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The Crystal Structure of the δ Phase, Mo-Ni*

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The crystal structure of the δ phase, Mo–Ni ($49{\cdot}2 \pm 0{\cdot}2$ at.% Mo) has been determined by single-crystal X-ray analysis. For the orthogonal cell $a = b = 9{\cdot}108 \pm 0{\cdot}005$, $c = 8{\cdot}852 \pm 0{\cdot}005$ Å, $Z(\text{exp}) = 55{\cdot}8 \pm 0{\cdot}2$. Earlier unsuccessful trials were based on space group $P4_22_12$, although there are significant deviations toward orthorhombic symmetry in some intensities. The present structure, based on $P2_12_12_1$, has been refined by several cycles of full-matrix least-squares to a final R of 0·146 including, or of 0·118 excluding, non-observed reflections. The resulting structure does not have pseudo-fourfold rotation or screw axes. The almost planar atomic layers parallel to the (041) and (401) planes are closely similar, and are related to layers observed in the σ, P, R, and μ phases. As in these phases, the coordinations are limited to CN12, 14, 15, and 16, and all interstices are tetrahedral. Considerable ordering occurs, Ni occupying the six CN12 positions, Mo the one CN16 and the two CN15 positions, and a mixture occupying the five CN14 positions. The relative numbers of atoms of a given CN are the same as in the P phase. The interatomic distances agree with the sums of characteristic radii, obtained by assuming different radii for five- and six-coordinated ligands (minor and major ligands) for each coordination type; the agreement is about as good as in the R phase. The major ligands form four interwoven non-interconnected three-dimensional networks.

Introduction

In a previous communication (Shoemaker, Fox & Shoemaker, 1960) we described X-ray diffraction studies of the δ phase in the Mo–Ni system. These studies led to an elucidation of some structural features and to the establishment of close structural relationships with the σ phase and other related phases (P, R, μ, χ phases; β-tungsten; Laves phases), but stopped short of a determination of the complete structure.

The crystal data of the δ phase, as given before, are:

$$a = b = 9{\cdot}108 \pm 0{\cdot}005,\ c = 8{\cdot}852 \pm 0{\cdot}005\ \text{Å};$$
$$\alpha = \beta = \gamma = 90^\circ.$$
$$d(\text{exp.}) = 9{\cdot}71 \pm 0{\cdot}01\ \text{g.cm}^{-3},\ Z(\text{exp.}) = 55{\cdot}8 \pm 0{\cdot}2.$$

At.% of Mo as determined by analysis: $49{\cdot}2 \pm 0{\cdot}2$.
Assumed space group: $P4_22_12$ (D_4^6).

No splitting of lines, such as would be attributable to a difference in length between the a and b repeats, was observed in the powder diagrams. Close inspection of the single-crystal diffraction diagrams showed, however, that the true diffraction symmetry is orthorhombic. The deviations from the tetragonal symmetry are most noticeable for weak and medium reflections and do not appear to increase with scattering angle. We therefore concluded at that time that the positions of the atoms conform to tetragonal symmetry, but that occupancy of the sites by the different atomic species might be such as to lower the symmetry to orthorhombic. However, attempts to solve the structure in the tetragonal space group were unsuccessful.

In our new attempts to solve the structure we disregarded at the outset the (pseudo-)tetragonal appearance of the diffraction pattern and considered arrangements of atoms in orthorhombic space groups. It seemed attractive to replace the 4_2 axes by twofold axes as in space group $P2_12_12$, a subgroup of $P4_22_12$. The extinctions of the $00l$ reflections would then be accidental, caused by some special features of the structure rather than by space-group symmetry. (Only reflections 004, 006 and 0,0,12 are observed.) The structure formulated in this space group failed to explain some of the high peaks of the three-dimensional Patterson function. It appeared that it was possible to remove these discrepancies by replacing the twofold axes in the z direction by twofold screw axes. This finally led to the determination of the structure in space group $P2_12_12_1$, which is not a subgroup of $P4_22_12$. However, it is the space group indicated by the true (orthorhombic) diffraction symmetry and the systematic extinctions.

Experimental

The intensities were visually estimated on equi-inclination Weissenberg films, Cu $K\alpha$ radiation, layers $hk0$–$hk5$ and $0kl$–$5kl$. Altogether 626 reflections were observed out of a total of 892 accessible to observation on these photographs. Two crystals, both irregular

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fragments no larger than 0·1 mm in size, were used. No absorption corrections were applied.

Structure determination

The three-dimensional Patterson function of the δ phase, computed on the IBM 704 with the Fourier program MIFR1 (Shoemaker & Sly, 1961), shows very small deviations from tetragonal symmetry and has some very striking features: (*a*) there are very strong peaks at $(\frac{1}{2}, \frac{1}{2}, 0)$, $(0, \frac{1}{2}, \frac{1}{8})$ and $(\frac{1}{2}, 0, \frac{1}{8})$, (*b*) there are strong peaks forming pseudo-hexagonal σ-phase type nets, tipped by about 15° with respect to the (100) and (010) planes.

In the tetragonal σ phase (Bergman & Shoemaker, 1954) there are perpendicular to the *z* axis two planar hexagonal nets which are rotated by 90° with respect to each other and slightly distorted to fit into the tetragonal cell. Four of the fifteen atoms of each net are displaced to positions between the nets, locking them together.

The three-dimensional Patterson function for the δ phase indicates that here the pseudo-hexagonal nets must be nearly perpendicular to the *x* and the *y* axes. This means that these layers must be puckered, perhaps in a way somewhat similar to the arrangement in α-Mn (χ phase) which is cubic and has σ-type layers in three perpendicular directions (Shoemaker, Shoemaker & Wilson, 1957).

The length of the *a* (or *b*) repeat of the δ phase is about twice the length of the *c* repeat of the σ phase, indicating that four σ-type layers have to be placed perpendicular to these axes. The structure determination consisted of two parts: (1) finding the position, with respect to the symmetry elements of the assumed space group, of the σ-type nets perpendicular to (say) the *x* axis; and (2) puckering and tilting the nets such that a good packing resulted and the pseudo-tetragonal appearance of the diffraction pattern was explained.

Ad (1). The position of the layer at, say, $x \sim \frac{1}{8}$ was taken such that the 2_1 axes in the *x* direction (at $x, \frac{1}{4}, 0$, *etc*) produced another layer at $x \sim \frac{5}{8}$, which was shifted with respect to the first layer by $(\frac{1}{2}, 0, \frac{1}{8})$, thus explaining the high peaks in the Patterson function at $(\frac{1}{2}, 0, \frac{1}{8})$ and at $(\frac{1}{2}, \frac{1}{2}, 0)$.

The 2_1 axes between the layers could be assumed to take over the function of the *n*-glides in the σ phase. With the layer in the chosen position at $x \sim \frac{1}{8}$, the 2_1 axes in the *z* direction (at $\frac{1}{4}, 0, z$, *etc*) produced a layer at $x \sim \frac{3}{8}$ which had a σ-phase-like relation to the layer at $x \sim \frac{1}{8}$. Similarly the layers at $x \sim \frac{5}{8}$ and $x \sim \frac{7}{8}$ packed in σ-phase fashion. The 2_1 axes in the *y* direction (at $0, y, \frac{1}{4}$, *etc*) related the layer at $x \sim \frac{1}{8}$ with the one at $x \sim \frac{7}{8}$ (and similarly the one at $x \sim \frac{3}{8}$ with the one at $x \sim \frac{5}{8}$). In the chosen position these layers were also related in a σ-phase fashion if the atoms corresponding to the inter-layer atoms of the σ phase were chosen in a different way. The layers of the δ phase must be sufficiently puckered, however, that the concept of inter-layer atoms has lost much of its meaning. The three-dimensional Patterson function supported this manner of stacking the layers. Several high peaks, corresponding to vectors between atoms in successive layers, were explained for the first time by this structure.

Ad (2). The puckering of the layers was achieved after building a model with the *x* axis vertical. Study of the model showed that the atoms could be moved out of the planes in such a way that one of the atoms (number VI) was surrounded by an almost perfect icosahedron. At the same time σ-type row lines of atoms appeared approximately in the *x*–*z* plane. On making the corresponding *x* changes for symmetry-related atoms, it was found that two fourfold atomic positions collapsed into one, thus arriving at 56 atoms per unit cell as demanded by the crystal density. A structure resulted in which all 14 non-equivalent atoms had recognizable CN12, 14, 15 or 16 polyhedra similar to those found in the σ phase and related phases. Now σ-type layers were found also perpendicular to the *y* axis, puckered differently but stacked similarly to those perpendicular to the *x* axis. Thus the pseudo-tetragonal character of the diffraction pattern was at least qualitatively explained.

Refinement of the structure

The atoms were given coordinates on the basis of the trial structure above described. The seven Mo atoms were placed in one 16-, two 15- and four 14-coordinated positions, and the seven Ni atoms in the remaining seven positions, which were assumed to be all 12-coordinated.

