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A note on the structure of Zr_2Co.*

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Weissenberg and precession diffraction data from a single crystal of Zr_2Co were found to corroborate the Strukturbericht Type C16 ($CuAl_2$) structure (Pearson, 1958) reported by Nevitt & Downey (1961):

$$\text{Space group } D_{4h}^{18}\text{-}I4/mcm\,,$$

$$4\ \text{Co at}\ (0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}) \pm (0, 0, \tfrac{1}{4})\,,$$

$$8\ \text{Zr at}\ (0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}) \pm (x, \tfrac{1}{2}+x, 0;\ \tfrac{1}{2}+x, \bar{x}, 0)\,.$$

Eighteen ($h0l$) reflections were used with a least-squares program to determine the single structural parameter as $x = 0{\cdot}1679 \pm 0{\cdot}0019$. Extrapolation of spacings obtained from Debye–Scherrer patterns against the Nelson–Riley function (1945) resulted in the tetragonal lattice parameters: $a_0 = 6{\cdot}363$ Å and $c_0 = 5{\cdot}469$ Å.

Table 1. *Comparison of observed and calculated structure factors for* Zr_2Co

$h0l$	$\lvert F_o \rvert$	F_c	$h0l$	$\lvert F_o \rvert$	F_c
002	41·0	+43·2	402	40·8	−37·0
004	60·6	+61·6	404	4·8	− 6·6
006	22·8	+24·4	406	20·6	−23·4
200	12·8	−12·2	600	53·4	+51·4
202	57·0	−48·2	602	27·0	+26·0
204	7·6	− 9·0	604	37·6	+41·8
206	26·2	−27·2	800	9·0	− 8·0
400	4·8	− 8·2	802	20·6	−25·0

The ($h0l$) intensities were visually estimated from a series of timed exposures of precession patterns obtained with Mo $K\alpha$ radiation. Lorentz and polarization corrections were made in the manner of Lu (1943), and absorption corrections were made in the manner of Bradley (1935) with the approximation of cylindrical symmetry for the needle-shaped crystal. The scattering factors of Thomas & Umeda (1957) were modified for dispersion corrections in the manner of Dauben & Templeton (1955), and the structure was refined on an IBM–650 with the least-squares program of Senko as modified by Fitzwater (1958). A comparison of observed and calculated structure factors per unit formula is shown in Table 1. The tabulated values give rise to the discrepancy indices:

$$R_1 = \Sigma \big| |F_o| - |F_c| \big| / \Sigma |F_o| = 0{\cdot}089$$

and

$$R_2 = \Sigma (|F_o| - |F_c|)^2 / \Sigma F_o^2 = 0{\cdot}009\,.$$

Isotropic temperature factors, $B_{Co} = 4{\cdot}08$ Å^2 and $B_{Zr} = 3{\cdot}06$ Å^2, were obtained and are rather large. On this basis one would expect appreciable vibrational amplitudes in the compound with a relatively high value for the entropy of formation. No thermodynamic data are available for corroboration. However, it may be noted that the temperature factors for the isostructural compound, Zr_2Ni, (Kirkpatrick, Bailey & Smith, 1961) are of comparable magnitude.

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The crystal structure of Ce_7Ni_3.*

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Table 1. *Final least-squares parameters for* Ce_7Ni_3

	Position	x	z	B (Å^2)
Ce_1	2(b)	1/3	0·7888 ± 0·0024	1·87 ± 0·24
Ce_2	6(c)	0·1250 ± 0·0005	0·0	1·52 ± 0·14
Ce_3	6(c)	0·5391 ± 0·0005	0·8011 ± 0·0012	1·85 ± 0·14
Ni	6(c)	0·8118 ± 0·0011	0·0496 ± 0·0026	1·76 ± 0·32

Vogel (1947), in a study of the Ce–Ni phase diagram, reported the existence of six binary compounds in this system. Of these, $CeNi_3$ and $CeNi_4$ were listed as having uncertain compositions. The existence of $CeNi_3$ has been verified (Cromer & Olsen, 1959), and what was thought to be $CeNi_4$ has been shown to be Ce_2Ni_7 (Cromer & Larson, 1959). The most Ce-rich compound was reported by Vogel to be Ce_3Ni. We find this compound to be Ce_7Ni_3. In attempting to prepare Ce_3Ni, Coffinberry (1960) was

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Table 2. *Observed and calculated structure factors for* Ce_7Ni_3

