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The Crystal Structure of the *M* Phase, Nb–Ni–Al*

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The crystal structure of the *M* phase ($Nb_{48}Ni_{39}Al_{13}$) has been determined by single-crystal X-ray analysis. The lattice constants are $a_0=9{\cdot}303(6)$, $b_0=16{\cdot}266(10)$, $c_0=4{\cdot}933(2)$ Å, and the space group is *Pnam* (D_{2h}^{16}). The crystal structure resembles that of the (Mo–Ni–Cr) *P* phase [space group *Pbnm* (D_{2h}^{16})], except that there are fewer atoms per unit cell (52 for the *M* phase, 56 for the *P* phase), the glide plane types are interchanged between the *a* and *b* axes, and five-membered rings replace all six-membered rings in the main layers. The structure has been refined by full-matrix least-squares analysis to a final *R* of 0·115, based on the 420 observed reflections. The atoms have characteristic coordination polyhedra with 12, 14, 15 and 16 vertices in the same relative numbers as in the μ phase. All positions with C.N.14, C.N.15, and C.N.16, are occupied essentially completely by Nb; the positions with C.N.12 are occupied by a mixture of Ni and Al and possibly some excess Nb. The atomic radii calculated from the observed distances are about 4% larger than those in the (Mo–Ni–Cr) *P* phase, the (Mo–Ni) δ phase, the (Mo–Co) μ phase, and about 5% smaller than those in the (Nb_2Al) σ phase. This structure turns out to be one of several predicted on geometrical grounds by Frank & Kasper (*Acta Cryst.* **12**, 483).

Introduction

The *M* phase was discovered by Benjamin, Giessen & Grant (1966) in ternary systems of Nb and Ni with Al, Ga or Cu. The *M*-phase field in the Nb–Ni–Al system appears in the vicinity of a μ-phase field and both fields are elongated approximately parallel to the Ni–Al binary line, suggesting that Al and Ni occupy the same kinds of site in the structure. A Laves-phase (*C*14) field in the same diagram is elongated in the same direction. The powder diffraction diagram of the *M* phase is very complex and shows the same bunching of strong lines as has been observed in powder diagrams for the σ-phase related structures μ, *P*, δ, *R etc.* Thus it appeared that the *M* phase was a new member of the family of σ-phase related structures, of which many members have been found in studies of ternary systems of transition metals with non-transition elements, notably Si (*e.g.* Bardos & Beck, 1966).

A specimen of the *M* phase of Nb–Ni–Al in stated atomic ratio 48:39:13, annealed at 1140°C for 20 hours, was kindly made available to us by Dr Bill C. Giessen of M.I.T. for single-crystal study. The composition was estimated from ratios of the constituent elements used, with allowance for estimated weight losses; no analysis was made.

Experimental

Approximate values for the cell dimensions were obtained from precession photographs of a single-crystal fragment and were refined by a least-squares fit of the diffraction peaks observed on a spectrogoniometer trace taken with Cu $K\alpha$ radiation, using our program 'LSCELP' (Shoemaker & Shoemaker, 1965). The dimensions of the orthorhombic cell are:*

$$a_0=9{\cdot}303(6),\ b_0=16{\cdot}266(10),\ c_0=4{\cdot}933(2)\ \text{Å}\,.$$

Table 1 is the output of LSCELP and shows the indexing of the powder diagram and the agreement obtained for the observed and calculated θ values. The cell dimensions of the *M* phase are very similar to those for the *P* phase (Shoemaker, Shoemaker & Wilson, 1957): a_0 and c_0 are about 3% larger, but b_0 is about 5% shorter. The systematic absences show that the same glide planes occur in the *M* and the *P* phases but that the types are interchanged between the *a* and *b* axes. The space group for the *P* phase is *Pbnm* (D_{2h}^{16}), and the possible space groups indicated by the extinctions for the *M* phase are *Pnam* (D_{2h}^{16}) and *Pna*2_1 (C_{2v}^{9}).