The structure factors were calculated by means of the Mo and Ni scattering factors published by Thomas & Umeda (1957), with an anomalous dispersion correction of −0·5 electron for Mo and −3·0 electrons for Ni (Dauben & Templeton, 1955). No $\Delta f''$ could be applied, as at the time the photographs were taken (1953) no consideration was given to the sign of the axes. The initial *R* index, defined as $\Sigma|\Delta|/\Sigma|F_o|$, was 0·326 for the observed reflections. The calculated structure factor magnitudes conformed so nearly to tetragonal symmetry that it was impossible to decide at that time whether the right choice of *x* and *y* axes was made.

The structure was refined by several cycles of full-matrix least-squares analysis on the IBM 704 with the program ORXLS, written by Busing & Levy (1959*a*). In the first three cycles the non-observed reflections and the markedly asymmetric (non-tetragonal) reflections were left out, leaving 504 independent structure factors. The positional parameters, one scale factor and one overall temperature factor were varied. After one cycle the *R* index for all the observed reflections dropped to 0·242, even though the structure factors now clearly showed that the wrong choice of x and y axes had been made and that the coordinates of the atoms accordingly had to be changed.

From the second cycle onward the atoms were given individual isotropic temperature factors. The temperature factor of atom 11 became negative in the second and third cycles, indicating that this atom should be given a larger weight. Inspection of the model showed that this atom had actually CN14 rather than CN12 as erroneously concluded at first. Its weight was increased at the expense of the other four CN14 atoms (giving all CN14 atoms 80% Mo occupancy) and in the following cycles its temperature factor remained positive but higher than those for the other CN14 atoms, indicating that its weight was now too high. The R index after cycle 3 was 0·136, all observed reflections included.

From cycle 5 onward all reflections were included in the refinement, the non-observed hkl reflections with $|F_o| = \frac{2}{3}|F(\min)|$ and the non-observed zonal reflections with $|F_o| = \frac{1}{2}|F(\min)|$. The standard errors, on which the weights were based, were set equal to 20 for all reflections with $|F_o| \leq 80$, to 15 for $80 < |F_o| \leq 150$, and to $\frac{1}{10}|F_o|$ for $|F_o| > 150$.

In order to determine the occupancy of the different sites by molybdenum and nickel, the scattering factors were varied in cycles 6 and 7. In the least-squares program ORXLS the scattering factors can be varied for a neutron, but not for an X-ray, diffraction problem. Therefore the F_o were divided by $\bar{f}$ (average scattering factor for Mo and Ni, with anomalous dispersion corrections applied as above) and the least-squares program was then run as for a neutron diffraction problem (at the suggestion of Dr Busing). In cycle 6, the individual isotropic B's, the scattering factors ($f/\bar{f}$) and the positional parameters were varied. The resulting parameters are given in Table 1. A strong interaction between the temperature and the scattering factors was shown by the standard deviations, which varied for the temperature factors between 0·18 and 0·39, and for the scattering factors $f/\bar{f}$ between 0·04 and 0·05. The temperature factors cover a large range for a particular coordination type and therefore in cycle 7 only the scattering factors and the positional parameters were varied and the temperature factors were set at the average values obtained in cycle 6 for the corresponding coordinations. (The B values marked by an asterisk were excluded in the calculation of the average). The standard deviations in the scattering factors were now about half the values obtained in the previous cycle.

Table 1. *Result of the refinement of the scattering factors for the δ phase*

Atom	CN	B cycle 6	$f/\bar{f}$ cycle 6	$f/\bar{f}$ cycle 7	% Mo estimated
IV	12	1·65	0·75	0·73	0
VI	12	1·80	0·71	0·73	0
VIII	12	0·69*	0·65	0·73	0
IX	12	1·42	0·75	0·77	0
X	12	1·48	0·69	0·72	0
XII	12	1·34	0·70	0·71	0
	Average	1·54			
(Limiting value, 0% Mo)			0·75		
I	14	−0·00*	1·09	1·21	80
XIII	14	0·45	1·14	1·18	80
II	14	0·87	1·27	1·27	91
V	14	0·65	1·22	1·25	91
XI	14	1·05	1·10	1·07	58
	Average	0·75			
VII	15	0·33	1·29	1·31	100
XIV	15	0·44	1·28	1·26	100
	Average	0·38			
III	16	0·09	1·20	1·25	100
	Assumed	0·20			
(Limiting value, 100% Mo)			1·25		

* Omitted from average; see text.

Table 1 shows that in cycle 7 the values obtained for $f/\bar{f}$ for the CN16 and the two CN15 positions are larger or equal to the value for 100% Mo, and for all but one of the CN12 positions the values of $f/\bar{f}$ are slightly smaller than the value for 0% Mo. For the five CN14 positions two $f/\bar{f}$ values are very close to the limiting value for 100% Mo. The last column of Table 1 contains the estimated percentages of Mo that were used in all subsequent least-squares and structure-factor calculations. All CN12 positions were assumed to contain 0% Mo and all CN16 and CN15 positions were assumed to contain 100% Mo. The values for the CN14 positions were obtained by interpolating between these values, normalizing so as to distribute four Mo atoms over the five kinds of CN14 positions. (Almost equal values for two pairs of CN14 atoms were averaged in order to minimize the number of scattering factor curves required in the calculations.)

After one more cycle (8) in which the scale factor, the positional parameters, and individual isotropic temperature factors were varied, anisotropic temperature factors were introduced in cycle 9. The shifts in the atomic positions were all smaller than the standard deviations, while the shifts in the thermal parameters were generally of the order of magnitude of the standard deviations, although some shifts were as large as three times the standard deviations. These values for the anisotropic temperature factors did not seem to correspond to the expectations based on the different surroundings and local symmetries of the atoms (see below under *Thermal parameters*).

In order to test the treatment of the non-observed reflections, one more cycle (9′) was calculated with isotropic temperature factors and starting with parameters as obtained from cycle 8. Of the non-observed reflections only the five with $|F_c| > |F(\min)|$

Table 2. *Atomic parameters of the δ phase*

Atom	x	$\sigma_x.10^4$	y	$\sigma_y.10^4$	z	$\sigma_z.10^4$	B	$\sigma_B.10^2$	% Mo	CN
IV	0·4519	16	0·1153	18	0·5322	21	1·20	24	0	12
VI	0·4424	16	0·3662	16	0·5971	20	1·38	27	0	12
VIII	0·3882	16	0·0523	16	0·2748	18	0·93	26	0	12
IX	0·1337	17	0·0707	15	0·2157	18	0·97	24	0	12
X	0·3768	17	0·4358	16	0·8567	20	1·24	27	0	12
XII	0·0680	17	0·1442	16	0·9529	18	1·32	27	0	12
I	0·2648	8	0·1993	7	0·7486	9	0·50	12	80	14
XIII	0·3136	8	0·2464	8	0·0740	10	0·67	12	80	14
II	0·0029	8	0·1969	8	0·6767	9	0·82	13	91	14
V	0·1885	8	0·0157	8	0·4960	9	0·77	12	91	14
XI	0·1031	10	0·4192	9	0·9133	12	0·84	15	58	14
VII	0·1763	7	0·4832	6	0·6425	8	0·49	10	100	15
XIV	0·0338	7	0·3398	8	0·1807	8	0·63	11	100	15
III	0·2289	7	0·2865	7	0·4098	8	0·56	11	100	16

were included, with $|F_o|$ set equal to $|F(\text{min})|$. (The weighting was also slightly changed: σ was taken $=15$ for all reflections with $|F_o|<150$, and $=\frac{1}{10}|F_o|$ for $|F_o|\geq 150$.) All but six of the resulting parameter shifts were smaller than the standard deviations, and the final atomic coordinates listed in Table 2 were taken to be the average of the values obtained by cycle 9′ and cycle 8. The standard deviations listed are those calculated in cycle 9′.

The R index calculated for all 892 reflections (with the non-observed reflections taken again with $|F_o|=\frac{2}{3}|F(\text{min})|$ for hkl reflections and with $|F_o|=\frac{1}{2}|F(\text{min})|$ for zonal reflections) was 0·146, and the R index calculated for all 626 observed reflections was 0·118. The observed and calculated structure factor magnitudes are given in Table 3.

Description of the structure

An interesting feature of this orthorhombic structure is its pseudo-tetragonal appearance, as evident in Figs. 1, 2 and 3.

Fig. 1(*a*) is a projection of the structure down the z axis. Important features in relation to the Patterson function are the pseudo-repeat of $\frac{1}{2}, \frac{1}{2}, 0$ and strong vectors of $\frac{1}{2}, 0, \frac{1}{8}$ and $0, \frac{1}{2}, \frac{1}{8}$. The structure is clearly in accord with the very strong 420 and 240 reflections.