If F_o is negative the minus sign should be interpreted as "less than"

h	F_o	F_c
	$h0l$	
	$l=0$	
2	25	17
3	216	216
4	106	98
5	176	156
6	−31	15
7	−34	15
8	36	36
9	98	103
10	73	70
11	37	32
	$l=1$	
2	79	87
3	299	300
4	139	140
5	328	317
6	144	141
7	88	91
8	74	71
9	47	54
10	122	130
11	51	65
	$l=2$	
0	167	162
1	282	269
2	309	291
3	120	130
4	121	111
5	139	126
6	41	48
7	79	92
8	177	183
9	38	48
10	47	47
11	49	57
	$l=3$	
1	35	35
2	187	176
3	324	331
4	113	115
5	118	113
6	184	183
7	36	51
8	54	62
9	47	51
10	45	53
11	51	75
	$l=4$	
0	416	448
1	104	106
2	105	91
3	107	100
4	69	66
5	112	94
6	36	34
7	84	68
8	120	107
9	84	68
10	41	45
	$l=5$	
1	50	44
2	95	78
3	−36	28
4	63	72
5	212	236
6	−37	15
7	65	61
8	37	49
9	−33	23
	$l=6$	
0	187	192
1	92	79
2	106	89
3	92	76
4	−37	31
5	124	120
6	46	49
7	36	44
8	85	79
	$l=7$	
1	−37	20
2	129	115
3	138	140
4	51	53
5	35	45
6	81	90
	$l=8$	
0	84	84
1	76	72
2	75	62
	$h1l$	
	$l=0$	
2	121	159
3	−24	9
4	40	51
5	−31	18
6	56	58
7	182	201
8	41	46
9	31	26
10	−45	20
	$l=1$	
2	267	284
3	115	106
4	149	123
5	90	86
6	44	52
7	−38	10
8	−41	20
9	44	45
10	46	46
	$l=2$	
0	259	269
1	129	116
2	108	95
3	21	22
4	89	78
5	111	103
6	26	29
7	40	53
8	85	85
9	−44	27
10	32	31
	$l=3$	
0	31	35
2	128	105
3	94	86
4	161	132
5	134	121
6	40	41
7	−41	26
8	−43	7
9	45	40
10	72	69
	$l=4$	
0	115	106
1	−36	8
2	102	86
3	−38	11
4	28	36
5	50	69
6	30	37
7	137	127
	$l=5$	
0	50	44
2	195	185
3	29	43
4	−41	20
5	−42	17
6	31	35
7	−44	9
	$l=6$	
0	87	79
1	31	43
2	93	87
3	−43	14
4	31	40
5	−44	31
6	−44	7
7	83	71
	$l=7$	
0	−44	20
2	32	38
3	45	42
4	55	56
5	63	69
	$l=8$	
0	55	72
1	−44	12
2	−44	22
3	−43	8
4	−42	16
5	41	49
	hhl	
	$l=0$	
1	28	31
2	327	371
3	366	387
4	20	32
5	273	271
6	60	65
	$l=2$	
0	182	162
1	127	116
2	33	43
3	102	102
4	51	43
5	64	59
6	22	23
	$l=4$	
0	472	448
1	−27	8
2	201	203
3	259	224
4	−31	27
5	158	172
6	49	44
	$l=6$	
0	221	192
1	31	43
2	50	60
3	131	141
4	37	45
5	93	92
	$l=8$	
0	86	84
1	−28	12
2	82	53

unable to obtain a single phase at 25 at.% Ni. A single phase was not obtained until the alloy contained ca. 30 at.% Ni.

Single crystals of the phase in question were obtained from an alloy containing 30·8 at.% Ni.* This alloy was