The density of the *M* phase as measured with a pycnometer is 8·03(5) g.cm^{-3}. The corresponding calculated number of atoms per unit cell is 50·8(0·3). Since the number of atoms is required by these space groups to be a multiple of four, and since our experience with other phases in this family is that the measured density is generally on the low side, the number of atoms per unit cell was taken to be 52.

A trial structure for the *M* phase in space group *Pnam* was obtained which resembles the *P* phase, except that there are fewer atoms per cell (52 for the *M* phase, 56 for the *P* phase) and five-membered rings replace all six-membered rings in the main layers.

The search for a good single crystal in the crushed material was unsuccessful and the intensity data were

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* Figures in parentheses are standard deviations.

Table 1. *X-ray powder data for the M phase*, Nb–Ni–Al

* THETA OBS is the observed value for the Bragg angle θ (°).
** ICAL is the calculated powder intensity multiplied by 10^{-4}. T = member of triplet, D = member of doublet, B = broad.

IOBS		THETA OBS*	H	K	L	THETA CAL	DELTA THETA	ICAL**
			1	4	0	11.940		16
			1	4	1	15.027		53
			0	5	1	16.491		11
			2	5	0	16.808		20
W		17.175	1	5	1	17.200	-.025	416
			1	6	0	17.229	-.054	10
			3	1	1	17.303	-.128	63
			3	2	1	17.972		14
M		18.200	0	0	2	18.212	-.012	705
VW		19.050	3	3	1	19.041	.009	104
			1	1	2	19.074	-.024	21
			2	5	1	19.189	-.139	17
			2	6	0	19.216		43
S		19.525	4	1	0	19.562	-.037	33
			1	6	1	19.566	-.041	1584
			1	2	2	19.691		17
S	T	20.125	1	7	0	19.996	.129	123
			3	5	0	20.087	.038	77
			4	2	0	20.166	-.041	837
SS	T	20.400	3	4	1	20.457	-.057	1561
W	T	20.825	1	3	2	20.684	.141	150
			2	0	2	20.718	.107	163
			2	1	2	20.911	-.086	392
			4	3	0	21.141		19
SS		21.425	2	6	1	21.367	.058	38
			0	4	2	21.441	-.016	157
			2	2	2	21.484	-.059	394
			4	0	1	21.496	-.071	967
			0	7	1	21.513	-.088	12
			4	1	1	21.684		49
			2	7	0	21.768		52
S	D	22.000	1	4	2	22.013	-.013	854
			1	7	1	22.084	-.084	154
S	D	22.100	3	5	1	22.168	-.068	64
			3	6	0	22.192	-.092	714
			0	8	0	22.281		142
			2	3	2	22.412		122
W		22.800	1	8	0	22.837	-.037	246
			4	3	1	23.145		11
W		23.625	1	5	2	23.633	-.008	164
			2	4	2	23.663	-.038	38
			2	7	1	23.730	-.105	62
W		24.250	3	2	2	24.233	.017	305
			4	4	1	24.367	-.117	157
			3	7	0	24.492		12
			5	1	0	24.646		11
VW		25.150	3	3	2	25.081	.069	34
			5	2	0	25.152	-.002	36
			2	5	2	25.201	-.051	43
			1	9	0	25.755		22
			4	6	0	25.895		16
			2	8	1	26.252		27
			2	6	2	26.993		13
VW	B?	27.700	4	2	2	27.731	-.031	16
VW		30.125	2	10	0	30.138	-.013	41
			2	8	2	31.236		10
VW	?	31.675	2	10	1	31.725	-.050	34
			5	6	1	31.752	-.077	15
VW	B	32.100	6	2	1	31.985	.115	16
			1	5	3	32.127	-.027	53
VW	B	33.200	2	11	0	33.164	.036	53
			3	3	3	33.323	-.123	16
			1	11	1	33.403		13
M		33.650	5	4	2	33.540	.110	16