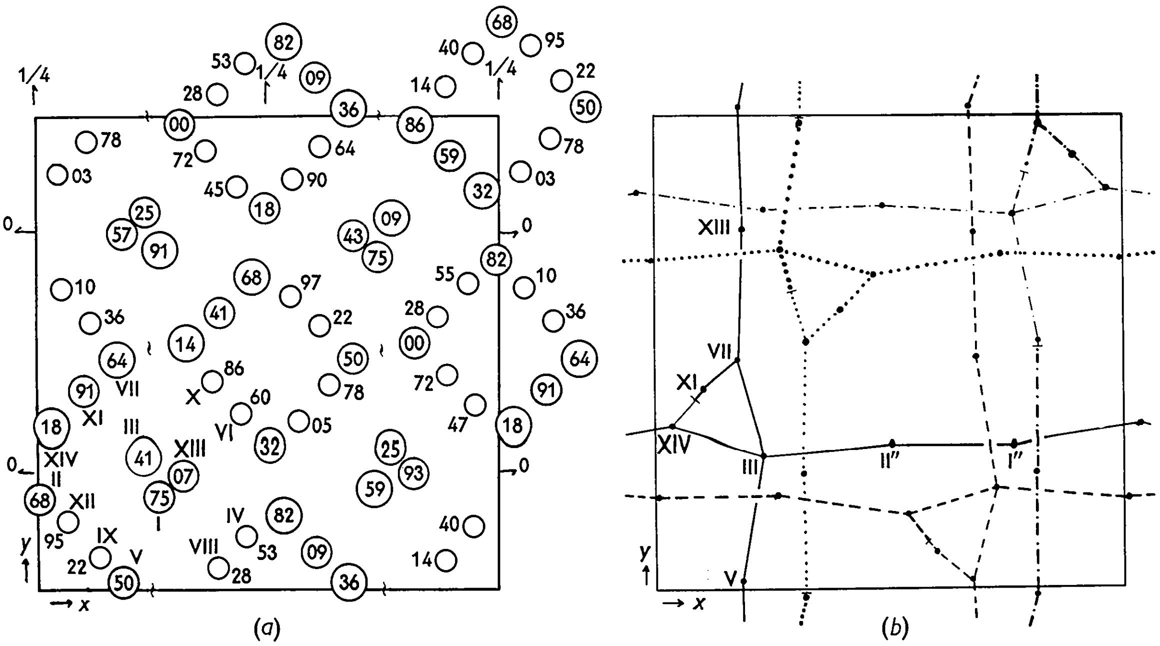

Fig. 1. (*a*) Delta phase structure: projection down the z axis. Large circles: Mo, small circles: Ni, intermediate circles: various mixtures of Mo and Ni. The numbers in the circles are the z coordinates in hundredths of the cell length c. (*b*) Networks of major ligands projected down the z axis. There are four three-dimensional networks indicated by different types of lines. Numbering of the atoms is as in Table 4.

Table 3. *Observed and calculated structure factor magnitudes for the δ phase*

Asterisks indicate non-observed reflections, which are entered under OBS with ½ or ⅔ of F(min)

H K	OBS	CAL
L=0		
0 2	41	44
2 0	41	58
0 4	157	172
4 0	121	126
0 6	68	74
6 0	68	54
0 8	* 38	47
8 0	* 38	28
0·10	88	69
10 0	78	61
1 1	* 16	9
1 2	44	26
2 1	* 18	4
1 3	* 20	1
3 1	88	76
1 4	99	91
4 1	117	132
1 5	* 25	28
5 1	* 25	10
1 6	52	43
6 1	* 26	11
1 7	* 32	22
7 1	* 32	19
1 8	* 35	33
8 1	* 35	17
1 9	* 36	33
9 1	* 36	19
1·10	* 34	23
10 1	102	100
1·11	* 28	16
11 1	* 28	2
2 2	* 14	13
2 3	166	147
3 2	* 15	18
2 4	497	531
4 2	404	525
2 5	55	32
5 2	29	36
2 6	85	74
6 2	107	104
2 7	150	133
7 2	126	108
2 8	76	73
8 2	111	117
2 9	* 30	18
9 2	* 30	50
2·10	140	115
10 2	72	63
2·11	70	57
11 2	78	76
3 3	33	45
3 4	185	156
4 3	178	189
3 5	* 25	6
5 3	57	69
3 6	188	172
6 3	* 29	3
3 7	* 32	17
7 3	80	60
3 8	123	110
8 3	* 31	2
3 9	74	66
9 3	* 34	30
3·10	107	82
10 3	125	112
3·11	117	99
11 3	120	114
4 4	50	50
4 5	88	89
5 4	112	119
4 6	240	235
6 4	213	223
4 7	94	94
7 4	92	100
4 8	* 25	28
8 4	80	67
4 9	105	68
9 4	* 34	16
4·10	188	149
10 4	159	137
4·11	166	235
11 4	166	228
5 5	* 25	2
5 6	* 28	29
6 5	* 28	22
5 7	* 28	6
7 5	92	103
5 8	47	25
8 5	76	54
5 9	68	55
9 5	64	52
5·10	62	59
10 5	* 26	37
6 6	100	120
6 7	260	219
7 6	224	202
6 8	124	117
8 6	105	111
6 9	66	71
9 6	66	28
6·10	* 24	8
10 6	48	55
7 7	122	114
7 8	207	186
8 7	154	149
7 9	106	105
9 7	106	98
8 8	313	333
L=1		
0 1	* 14	0
1 0	* 14	19
0 2	70	66
2 0	57	37
0 3	33	31
3 0	70	58
0 4	602	649
4 0	602	638
0 5	* 22	15
5 0	44	26
0 6	64	51
6 0	92	104
0 7	151	142
7 0	107	113
0 8	92	71
8 0	* 38	40
0 9	* 38	29
9 0	* 38	24
0·10	* 32	11
10 0	68	61
0·11	423	308
11 0	308	311
1 1	33	18
1 2	* 29	9
2 1	41	30
1 3	88	77
3 1	41	31
1 4	301	271
4 1	251	280
1 5	97	88
5 1	72	64
1 6	68	60
6 1	* 39	54
1 7	105	93
7 1	110	120
1 8	91	63
8 1	110	91
1 9	* 48	47
9 1	* 48	46
1·10	174	123
10 1	109	96
1·11	158	117
11 1	113	96
2 2	95	78
2 3	144	130
3 2	174	167
2 4	378	385
4 2	378	390
2 5	* 29	23
5 2	55	41
2 6	84	72
6 2	* 33	30
2 7	177	154
7 2	177	151
2 8	208	170
8 2	118	110
2 9	99	77
9 2	* 40	34
2·10	62	40
10 2	110	104
2·11	122	102
11 2	127	115
3 3	120	107
3 4	52	33
4 3	52	40
3 5	88	87
5 3	* 33	11
3 6	152	142
6 3	207	218
3 7	162	156
7 3	162	159
3 8	246	228
8 3	246	262
3 9	70	55
9 3	103	96
3·10	158	116
10 3	* 40	39
3·11	* 37	12
11 3	* 37	25
4 4	119	125
4 5	132	138
5 4	132	114
4 6	260	282
6 4	254	261
4 7	137	124
7 4	137	124
4 8	223	197
8 4	223	199
4 9	151	120
9 4	151	118
4·10	74	62
10 4	112	85
4·11	29	37
11 4	60	62
5 5	91	89
5 6	57	46
6 5	* 37	30
5 7	111	97
7 5	111	98
5 8	74	63
8 5	* 32	16
5 9	94	77
9 5	94	70
5·10	55	42
10 5	83	70
6 6	92	87
6 7	123	120
7 6	88	83
6 8	* 45	16
8 6	98	100
6 9	* 39	27
9 6	68	54
6·10	86	103
10 6	41	39
7 7	* 45	52
7 8	* 40	51
8 7	60	63
7 9	55	67
9 7	57	51
L=2		
0 0	* 15	8
0 1	* 16	21
1 0	* 16	24
0 2	84	82
2 0	116	98
0 3	107	102
3 0	33	21
0 4	* 26	32
4 0	70	65
0 5	* 30	30
5 0	* 30	26
0 6	72	73
6 0	* 33	16
0 7	408	437
7 0	408	420
0 8	312	311
8 0	312	312
0 9	76	64
9 0	* 37	17
0·10	* 30	17
10 0	64	60
0·11	* 25	9
11 0	* 25	19
1 1	70	44
1 2	74	59
2 1	37	32
1 3	246	199
3 1	246	236
1 4	118	112
4 1	101	88
1 5	* 36	7
5 1	62	51
1 6	89	97
6 1	89	117
1 7	322	338
7 1	322	348
1 8	257	254
8 1	257	269
1 9	80	57
9 1	80	86
1·10	88	62
10 1	68	76
1·11	* 35	20
11 1	* 35	27
2 2	37	28
2 3	226	226
3 2	197	191
2 4	186	179
4 2	216	207
2 5	57	52
5 2	41	32
2 6	70	59
6 2	70	72
2 7	107	100
7 2	107	96
2 8	127	131
8 2	127	125
2 9	* 40	29
9 2	* 40	43
2·10	94	75
10 2	* 39	21
2·11	116	113
11 2	81	100
3 3	384	405
3 4	50	29
4 3	83	74
3 5	128	119
5 3	128	132
3 6	154	158
6 3	154	139
3 7	* 45	37
7 3	* 45	29
3 8	* 47	29
8 3	* 47	44
3 9	106	88
9 3	76	58
3·10	126	96
10 3	118	120
3·11	66	65
11 3	43	52
4 4	159	151
4 5	218	246
5 4	218	230
4 6	117	128
6 4	117	143
4 7	88	98
7 4	88	83
4 8	70	59
8 4	81	68
4 9	154	132
9 4	154	142
4·10	110	97
10 4	72	63
5 5	189	227
5 6	* 37	31
6 5	* 37	54
5 7	119	134
7 5	119	120
5 8	74	67
8 5	97	92
5 9	133	107
9 5	133	117
5·10	66	64
10 5	64	77
6 6	* 41	46
6 7	64	58
7 6	64	62
6 8	84	85
8 6	72	67
6 9	66	69
9 6	66	55
7 7	* 39	23
7 8	* 37	35
8 7	62	58
7 9	37	40
9 7	37	41
L=3		
0 1	* 20	24
1 0	94	76
0 2	80	83
2 0	33	13
0 3	193	212
3 0	246	204
0 4	* 27	31
4 0	* 27	11
0 5	* 30	41
5 0	52	34
0 6	* 32	12
6 0	64	68
0 7	* 38	20
7 0	* 38	1
0 8	* 39	17
8 0	* 39	19
0 9	* 36	29
9 0	* 36	49
0·10	57	50
10 0	60	61
0·11	133	112
11 0	97	102
1 1	287	238
1 2	* 29	10
2 1	89	78
1 3	574	631
3 1	574	638
1 4	78	74
4 1	84	68
1 5	57	62
5 1	112	81
1 6	94	88
6 1	57	61
1 7	70	59
7 1	* 45	45
1 8	66	59
8 1	* 49	45
1 9	72	51
9 1	* 48	22
1·10	148	118
10 1	91	99
1·11	85	81
11 1	74	98
2 2	37	31
2 3	166	157
3 2	124	106
2 4	44	26
4 2	44	34
2 5	78	68
5 2	99	75
2 6	* 37	10
6 2	* 37	20
2 7	* 40	39
7 2	* 40	24
2 8	60	50
8 2	72	82
2 9	91	75
9 2	70	72
2·10	57	32
10 2	* 37	32
2·11	94	97
11 2	52	60
3 3	91	61
3 4	70	72
4 3	81	77
3 5	226	241
5 3	221	234
3 6	110	111
6 3	109	117
3 7	72	70
7 3	70	85
3 8	124	120
8 3	101	125
3 9	98	85
9 3	66	65
3·10	* 39	9
10 3	* 39	21
4 4	60	58
4 5	94	91
5 4	198	130
4 6	60	73
6 4	* 36	39
4 7	156	187
7 4	147	173
4 8	99	89
8 4	98	87
4 9	148	128
9 4	117	125
4·10	52	51
10 4	70	63
5 5	148	157
5 6	* 37	46
6 5	70	78
5 7	202	189
7 5	218	208
5 8	162	146
8 5	163	165
5 9	192	189
9 5	152	140
5·10	78	83
10 5	102	120
6 6	78	98
6 7	97	101
7 6	88	80
6 8	* 40	42
8 6	* 40	41
6 9	57	66
9 6	66	55
7 7	86	99
7 8	* 37	33
8 7	55	44
L=4		
0 0	52	46
0 1	107	102
1 0	151	128
0 2	52	55
2 0	86	76
0 3	* 27	11
3 0	62	43