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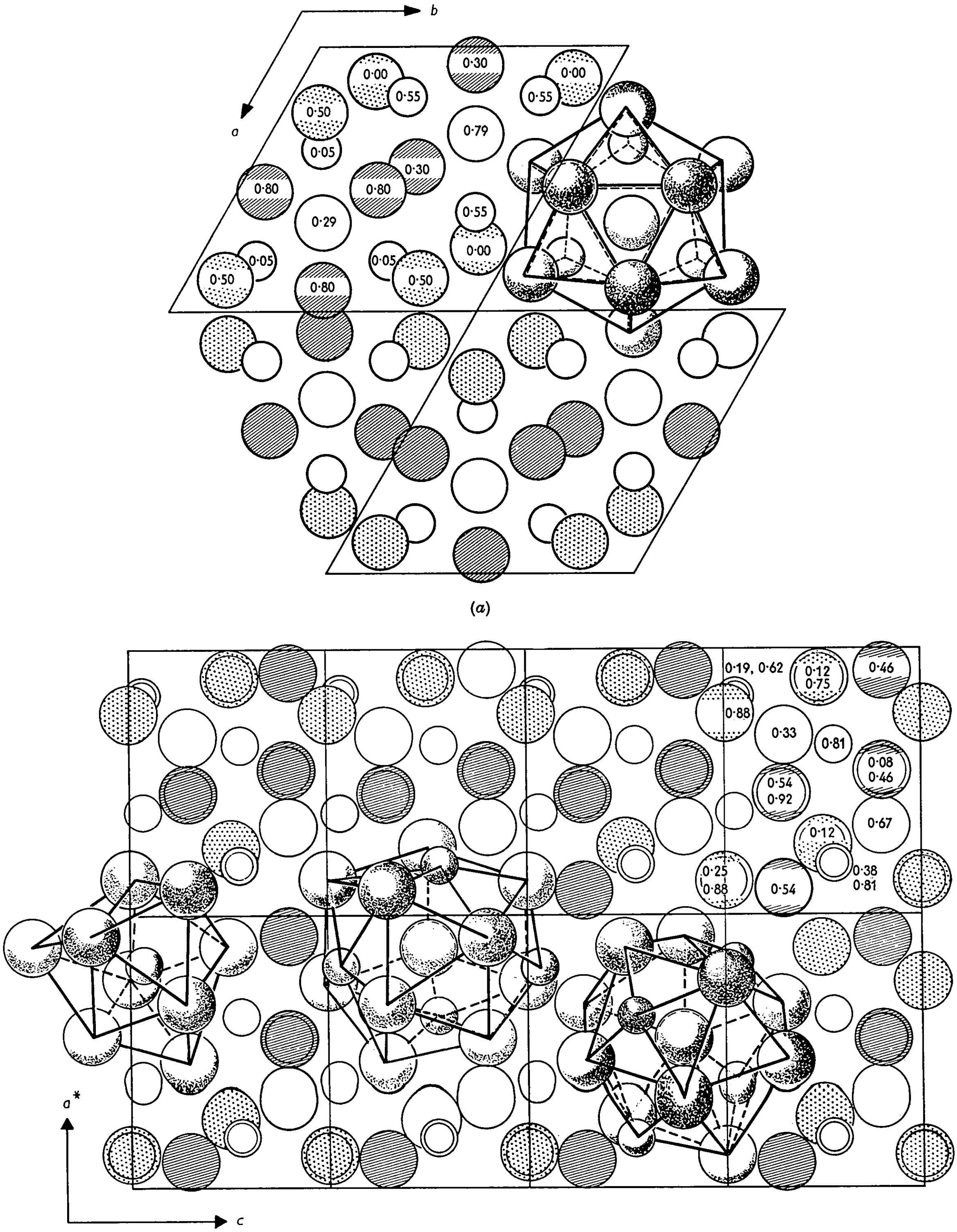
* At the time this alloy was made the compound was thought to be Ce_9Ni_4; hence the composition 30·8 at.% Ni.



(b)

Fig. 1. (*a*) The structure in projection down the *c* axis showing the polyhedron about Ce_1. (*b*) The structure in projection down the *b* axis showing, from left to right, the polyhedra about Ni, Ce_2 and Ce_3.

The large open circles are Ce_1, the dotted circles are Ce_2, the lined circles are Ce_3 and the small open circles are Ni atoms. The *z* and *y* coordinates are given.

arc melted and then heat treated in an evacuated quartz tube for about two months at 450 °C. Because the alloy is slowly oxidized by air, fragments were sealed in thin pyrex capillaries for X-ray examination. Using Mo $K\alpha$ X-rays ($\lambda = 0{\cdot}7107$ Å) and a precession camera, the crystals were found to be hexagonal with $a = 9{\cdot}92 \pm 0{\cdot}02$ and $c = 6{\cdot}33 \pm 0{\cdot}02$ Å. With two Ce_7Ni_3 per unit cell the calculated density is 7·12 g.cm.$^{-3}$, and the measured density of the gross alloy was 7·12 g.cm.$^{-3}$. Reflections of type *hhl* with $l = 2n+1$ were systematically absent. Thus the space group is $P6_3mc$, $P\bar{6}2c$ or $P6_3/mmc$. For intensity data, sets of timed exposures for each of the levels *h0l*, *hhl* and *h1l* were made with a precession camera and Mo $K\alpha$ radiation. Intensities were estimated visually by comparison with a series of spots of known relative intensity. *Lp* corrections (Waser, 1951) were computed with an IBM 704. No absorption corrections were made.