			5	7	1	33.594	.056	73
			2	9	2	33.652	-.002	58
			1	6	3	33.679	-.029	253
MW		34.300	3	4	3	34.297	.003	269
W	D	34.600	0	12	0	34.662	-.062	72
			2	11	1	34.675	-.075	126
W	D	34.750	5	5	2	34.787	-.037	84
W		35.000	4	0	3	35.040	-.040	184
W		35.325	4	1	3	35.177	.148	10
			4	10	0	35.334	-.009	131
			1	7	3	35.470	-.145	30
			3	5	3	35.532		13
W		35.700	5	8	1	35.658	.042	114
W	D	36.000	6	0	2	35.962	.038	79
			6	1	2	36.097	-.097	45
M	D	36.275	2	10	2	36.257	.018	230
			5	6	2	36.283	-.008	185
			2	12	0	36.326	-.051	10
			6	6	1	36.419	-.144	16
			6	2	2	36.502		18
			2	7	3	36.710		14
W	D	37.200	6	3	2	37.172	.028	48
			4	4	3	37.203	-.003	38
MW	D	37.525	7	2	1	37.456	.069	128
			7	4	0	37.606	-.081	187
			2	12	1	37.781		31
W		38.000	5	9	1	37.940	.060	43
			5	7	2	38.021	-.021	78
			6	4	2	38.104	-.104	37
MW		38.650	0	0	4	38.689	-.039	212
			6	8	0	38.701	-.051	11
MW		39.075	2	11	2	39.053	.022	217
VW	B	42.000	2	12	2	42.050	-.050	75
			6	7	2	42.414		17
			7	4	2	43.284		26
W	B	43.450	1	14	1	43.369	.081	22
			2	10	3	43.388	.062	12
			8	2	1	43.443	.007	39
			8	4	0	43.588	-.138	50
			7	8	0	43.865		13
VW		44.375	6	8	2	44.348	.027	89
VW		44.775	6	10	1	44.784	-.009	62
			5	7	3	45.086		29
			3	14	0	45.118		17
			2	13	2	45.272		37
W	B	45.500	1	7	4	45.439	.061	17
			3	5	4	45.497	.003	10
			4	2	4	45.549	-.049	117
			1	15	0	45.703		17
VW	B	46.100	6	11	0	46.087	.013	15
			2	11	3	46.092	.008	54
			5	12	1	46.119	-.019	10
			6	9	2	46.537		15
			2	7	4	46.620		10
MW	B	47.000	3	6	4	46.915	.085	132
			0	8	4	46.978	.022	25
			5	8	3	47.019	-.019	52
			1	15	1	47.103	-.103	32
			8	0	2	47.128	-.128	42
VW	B	47.400	8	1	2	47.258	.142	10
			1	8	4	47.372	.028	51
			6	11	1	47.489	-.089	35
VW		47.900	4	14	0	47.876	.024	31
			5	13	0	47.942	-.042	11
VW	B	48.750	7	2	3	48.747	.003	64
			2	12	3	49.065		16
			5	2	4	49.103		10
			8	4	2	49.201		24
			5	9	3	49.220		22
			7	8	2	49.480		11
			8	8	0	49.789		20
			5	14	1	52.911		10
			2	10	4	53.299		16
			6	13	1	53.801		17
			3	16	1	54.407		23
			1	14	3	54.751		15
			8	2	3	54.829		26
			6	12	2	54.836		14
			1	5	5	55.155		13
			1	16	2	55.524		17
			1	17	1	55.577		27
			8	10	1	56.072		15
VW	B	56.250	2	11	4	56.166	.084	30
			6	10	3	56.266	-.016	45
VW	B	56.700	1	6	5	56.680	.020	73
			5	15	1	56.881		23
VW	B	57.300	3	4	5	57.307	-.007	83
			5	14	2	57.392	-.092	15
			9	5	2	57.417	-.117	10
W	D	57.575	3	17	0	57.477	.098	18
			10	0	1	57.483	.092	15
W	D	57.675	0	12	4	57.682	-.007	47
W	T	58.050	4	0	5	58.076	-.026	63
MW	T	58.375	6	13	2	58.338	.037	30
			4	10	4	58.386	-.011	91
W	T	58.650	1	7	5	58.530	.120	10
			10	3	1	58.774	-.124	11
			1	15	3	58.826		26
			9	6	2	58.998		24
			3	17	1	59.041		26
			6	11	3	59.262		30
			10	4	1	59.800		16
			1	17	2	60.246		43
			4	4	5	60.420		17
			1	18	1	60.603		15
M	D	60.900	9	9	1	60.836	.064	10
			8	12	0	60.860	.040	36
			7	4	4	60.876	.024	166
			9	7	2	60.928	-.028	50