Table 3 (*cont.*)

H	K	OBS	CAL
0	4	* 30	19
4	0	57	42
0	5	* 32	17
5	0	116	122
0	6	88	60
6	0	88	76
0	7	* 39	3
7	0	* 39	33
0	8	* 39	36
8	0	* 39	14
0	9	92	26
9	0	102	102
0	10	* 28	31
10	0	* 28	33
1	1	598	626
1	2	97	78
2	1	* 32	11
1	3	156	139
3	1	150	111
1	4	55	38
4	1	55	31
1	5	214	237
5	1	208	191
1	6	101	91
6	1	101	81
1	7	91	88
7	1	91	72
1	8	105	84
8	1	108	92
1	9	107	88
9	1	66	69
1	10	124	100
10	1	106	112
2	2	55	42
2	3	68	60
3	2	95	79
2	4	* 32	22
4	2	50	46
2	5	173	175
5	2	173	183
2	6	84	86
6	2	84	75
2	7	112	120
7	2	86	94
2	8	98	79
8	2	* 50	34
2	9	144	122
9	2	144	129
2	10	84	55
10	2	99	92
3	3	* 33	30
3	4	95	99
4	3	95	78
3	5	340	398
5	3	340	380
3	6	76	70
6	3	76	61
3	7	106	112
7	3	106	143
3	8	* 45	42
8	3	* 45	35
3	9	142	127
9	3	142	131
3	10	155	136
10	3	110	114
4	4	* 36	9
4	5	76	57
5	4	99	93
4	6	* 36	35
6	4	97	100
4	7	60	60
7	4	* 53	39
4	8	* 29	27
8	4	* 46	43
4	9	* 24	15
9	4	* 40	29
4	10	88	94
10	4	88	101
5	5	* 37	31
5	6	70	98
6	5	* 47	40
5	7	97	61
7	5	* 50	54
5	8	133	115
8	5	91	75
5	9	79	63
9	5	79	82
6	6	107	80
6	7	190	175
7	6	190	207
6	8	* 40	64
8	6	* 40	54
6	9	68	86
9	6	68	100
7	7	227	253
7	8	* 32	43
8	7	* 32	34
L=5			
0	1	* 28	18
1	0	* 28	36
0	2	60	52
2	0	76	72
0	3	* 31	45
3	0	* 31	9
0	4	* 33	15
4	0	47	38
0	5	186	196
5	0	210	220
0	6	* 39	33
6	0	* 39	73
0	7	* 39	29
7	0	* 39	10
0	8	* 35	2
8	0	* 35	48
0	9	* 30	9
9	0	* 30	19
0	10	141	115
10	0	141	126
1	1	62	43
1	2	64	61
2	1	60	44
1	3	74	79
3	1	74	48
1	4	124	137
4	1	134	131
1	5	292	310
5	1	292	323
1	6	110	129
6	1	118	121
1	7	* 49	61
7	1	* 59	38
1	8	* 48	35
8	1	* 48	10
1	9	144	128
9	1	91	89
1	10	218	206
10	1	218	182
2	2	137	155
2	3	111	100
3	2	125	135
2	4	161	172
4	2	141	143
2	5	124	129
5	2	183	201
2	6	190	207
6	2	187	208
2	7	107	101
7	2	107	137
2	8	* 40	33
8	2	* 40	84
2	9	208	176
9	2	230	216
2	10	101	77
10	2	101	70
3	3	157	167
3	4	62	47
4	3	62	66
3	5	102	95
5	3	81	72
3	6	191	227
6	3	165	182
3	7	124	134
7	3	124	124
3	8	128	136
8	3	128	84
3	9	178	160
9	3	153	143
4	4	50	28
4	5	* 36	46
5	4	89	101
4	6	152	168
6	4	162	195
4	7	47	42
7	4	* 51	48
4	8	99	86
8	4	99	96
4	9	60	48
9	4	103	90
5	5	104	118
5	6	76	71
6	5	* 47	41
5	7	81	81
7	5	80	99
5	8	110	96
8	5	110	96
5	9	50	41
9	5	64	69
6	6	* 43	51
6	7	* 40	32
7	6	* 40	35
6	8	76	76
8	6	76	24
L=6			
0	0	68	74
0	1	* 32	31
1	0	* 32	13
0	2	222	256
2	0	245	264
0	3	* 35	67
3	0	* 35	12
0	4	* 37	3
4	0	60	35
0	5	* 39	16
5	0	* 39	48
0	6	277	303
0	7	* 38	14
0	8	* 32	46
0	9	117	101
1	1	* 40	37
1	2	123	115
2	1	78	74
1	3	* 43	38
3	1	70	60
1	4	* 44	68
4	1	* 44	29
1	5	* 47	19
5	1	* 47	33
1	6	226	211
1	7	* 49	58
1	8	132	142
1	9	102	97
2	2	386	424
2	3	101	103
3	2	138	132
2	4	160	157
4	2	151	150
2	5	* 41	23
5	2	* 41	12
2	6	124	128
2	7	78	96
2	8	154	141
2	9	198	170
3	3	* 44	68
3	4	* 47	26
4	3	* 47	0
3	5	72	77
5	3	72	77
3	6	* 47	18
3	7	66	76
3	8	* 40	33
3	9	68	62
4	4	94	108
4	5	180	180
5	4	185	194
4	6	57	58
4	7	* 27	42
4	8	84	78
4	9	62	71
5	5	112	108
5	6	115	139
5	7	44	45
5	8	68	67
L=7			
0	1	81	73
1	0	* 36	19
0	2	174	219
2	0	230	266
0	3	* 38	49
3	0	* 38	10
0	4	* 39	20
4	0	* 39	6
0	5	97	103
5	0	97	111
0	6	155	138
0	7	* 32	10
0	8	105	107
0	9	111	121
1	1	* 44	33
1	2	98	101
2	1	* 45	22
1	3	* 47	23
3	1	* 47	17
1	4	* 48	76
4	1	52	68
1	5	* 40	48
5	1	62	61
1	6	* 48	49
1	7	* 44	50
1	8	83	57
1	9	* 35	45
2	2	362	425
2	3	* 40	52
3	2	* 40	26
2	4	224	243
4	2	202	244
2	5	74	87
5	2	74	71
2	6	119	122
2	7	* 37	12
2	8	68	65
2	9	94	133
3	3	* 47	21
3	4	* 47	53
4	3	* 47	40
3	5	* 47	2
5	3	* 47	20
3	6	86	80
3	7	* 41	27
3	8	* 39	53
4	4	89	93
4	5	60	56
5	4	81	76
4	6	179	191
4	7	* 24	30
4	8	81	96
5	5	57	57
5	6	* 27	50
5	7	68	88
L=8			
0	0	* 39	29
0	1	95	95
1	0	95	91
0	2	212	241
2	0	236	257
0	3	* 39	29
3	0	* 39	25
0	4	116	126
4	0	74	69
0	5	114	100
5	0	70	70
0	6	76	72
0	7	* 28	32
0	8	* 25	15
1	1	95	98
1	2	* 49	34
2	1	103	101
1	3	* 49	61
3	1	* 49	39
1	4	* 49	60
4	1	134	118
1	5	102	94
5	1	130	124
1	6	91	65
1	7	* 39	45
1	8	52	55
2	2	192	204
2	3	72	75
3	2	72	69
2	4	146	129
4	2	104	90
2	5	141	141
5	2	78	83
2	6	205	204
2	7	68	59
2	8	50	76
3	3	* 45	35
3	4	* 44	32
4	3	* 44	32
3	5	91	106
5	3	124	126
3	6	74	69
3	7	60	66
4	4	* 28	6
4	5	84	77
5	4	* 27	31
4	6	114	123
5	5	72	92
5	6	62	90
L=9			
0	1	91	90
1	0	* 37	25
0	2	* 35	17
2	0	* 35	33
0	3	* 34	3
3	0	* 34	12
0	4	* 32	43
4	0	* 32	6
0	5	* 29	4
5	0	* 29	38
0	6	117	113
0	7	* 25	22
1	1	210	203
1	2	* 48	16
2	1	* 48	53
1	3	148	146
3	1	131	139
1	4	* 44	47
4	1	76	77
1	5	102	102
5	1	103	120
1	6	131	126
1	7	64	83
2	2	* 40	15
2	3	94	84
3	2	60	80
2	4	110	109
4	2	110	99
2	5	169	161
5	2	112	123
2	6	117	107
3	3	76	90
3	4	89	47
4	3	89	91
3	5	133	144
5	3	151	171
3	6	60	64
4	4	64	61
4	5	89	111
5	4	47	50
5	5	52	75
L=10			
0	0	* 31	29
0	1	* 31	52
1	0	* 31	7
0	2	* 29	2
2	0	* 29	31
0	3	100	51
3	0	* 28	34
0	4	* 26	11
4	0	* 26	13
0	5	98	112
5	0	* 25	7
1	1	102	95
1	2	* 41	44
2	1	60	65
1	3	203	220
3	1	186	199
1	4	* 37	27
4	1	60	63
1	5	118	141
5	1	101	145
2	2	* 37	20
2	3	* 36	34
3	2	* 36	40
2	4	* 35	31
4	2	* 35	12
2	5	55	61
5	2	33	61
L=11			
0	1	* 25	38
1	0	78	83
0	2	* 25	36
2	0	* 25	8
0	3	50	77
3	0	* 24	46
1	1	162	194