Considerations of atomic volumes had indicated that the most likely formula of the compound was Ce_7Ni_3. An *h0l* Patterson projection was computed. Inspection of this Patterson quickly showed that the space group could not be $P6_3/mmc$, and a tentative structure was deduced by using space group $P6_3mc$. It was then realized that the compound is isostructural with the Th_7M_3 compounds described by Florio *et al.* (1956).

The structure was refined by least-squares using an IBM-704. Separate scale factors for each of the three reciprocal lattice levels and individual isotropic temperature factors were used as parameters in addition to the position parameters. The full matrix was used to determine parameter shifts and standard deviations. Form factors were used in functional form with the parameters given by Forsyth & Wells (1959). $P6_3mc$ is a polar space group, thus the value of one z parameter is arbitrary. The z of Ce_2 was, therefore, held fixed at zero. The results of the least-squares calculations are given in Table 1. These values may be compared with those of Florio *et al.* by adding $\frac{1}{4}$ to the present z parameters. The list of observed and calculated structure factors is given in Table 2. With unobserved reflections omitted, the overall value of R is 9·1%. For the levels *h0l*, *hhl* and *h1l*, R is respectively 7·7, 9·1 and 11·7%.

The interatomic distances are given in Table 3. The atoms listed are those which satisfy the definition of a neighbor given by Frank & Kasper (1958). The Ni atom has nine Ce neighbors forming a polyhedron with 14 three-sided faces. The six closest atoms are at the corners of a distorted trigonal prism, and the other three atoms lie outward from the rectangular faces of this prism. Each Ce atom has 15 neighbors. Ce_1 has three Ni and 12 Ce neighbors which form a polyhedron with 26 three-sided faces. Ce_3 has four Ni and 11 Ce neighbors also forming a polyhedron with 26 three-sided faces but different from that about Ce_1. Ce_2 has four Ni and 11 Ce neighbors which form a polyhedron having 22 three-sided faces and two four-sided faces. These polyhedra are outlined in Fig. 1. All of the edges of the convex polyhedra about the Ni atom and Ce_2 join common neighbors but this is not the case for Ce_1 and Ce_3.

Table 3. *Interatomic distances in* Ce_7Ni_3

The numerals in parentheses denote the number of crystallographically equivalent distances. The standard deviation of these distances is about 0·025 Å.

Ce_1–Ni	(3)	2·92 Å	Ce_3–Ni	(2)	2·83 Å
–Ce_2	(3)	3·82	–Ni	(2)	3·53
–Ce_3	(3)	3·54	–Ce_1		3·54
–Ce_3	(3)	3·79	–Ce_1		3·79
–Ce_3	(3)	3·91	–Ce_1		3·91
			–Ce_2	(2)	3·66
			–Ce_2	(2)	3·77
Ce_2–Ni	(2)	2·87	–Ce_3	(2)	3·44
–Ni		3·05	–Ce_3	(2)	3·80
–Ni		3·64			
–Ce_1		3·82	Ni–Ce_1		2·92
–Ce_2	(2)	3·72	–Ce_2	(2)	2·87
–Ce_2	(4)	3·82	–Ce_2		3·05
–Ce_3	(2)	3·66	–Ce_2		3·64
–Ce_3	(2)	3·77	–Ce_3	(2)	2·83
			–Ce_3	(2)	3·53

In the paper by Florio *et al.* (1956), Table 1, which lists the interatomic distances in Th_7Fe_3, is in error with respect to both the distance given and the identification of the neighbors. The neighbors in Th_7Fe_3 correspond with those given in our Table 3, and the actual distances, in most cases, differ by about 0·05 Å.

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On the nature of the omega phase in quenched titanium alloys.

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There was a time when the crystal structure of the omega phase in titanium alloys was the subject of some doubt (Silcock, Davies & Hardy, 1955; Bagarjatskij, Tagunova & Nosova, 1955; Yoshida, 1956; Austin & Doig, 1957; Spachner, 1958), but it has now been established (Bagarjatskij & Nosova, 1958; Silcock, 1958). The omega phase has a hexagonal lattice with $c/a = 0{\cdot}612$–$0{\cdot}613$ in Ti-base alloys (Silcock *et al.*, 1955; Bagarjatskij *et al.*, 1955;