 (3)
Cu(3)	1	3·112 (3)	Cu(1)	2	2·617 (3)
Cu(4)	1	3·036 (3)	Cu(2)	2	2·527 (2)
Cu(5)	1	2·886 (3)	Cu(4)	1	2·403 (4)
Cu(6)	1	2·906 (3)	Cu(4)	1	2·558 (4)
			Cu(6)	1	2·501 (3)
Cu(1)–Hf(1)	1	2·666 (2)			
Hf(1)	1	2·697 (2)	Cu(6)–Hf(1)	2	2·895 (1)
Hf(2)	1	2·793 (2)	Hf(1)	2	2·909 (2)
Hf(2)	1	2·941 (2)	Hf(2)	1	2·906 (3)
Cu(1)	1	2·817 (4)	Cu(1)	2	2·552 (3)
Cu(2)	1	2·658 (3)	Cu(2)	2	2·492 (2)
Cu(2)	1	2·668 (2)	Cu(3)	1	2·438 (3)
Cu(2)	1	2·895 (2)	Cu(4)	1	2·430 (4)
Cu(3)	1	2·964 (2)	Cu(5)	1	2·501 (3)
Cu(4)	1	2·798 (3)			
Cu(5)	1	2·617 (3)			
Cu(5)	1	2·528 (3)			
Cu(6)	1	2·552 (3)			
Cu(2)–Hf(1)	1	2·910 (2)			
Hf(1)	1	2·886 (2)			
Hf(1)	1	3·014 (2)			
Hf(2)	1	2·760 (2)			
Hf(2)	1	2·789 (2)			
Cu(1)	1	2·658 (2)			
Cu(1)	1	2·668 (2)			
Cu(1)	1	2·895 (2)			
Cu(3)	1	2·506 (2)			
Cu(4)	1	2·492 (2)			
Cu(5)	1	2·527 (2)			
Cu(6)	1	2·492 (2)			

sequence repeated after four layers. The atoms in the fourfold positions are situated on the mirror planes at $y=\frac{1}{4}$ and $y=\frac{3}{4}$, forming planar layers. The atoms in the eightfold positions, with approximate y coordinates of 0 and $\frac{1}{2}$, form puckered layers sandwiched between the mirror planes. A projection on (010) of the puckered layer near $y=0$ together with the planar layer at $y=\frac{1}{4}$ is shown in Fig. 1. Fig. 1 also shows a projection of the puckered layer near $y=\frac{1}{2}$ together with the planar layer at $y=\frac{3}{4}$.

The various interatomic distances in Hf_3Cu_8 are given in Table 4. Only distances shorter than 3·5 Å are included.

With the exception of the eightfold Hf(1) and Cu(1) atoms, which have, respectively, one Hf(1) and one Cu(1) contact across a mirror plane, the atoms in one layer have near neighbours only within the same layer and in the two adjacent layers. The Hf(1) atoms are coordinated to two other Hf(1) at 3·083 and 3·175 Å and to 12 Cu atoms, while the Hf(2) atoms have 13 Cu neighbours. The Hf–Cu distances are between 2·633 and 3·112 Å. The coordination numbers for the six non-equivalent types of Cu atoms vary from 11 to 13, with Cu–Cu distances from 2·403 to 2·964 Å.

The coordination of the atoms in Hf_3Cu_8 may be compared with that in $Hf_{14}Cu_{51}$ (Gabathuler, White & Parthé, 1975). In $Hf_{14}Cu_{51}$ there is only one Hf–Hf contact at a distance of 3·106 Å. The coordination numbers for the three non-equivalent Hf atoms are 16, 14 and 14, while the coordination numbers for the Cu atoms vary from 11 to 13. The Hf–Cu and Cu–Cu distances range from 2·660 to 2·974 Å, and from 2·413 to 3·269 Å respectively. Apart from the larger number of neighbours to the Hf atoms in $Hf_{14}Cu_{51}$, the coordination numbers and interatomic

distances are evidently quite similar in $Hf_{14}Cu_{51}$ and Hf_3Cu_8.

References

BAILEY, D. M. & KLINE, G. R. (1971). *Acta Cryst.* B27, 650–653.
BSENKO, L. (1975). *J. Less-Common. Met.* 40, 365–366.
CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* 53, 1891–1898.
CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* 18, 104–109.
DONACHIE, M. J. (1963–1964). *J. Inst. Met.* 92, 180.
FROHNMEYER, G. & GLOCKER, R. (1953). *Acta Cryst.* 6, 19–24.
GABATHULER, J.-P., WHITE, P. & PARTHÉ, E. (1975). *Acta Cryst.* B31, 608–610.
HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* 17, 1040–1044.
LUNDGREN, J.-O. (1974). *Crystallographic Computer Programs.* UUIC-B13-4-01. Univ. of Uppsala, Sweden.
LUNDIN, C. E., McPHERSON, D. J. & HANSEN, M. (1953). *Trans. AIME,* 197, 273–278.
MALMROS, G. & WERNER, P.-E. (1973). *Acta Chem. Scand.* 27, 493–502.
MARKIV, V. YA., PETKOV, V. V., STOROZHENKO, A. I., IVANCHENKO, V. G. & GORSKII, V. V. (1974). *Izv. Akad. Nauk SSSR, Met.* 2, 209–213.
NEVITT, M. V. & DOWNEY, I. W. (1962). *Trans. AIME,* 224, 195–196.
PERRY, A. J. (1974). *Mater. Sci. Eng.* 13, 57–62.
PERRY, A. J. & HUGI, W. (1972). *J. Inst. Met.* 100, 378–380.
RUSSELL, R. B. (1953). *J. Appl. Phys.* 24, 232-233.