Notwithstanding the pseudo-tetragonal appearance, there are no pseudo-fourfold rotation or screw axes.

Fig. 1(*a*) shows that many atoms in the structure are related by pseudo-twofold axes in the direction [110] at $z=0{\cdot}09$ and $z=0{\cdot}59$ (through both $x=\frac{1}{2}$, $y=0$ and $x=\frac{1}{2}$, $y=\frac{1}{2}$). Also, many atoms are related by pseudo-twofold axes in the direction [$\bar{1}$10] at $z=0{\cdot}41$ and $z=0{\cdot}91$ (through both $x=\frac{1}{2}$, $y=0$ and $x=\frac{1}{2}$, $y=\frac{1}{2}$). If the structure were to be truly tetragonal the twofold axes governing all atoms would have to be at $z=\frac{1}{8}$ (and $\frac{5}{8}$) and $z=\frac{3}{8}$ (and $\frac{7}{8}$) respectively, and very drastic changes in the present structure would have to be made. A 4_1 axis would appear at $0, 0, z$ (and $\frac{1}{2}, \frac{1}{2}, z$) and the strong vectors at $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{8})$ and $(0, \frac{1}{2}, \frac{1}{8})$ would now represent real repeats of $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, 0)$ and $(0, \frac{1}{2}, 0)$. This would give a resulting tetragonal cell one fourth of the volume of the orthorhombic cell and lead to space group symmetry $P4_122$. The σ-phase type diffraction pattern would be destroyed since some of the very strong reflections caused by the σ-phase type nets have odd h or k, and would therefore be extinguished for the smaller tetragonal cell. The number of atoms per δ-phase cell would have to be decreased or increased, since there are eleven and three atoms respectively around the assumed positions for the 4_1 axes.

Related to the presence of the pseudo-twofold axes in the diagonal directions are pseudo-twofold screw axes in positions between the positions of the true twofold screw axes. The positions of these pseudo-twofold screw axes depend on what atoms one assumes are related to each other. From Fig. 1(*a*) it can be seen that these pseudo-screw axes are at: $\frac{1}{2}, \frac{3}{4}, z$; $\frac{3}{4}, y, 0{\cdot}18$ or $0{\cdot}32$; $x, \frac{1}{2}, 0{\cdot}07$ or $0{\cdot}43$. In many cases these pseudo-axes relate atoms of different weight.

A model of the refined structure showed that the atoms form an approximately planar arrangement of hexagons, pentagons and triangles in the (041) and (401) planes, which form angles of 14·4° with the (010) and (100) planes respectively, in agreement with the 15° angle of tip predicted for the σ-phase-type nets from the three-dimensional Patterson function. The arrangements followed through four unit cells in the z direction (shown in Figs. 2(*a*) and 2(*b*)) are similar but not identical with that found in the rhombohedral R phase in the ($\bar{1}\bar{3}5$) plane (Komura, Sly & Shoemaker, 1960). The vertical distances from the planes are smaller than 0·20 Å, except in the faulting regions where distances occur up to 0·65 Å. These faulting regions occur where the linear rows of interlayer atoms come to a stop at the transition from one unit cell to the next.

The arrangements of hexagon- and pentagon-strips and double triangles in the almost planar regions resemble some sequences considered for layered complex alloy structures by Frank & Kasper (1959). In the δ phase, as in the P and R phases, we find hexagon-strips followed by pentagon-strips without double triangles (denoted 'p strips' by Frank & Kasper) in between, but in the δ phase there are also pentagon-strips with double triangles on both sides (just as, in the R phase, there are hexagon-strips with double triangles on both sides).

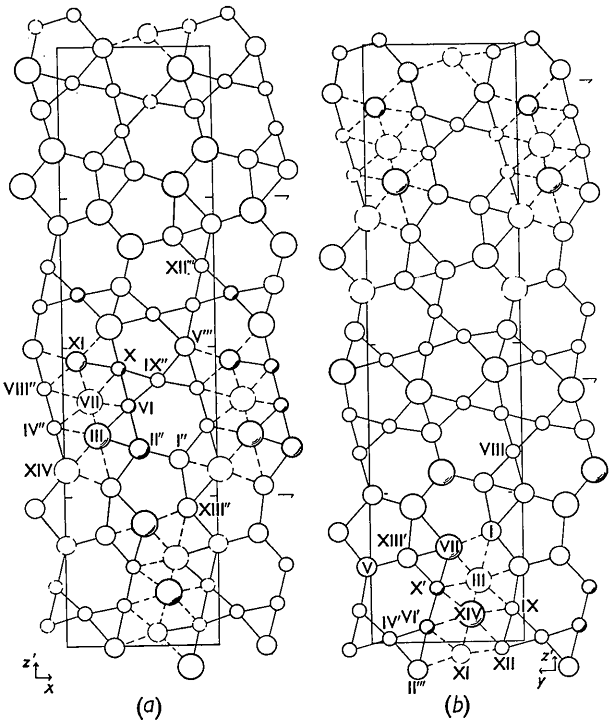

Fig. 2. (*a*) Delta phase: projection of nearby atoms normally onto the (04$\bar{1}$) plane passing through the origin. A right-handed system of axes is assumed. Dashed lines indicate ligands between atoms whose component of interatomic distance normal to the plane is larger than 0·35 Å. For clarity, atoms with normal distances to the plane larger than 0·65 Å have been omitted. Atoms with normal distances larger than 0·20 Å above the plane are shaded; those with normal distances larger than 0·20 Å below the plane are in broken lines. Numbering of the atoms is as in Table 4. (*b*) Delta phase: projection of nearby atoms normally onto the (40$\bar{1}$) plane passing through (0, 0, $-\frac{1}{4}$). A right-handed system of axes is assumed; conventions as in (*a*).