collected from a relatively large irregularly shaped crystal fragment (largest dimension 0·1 mm), which gave many spurious reflections from attached randomly oriented crystallites. Intensity data were collected with Mo $K\alpha$ radiation for layer lines $hk0$, $hk1$, $hk2$, and $0kl$, $1kl$, $2kl$ with the precession camera and were visually estimated by comparison with an intensity scale. As in the case of the σ phase and P phase the intensities for layer lines $l\pm4$ are equal to the corresponding ones for layer lines l (except for normal decline) indicating that the atoms are confined to layers parallel to (001) planes, quartering the cell. Therefore, no attempt was made to collect a complete set of three-dimensional intensity data. No absorption correction was applied, but an extinction correction was introduced at a later stage of the refinement.

Refinement of the structure

The trial structure was first 'refined' without recourse to the intensity data by adjusting the parameters by least squares to fit the distances to values predicted from the coordination numbers of the atoms, the type of the ligands, and the average 12-coordinated radius of the atoms (Shoemaker & Shoemaker, 1964).

The structure factors for this partially refined structure were calculated with the scattering factors tabulated in *International Tables for X-ray Crystallography* (1962). Anomalous dispersion corrections of $+0{\cdot}40$ for Ni and $-2{\cdot}18$ for Nb were applied (Cromer, 1965). Nb was assumed to occupy the C.N.16, C.N.15 and C.N.14 positions, and Ni, Al and the small amount of remaining Nb were assumed to be uniformly distributed among the C.N.12 positions. The R index for this structure was 0·24.

The refinement was carried out by several cycles of full-matrix least-squares analysis on the IBM 7094 computer with the program ORFLS (Busing, Martin & Levy, 1962). The function minimized was $\Sigma\, w(F_o-F_c)^2$. The standard errors in the structure amplitudes, on which the weights were based, were set equal to 10 for all reflections with $|F_o|\le100$ and to $0{\cdot}10|F_o|$ for $|F_o|>100$. In the first cycles the 420 observed reflections were used and 36 parameters were varied (one scale factor; for each atom x, y and isotropic B; and for atoms X and XI, also z). Since the calculated structure factors for the strong reflections were consistently higher than the observed values, a secondary extinction correction was applied of the form $F_o^{\text{corr}}=F_o(1+gF_o^2)$ with $g=1{\cdot}33\times10^{-6}$. No high intensities occur beyond 2θ of about 52° and g was therefore assumed to be independent of 2θ (Zachariasen, 1963). The final R index ($\Sigma\,|\Delta F|/\Sigma\,|F_o|$, observed reflections only) was 0·115. Including about 400 non-observed reflections with $F_o=\frac{1}{2}F_{\min}$ the R index is 0·178. No structure factors calculated for the non-observed reflections exceed significantly the estimated values of $F_{\min}$. The calculated structure factors are substantially higher than the observed ones for about a dozen strong reflections, principally with $l=2$; it is possible that the scale factor for this layer is somewhat in error.