On comparing the arrangements in Figs. 2(*a*), (*b*), which are very similar but not identical, one finds it understandable that the diffraction pattern should have nearly tetragonal symmetry, since practically the same vectors (with x and y component interchanged) occur in the two views of the structure (*i.e.* the structure is almost 'homometric' with its reflection in the $x=y$ plane). However, similar regions in the two kinds of layer are differently located with respect to the twofold screw axes lying in the layers.

As previously mentioned, the pseudo-twofold screw axes often relate atoms of different weight. Accordingly it may be postulated that the observed deviations from tetragonal symmetry are due in part to the ordering of the atoms. In support of this suggestion, a set of calculated structure factors based on a single scattering factor for all atoms has shown smaller deviations from tetragonality.

Interatomic distances and coordination polyhedra

The interatomic distances, calculated with the IBM 704 program ORXFE (Busing & Levy, 1959*b*), are listed in Table 4.

The close relationship anticipated before (Shoemaker, Fox & Shoemaker, 1960) between the δ phase and the other σ-type transition-metal alloys, shows up clearly in the kinds of coordination polyhedra actually found. As in the *P* phase (Shoemaker, Shoemaker & Wilson, 1957), the *R* phase (Komura, Sly & Shoemaker, 1960) and the μ phase (Arnfeld & Westgren, 1935) all the atoms are 12, 14, 15 or 16

Table 4. *Observed interatomic distances and differences with the predicted distances (see text) for the δ phase*

The standard deviation in the distances varies between 0·01 and 0·03 Å

Atom I

Atom†	Translation	D_o	$\Delta \times 10^3$
II		*2·469	12
III		3·120	43
IV		2·676	38
V		2·877	−5
V′	$0\bar{1}0$	2·968	86
VI		2·593	−44
VII		2·867	−121
VIII′	$0\bar{1}0$	2·692	54
IX′	$0\bar{1}0$	2·643	6
X		2·568	−69
XI		2·882	0
XII		2·595	−42
XIII	001	2·946	64
XIV″		*2·554	−7
14		Average	42

Atom II

Atom	Translation	D_o	$\Delta \times 10^3$
I		*2·469	12
III″	$\bar{1}00$	*2·615	−17
III		3·238	162
IV″	$\bar{1}00$	2·561	−76
V		2·853	−29
VI″	$\bar{1}00$	2·551	−86
VII‴	$\bar{1}\bar{1}0$	3·002	14
VII		3·064	76
VIII′	$0\bar{1}0$	2·625	−13
VIII″	$\bar{1}00$	2·548	−89
XI‴	$\bar{1}\bar{1}0$	2·822	−60
XI		3·053	171
XII		2·561	−76
XIII″	$\bar{1}00$	2·848	−34
14		Average	65

Atom III

Atom	Translation	D_o	$\Delta \times 10^3$
I		3·120	43
II″		*2·615	−17
II		3·238	162
IV″	$\bar{1}00$	2·726	−106
IV		2·780	−52
V		*2·608	−24
VI		2·656	−175
VI″	$\bar{1}00$	2·958	126
VII		*2·772	36
VII′	$00\bar{1}$	3·278	96
VIII		2·843	11
IX		2·751	−81
X′	$00\bar{1}$	2·747	−85
XI′	$00\bar{1}$	3·087	10
XIII		3·093	16
XIV		*2·740	4
16		Average	65

Atom IV

Atom	Translation	D_o	$\Delta \times 10^3$
I		2·676	38
II″		2·561	−76
III″		2·726	−106
III		2·780	−52
V		2·585	−53
VI		2·358	−35
VII″		2·715	−28
VIII		2·420	27
IX′	$0\bar{1}0$	2·473	80
X‴	$0\bar{1}0$	2·465	71
XII′	$0\bar{1}\bar{1}$	2·472	79
XIV″		2·680	−64
12		Average	59

Atom V

Atom	Translation	D_o	$\Delta \times 10^3$
I		2·877	−5
I′	$0\bar{1}\bar{1}$	2·968	86
II		2·853	−29
III		*2·608	−24
IV		2·585	−53
VI″	$\bar{1}00$	2·619	−18
VIII		2·693	56
VIII′	$0\bar{1}0$	2·639	1
IX		2·580	−58
IX′	$0\bar{1}0$	2·650	13
XI‴	$\bar{1}\bar{1}0$	2·910	28
XII′	$0\bar{1}\bar{1}$	2·680	43
XIII′	$0\bar{1}0$	*2·485	28
XIV‴	$\bar{1}\bar{1}\bar{1}$	3·019	31
14		Average	34

Atom VI

Atom	Translation	D_o	$\Delta \times 10^3$
I		2·593	−44
II″		2·551	−86
III		2·656	−175
III″		2·958	126
IV		2·358	−35
V″		2·619	−18
VII		2·678	−66
IX″		2·472	79
X		2·458	64
XI′	$00\bar{1}$	2·577	−61
XIV′		2·787	43
XIV″		2·843	99
12		Average	75

Table 4 (*cont.*)

Atom VII

Atom	Translation	D_o	$\Delta \times 10^3$
I		2·867	−121
II‴	$\bar{1}00$	3·002	14
II		3·064	76
III		*2·772	36
III′		3·278	96
IV″	$\bar{1}00$	2·715	−28
VI		2·678	−66
VIII″	$\bar{1}00$	2·743	0
X		2·668	−76
X′	$00\bar{1}$	2·679	−64
XI		*2·556	−5
XI′	$00\bar{1}$	2·991	3
XII‴	$\bar{1}00$	2·795	52
XIII′		*2·538	−22
XIV′		3·112	18
15		Average	45

Atom VIII

Atom	Translation	D_o	$\Delta \times 10^3$
I′	$0\bar{1}\bar{1}$	2·692	54
II′	$0\bar{1}\bar{1}$	2·625	−13
II″		2·548	−89
III		2·843	11
IV		2·420	27
V		2·693	56
V′	$0\bar{1}\bar{1}$	2·639	1
VII″		2·743	0
IX		2·382	−11
XI″		2·583	−55
XII′	$0\bar{1}\bar{1}$	2·418	25
XIII		2·597	−40
12		Average	32

Atom IX

Atom	Translation	D_o	$\Delta \times 10^3$
I′	$0\bar{1}\bar{1}$	2·643	6
III		2·751	−81
IV′	$0\bar{1}\bar{1}$	2·473	80
V		2·580	−58
V′	$0\bar{1}\bar{1}$	2·650	13
VI″	$\bar{1}00$	2·472	79
VIII		2·382	−11
X″	$\bar{1}00$	2·427	33
XII	$00\bar{1}$	2·494	100
XIII		2·611	−26
XIV‴	$\bar{1}\bar{1}\bar{1}$	2·755	11
XIV		2·633	−111
12		Average	51

Atom X

Atom	Translation	D_o	$\Delta \times 10^3$
I		2·568	−69
III′		2·747	−85
IV‴		2·465	71
VI		2·458	64
VII		2·668	−76
VII′		2·679	−64
IX″		2·427	33
XI		2·547	−90
XII″	001	2·533	139
XIII	001	2·647	10
XIV′		2·696	−48
XIV″		2·908	164
12		Average	76

Atom XI

Atom	Translation	D_o	$\Delta \times 10^3$
I		2·882	0
II‴	$\bar{1}00$	2·822	−60
II		3·053	171
III′		3·087	10
V‴	$\bar{1}00$	2·910	28
VI′		2·577	−61
VII		*2·556	−5
VII′		2·991	3
VIII′	$\bar{1}00$	2·583	−55
X		2·547	−90
XII		2·549	−88
XIII	001	2·859	−23
XIII″	$\bar{1}00$	3·040	158
XIV	001	*2·554	−6
14		Average	54

Atom XII

Atom	Translation	D_o	$\Delta \times 10^3$
I		2·595	−42
II		2·561	−76
IV′	$0\bar{1}0$	2·472	79
V′	$0\bar{1}0$	2·680	43
VII‴	$\bar{1}\bar{1}0$	2·795	52
VIII′	$0\bar{1}0$	2·418	25
IX	001	2·494	100
X″	$\bar{1}01$	2·533	139
XI		2·549	−88
XIII″	$\bar{1}00$	2·534	−104
XIII	001	2·649	12
XIV	001	2·709	−35
12		Average	66

coordinated. The symmetry of the coordination polyhedra is close to the ideal symmetry as described by Frank & Kasper (1958, 1959) and in connection with the P- and σ-phase structures by Shoemaker, Shoemaker & Wilson (1957). Thus all the coordination shells are triangulated and all the interstices are tetrahedral. No irregular CN13 polyhedra such as are found in the χ phase (α-Mn) occur.

In all related structures so far investigated some symmetry is imposed on the coordination polyhedra by the space groups. In the σ and P phases almost all atoms lie in mirror planes. In the R, μ and Laves phases several atoms lie on threefold axes, thus determining the direction of these axes in the CN12, 14, 15 or 16 polyhedra for these atoms. The δ phase is the first example in this class of structures where no symmetry is imposed on any of the coordination polyhedra by the space group.

The number of atoms per unit cell with a given coordination type is the same for the δ phase as was found previously for the P phase: per unit cell of 56 atoms there are 24 atoms with CN12, 20 with CN14, 8 with CN15 and 4 with CN16.

Table 4 (*cont.*)

Atom XIII

Atom	Translation	D_o	$\Delta \times 10^3$
I	$00\bar{1}$	2·946	64
II″		2·848	−34
III		3·093	16
V′	$0\bar{1}\bar{1}$	*2·485	28
VII′	$00\bar{1}$	*2·538	−22
VIII		2·597	−40
IX		2·611	−26
X	$00\bar{1}$	2·647	10
XI	$00\bar{1}$	2·859	−23
XI″		3·040	158
XII″		2·534	−104
XII	$00\bar{1}$	2·649	12
XIV		2·848	−140
XIV″	$00\bar{1}$	3·118	130
14		Average	58

Atom XIV

Atom	Translation	D_o	$\Delta \times 10^3$
I″	$\bar{1}00$	*2·554	−7
III		*2·740	4
IV″	$\bar{1}00$	2·680	−64
V‴	$\bar{1}0\bar{1}$	3·019	31
VI′	$00\bar{1}$	2·787	43
VI″	$\bar{1}00$	2·843	99
VII′	$00\bar{1}$	3·112	18
IX‴	$\bar{1}0\bar{1}$	2·755	11
IX		2·633	−111
X′	$00\bar{1}$	2·696	−48
X″	$\bar{1}00$	2·908	164
XI	$00\bar{1}$	*2·554	−6
XII	$00\bar{1}$	2·709	−35
XIII		2·848	−140
XIII″	$\bar{1}0\bar{1}$	3·118	130
15		Average	61

Number of different distances	94
Average distance	2·716
Largest distance	3·278
Smallest distance	2·358
Average deviation between observed and predicted distances	0·056
Largest deviation	0·175

† The unprimed atoms have coordinates as listed in Table 2. The primed atoms are obtained by the following symmetry operations: single prime: $0{\cdot}5-x,\ 1{\cdot}0-y,\ 0{\cdot}5+z$; double prime: $0{\cdot}5+x,\ 0{\cdot}5-y,\ 1{\cdot}0-z$; triple prime: $1{\cdot}0-x,\ 0{\cdot}5+y,\ 1{\cdot}5-z$. Applying the symmetry operation and then the translations to the coordinates of the atoms in Table 2 gives the coordinates of the coordinating atom.

* Asterisks indicate major ligands.

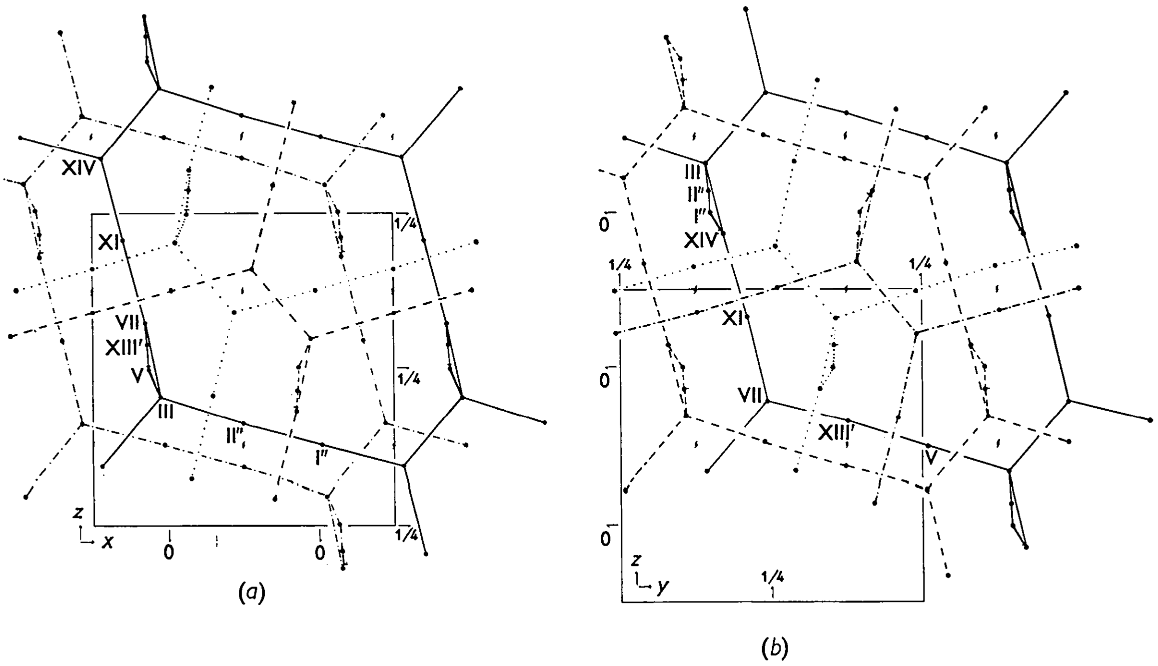

Fig. 3. (*a*) Projection of the major networks in the δ phase down the y axis. The y axis is pointing into the paper. The order of the 'kagomé tiles', proceeding in the positive y direction (into the paper), is: dashed line, solid line, dotted line, alternating dots and dashes. Numbering of the atoms is as in Table 4. (*b*) Projection of the major networks in the δ phase down the x axis. The x axis is pointing out of the paper. The order of the 'kagomé tiles', proceeding in the negative x direction (into the paper), is: alternating dots and dashes, dashed line, dotted line, solid line.

Major networks

In agreement with what was found before in the related structures, the ligands in the δ-phase structure can be divided into two types: 5-coordinated ('minor ligands') and 6-coordinated ('major ligands'), the latter being shorter for a particular pair of atoms and thus possibly giving stronger bonding. There are four non-interconnected three-dimensional networks formed by the major ligands in the δ phase ('major skeletons') (Fig. 1(*b*)). Three-dimensional networks of major ligands have been found before: in the R and Laves phases there is one three-dimensional major skeleton; in the P phase there are two non-interconnected three-dimensional nets with additional rows of major ligands; in the μ phase one three-dimensional net occurs with non-connected planes of major ligands.

The projections of these major skeletons down the x and y axes (Figs. 3(*a*) and 3(*b*)) show a striking resemblance to the major networks in the σ-phase. In that structure the major ligands form a repetition of two networks in parallel planes built up from 'kagomé tiles' and additional lines connecting atoms in rows perpendicular to these planes. In the δ phase there are the two 'kagomé tile' nets similar to the ones found in the σ phase, but these are then shifted and repeated once more. These networks are not planar in the δ phase; of the four CN14 atoms in the σ phase one is replaced by a CN15 atom in the δ phase and of the two CN15 atoms in the σ phase one is replaced by a CN16 atom in the δ phase. It is apparent in Figs. 3(*a*) and 3(*b*) that the row lines of CN14 atoms in the σ phase form part of the three-dimensional frameworks in the δ phase. There are four such CN14 atoms per network per cell in the σ phase, compared with two in the δ phase, the other two being replaced by two CN12 atoms. To the additional five CN12 atoms per network per cell of the σ phase correspond only four CN12 atoms in the δ phase, since one CN12 atom has been squeezed out by the CN16 atom. In sum, the σ phase has, per unit cell per 'layer', relatively fewer CN12 atoms (5 out of a total of 15 atoms) than the δ phase (6 out of a total of 14 atoms).

Figs. 3(*a*) and 3(*b*) show again the very strong similarity between views of the structure along the y axis and along the x axis. The network shown by solid lines in Fig. 3(*a*) is puckered in almost the same way as that shown by dashed lines in Fig. 3(*b*), atoms in corresponding positions having corresponding coordinations. These two networks have, however, a different orientation with respect to the twofold screw axes. This different orientation with respect to the screw axes in the y, and the x directions respectively, can be seen in Figs. 3(*a*) and 3(*b*); a twofold screw axis in the y direction (Fig. 3(*a*)) corresponds to a pseudo-twofold screw axis, roughly halfway between the true screw axes, in the x direction (Fig. 3(*b*)), and *vice versa*. In the same way pseudo-screw axes correspond to true screw axes in the z direction. As a result the 'kagomé' layers are stacked in a different fashion. (The pseudo-twofold screw axes show up better in Fig. 1(*a*) than in Fig. 3, because they relate in many cases atoms of different weight and the CN12 atoms are not shown in Fig. 3).

The angles between the major ligands were calculated on the IBM 709, using a program written by Peacor & Prewitt (1962), and are listed in Table 7. The largest deviations for the CN14 atoms occur for atoms I″ and V, which have major-ligand angles deviating about 8° from the ideal value of 180°. For both CN15 atoms the angles deviate up to 6·5° from the ideal 120° value. The major ligands around the CN16 atoms are very close to tetrahedral symmetry, the largest deviations being about 3·5° from the ideal value of 109·5°.

Fig. 3 shows that the CN14 atoms divide roughly into three types in relation to their environment: (1) atoms II and V, each of which is ligated with one CN16 and one CN14 atom (of type 2), (2) atoms I and XIII, each of which is ligated with one CN15 and one CN14 atom (of type 1), and (3) atom XI, which is ligated with two CN15 atoms. These are the same groupings as were made on the basis of scattering factor refinement and indicated in Table 1. Those groupings were made primarily for computational convenience, but may indeed have real significance in relation to the atomic environments.

Considering the similarity of the layers in the two directions, one wonders whether twinning might be expected to occur. One might for example imagine that twinning could arise from a 'stacking fault' which would interchange true and pseudo-screw axes. The deviation from tetragonality may be described by an R index defined by $\Sigma|\Delta|/\frac{1}{2}\Sigma|F|$, where $\Delta = |F(hkl)|-|F(khl)|$ and only those pairs of reflections are included for which both members have been observed. For the calculated structure factors this R index is 0·174, and for the observed ones 0·144. This slight difference can hardly be taken as strong evidence for twinning. Moreover, two crystals were used in the collection of intensity data and the amount of twinning in these two specimens would have to have been approximately the same.

Thermal parameters

All atoms have 12 minor ligands; in addition the CN14 atoms have two major ligands forming a straight line, the CN15 atoms have three major ligands in a plane and the CN16 atoms have four tetrahedrally oriented major ligands. It was therefore expected that the thermal motion of the CN12 and 16 atoms would be nearly isotropic, that the CN14 atoms would show the smaller displacements in the direction of the major ligands and that the CN15 atoms would show the larger displacements perpendicular to the plane formed by the major ligands. The anisotropic temperature factors arrived at, however, could not be interpreted in this way. If the atoms do have significantly anisotropic thermal motions in the expected sense, then these are apparently obscured by inadequacies in the data, caused for instance by scaling or neglect of absorption corrections. The crystals used were very small (no larger than 100 microns) but irregular in shape, and the linear absorption coefficient is large (for Cu $K\alpha$ about 1100 cm^{-1}). However, a least-squares cycle run with the lower order reflections left out gave similar disappointing results.

Any amount of twinning that may exist (see the previous section) might also obscure any anisotropy of the thermal motions and perhaps account for the lack of correspondence between the observed atomic anisotropies and the coordination symmetries.

The isotropic temperature factors appear to increase with decreasing coordination number, and hence with decreasing number of major ligands. This may reflect a tighter bonding for the higher-coordinated atoms. However there may be some question whether this observation is significant in view of the uncertainties in the scattering factors used for Ni and Mo.

Analysis of the interatomic distances

The distances occurring in the δ phase were analyzed in the same way as was done before for the σ, *P* and *R* phases. A least-squares program was written which derived, from the interatomic distances, 5-coordinated (minor) and 6-coordinated (major) radii for each kind of atom. There are 94 non-equivalent distances and 24 radii are to be determined (one for each CN12 atom, two for each CN14 and CN16 atom and three for each CN15 atom). All minor radii came out as expected but the result for the major radii was rather surprising: they were alternately very large and negative for atoms along a major row line. The particular arrangement of these atoms in this structure happens to put only a very weak constraint on the value of any individual major radius, with the result that the normal-equation matrix is nearly singular.

Table 5. *Summary of radii for the δ phase*

CN	Atom	r	r′	r*
12	IV	1·186		
	VI	1·190		
	VIII	1·195		
	IX	1·199		
	X	1·203		
	XII	1·207		
		1·197		
14	I	1·441		
	II	1·438		
	V	1·448		
	XI	1·440		
	XIII	1·438		
		1·441		1·228
15	VII	1·528	1·548	1·335
	XIV	1·548	1·565	1·329
		1·547		1·332
16	III	1·635		1·403

Table 7. *Angles between major ligands in the δ phase*

Atom	Angle	
II″	III–II″–I″	175·6°
V	III–V–XIII′	172·3
I″	XIV–I″–II″	171·5
XIII′	VII–XIII′–V	177·2
XI	XIV–XI–VII	176·7
VII	XI–VII–III	126·5
	III–VII–XIII′	116·3
	XI–VII–XIII′	117·1
XIV	XI–XIV–III	125·2
	III–XIV–I″	114·6
	XI–XIV–I″	120·2
III	VII–III–XIV	108·9
	VII–III–II″	110·2
	XIV–III–V	107·0
	VII–III–V	111·7
	XIV–III–II″	113·1
	V–III–II″	106·0

There are ten such independent distances in the major network and we had attempted to determine eight radii from these. In the next run only one major radius was determined for all CN14 atoms, thus reducing the number of variables by four. The resulting radii and their averages for each coordination type are given in Table 5. These agree very well with the results obtained before for the σ and *R* phases and particularly for the *P* phase. 'Predicted' interatomic distances, calculated with these average radii, are given in Table 6 and the observed interatomic distances and their differences with the 'predicted' distances in Table 4. These differences are of the same order as those found in the *R* phase (largest difference 0·175 Å, average difference 0·056 Å for both phases), and somewhat larger than those found previously in the *P* and σ phases.

Table 6. *Predicted interatomic distances in the δ phase*

	CN12	CN14		CN15		CN16	
CN12	2·393						
CN14	2·638	2·882	*2·457				
CN15	2·744	2·988	*2·561	3·094	*2·664		
CN16	2·832	3·076	*2·632	3·182	*2·735	3·270	*2·806

Conclusion

Both the δ and the R phases are examples of structures containing atoms with triangulated coordination shells and coordination numbers 12, 14, 15 and 16, but with regions where the planar layering of the atoms has been disturbed. Frank & Kasper (1958) anticipated that deviations from a planar arrangement might occur in structures of this type, but concluded that there was 'strong indication that structures containing exclusively "normal coordinations" will be "layer structures" having unlimited coplanar or approximately coplanar arrays of neighboring atoms'. Therefore in their analysis and classification of these complex alloy structures (Frank & Kasper, 1959) only structures based on the planar or approximately planar layering of the atoms were considered. Both the δ and the R phases show that large deviations from planarity may occur even with 'normal coordinations' for all of the atoms. It seems therefore that in any further classification of these alloy structures, an attempt should be made to take into account significant deviations from the planar layering of the atoms.

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Die Kristallstruktur von Dolerophanit, $Cu_2O(SO_4)$

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Dolerophanite, $Cu_2O(SO_4)$, crystallizes in the spacegroup $C2/m$ with the unit-cell dimensions:

$$a=9{\cdot}355,\ b=6{\cdot}312,\ c=7{\cdot}628\ \text{Å},\ \beta=122°\ 17{\cdot}5',\ Z=4\,.$$

The structure has been determined and refined by electron-density projections and a generalized projection. Two types of coordination around Cu have been found: Cu(2) surrounded by 5 oxygen atoms at approximately equal distances (1·87–2·14 Å) forming a trigonal dipyramid, and Cu(1) in [4 + 2] coordination (distorted octahedron) with oxygen. The $Cu^{[4+2]}O_6$ octahedra form chains along [010] connected by double groups of trigonal dipyramids.

Dolerophanit, $Cu_2O(SO_4)$ entstand als Sublimationsprodukt während des Vesuvausbruches im Jahre 1868 und wurde von Scacchi (1873) erstmals beschrieben. Bisher blieb dieses Vorkommen das einzige natürliche. Kristalle aus einem Hochofen in Åtvidaberg (Schweden) mit derselben chemischen Zusammensetzung wie Dolerophanit konnten von Strandmark (1902) vermessen werden. Als Pulver lässt sich Dolerophanit leicht durch Erhitzen von $CuSO_4.5H_2O$ auf 650 °C herstellen (Mrose, 1961).

Kristalle vom Vesuv, die zur Untersuchung zur Verfügung standen, sind fast durchwegs allseitig ausgebildet und von hell- bis dunkelbrauner Farbe.

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