The final parameters and their standard deviations are listed in Table 2. The z parameters for atoms X and XI are not significantly different from zero (the standard deviations in these parameters are about 0·01 Å). The temperature factors listed in Table 2 were obtained in the previous cycle. Because of the strong interactions between temperature factors and occupancy factors, average values for the temperature factors for atoms of a particular coordination type were taken and held constant in the last cycle, in which the scattering-factor multipliers and the positional parameters but not the overall scale factor were varied. In view of this procedure, the standard deviations given in Table 2 do not fully represent the uncertainties in these parameters. The f_0 values listed in Table 2 show that the positions with C.N.14, C.N.15, and C.N.16 are occupied by Nb (f_0 for Nb after anomalous dispersin correction is 38·8). The number of atoms in such positions per unit cell (24) is about the same as the number of Nb atoms per unit cell indicated by the overall composition (25). One C.N.15 position (position no. IV with $f_0=35{\cdot}5$) may have some Ni and/or some Al admixed in it, but the difference is perhaps not significant. The C.N.12 positions are occupied by essentially the same mixture of Ni and Al (f_0 for 0·75 Ni and 0·25 Al is 24·4), except that position VII has a higher scattering factor, indicating either that it is rich in Ni (f_0 for Ni is 28·4) or that it contains some Nb. Apparently, no position is rich in Al.

The observed and calculated structure factors (calculated with the parameters given in Table 2, except

Table 2. *Atomic parameters for the M phase*

Atom	Position	x	y	z	B	f_0	C.N.
I	4(*c*)	0·0593 (8)	0·1494 (4)	$\frac{1}{4}$	0·63 (0·12)	37·4 (0·9)	14
II	4(*c*)	0·2996 (8)	0·3984 (4)	$\frac{1}{4}$	0·84 (0·12)	37·7 (0·9)	14
III	4(*c*)	0·5242 (8)	0·5410 (4)	$\frac{1}{4}$	0·88 (0·13)	38·7 (0·9)	15
IV	4(*c*)	0·6164 (9)	0·7068 (4)	$\frac{1}{4}$	0·88 (0·13)	35·5 (0·9)	15
V	4(*c*)	0·0144 (9)	0·4482 (4)	$\frac{1}{4}$	1·19 (0·13)	37·2 (0·9)	16
VI	4(*c*)	0·8388 (9)	0·2938 (4)	$\frac{1}{4}$	1·14 (0·13)	38·9 (0·9)	16
VII	4(*c*)	0·0714 (12)	0·6225 (5)	$\frac{1}{4}$	0·72 (0·13)	30·4 (0·8)	12
VIII	4(*c*)	0·3255 (12)	0·6697 (6)	$\frac{1}{4}$	0·77 (0·16)	25·6 (0·8)	12
IX	4(*c*)	0·8168 (12)	0·5778 (6)	$\frac{1}{4}$	0·66 (0·16)	26·3 (0·8)	12
X	8(*d*)	0·1118 (8)	0·2951 (4)	0·0048 (23)	0·63 (0·12)	23·4 (0·6)	12
XI	8(*d*)	0·2550 (7)	0·5450 (4)	−0·0031 (18)	0·75 (0·12)	26·0 (0·6)	12

that *B*'s were averaged as stated above) are given in Table 3. An analysis of *R* as a function of *l* did not suggest that the agreement could be improved by abandoning the mirror planes and formulating a structure in the lower space group $Pna2_1$. It was therefore concluded that *Pnam* is the correct space group.

Description of the structure

The structure is shown, in projection down the *c* axis, in Fig. 1. Atoms X and XI are located at $z=0$ and $z=\frac{1}{2}$ and all other atoms are situated in the mirror planes at $z=\frac{1}{4}$ and $z=\frac{3}{4}$ perpendicular to the *z* axis. In the σ phase, the atoms in the main layers form hexagons and triangles. All the atoms between the main layers center the hexagons in projection and are therefore 14-coordinated. In the *P* phase the atoms in the main layers form hexagons, pentagons and triangles and half of the atoms between the main layers now center pentagons and are therefore 12-coordinated. In the *M* phase the atoms in the main layers form only pentagons and triangles and all the in-between atoms have now C.N.12.

The coordination polyhedra are of the same type as those found previously in the *P* phase (Shoemaker, Shoemaker & Wilson, 1957), the *R* phase (Komura, Sly & Shoemaker, 1960), the μ phase (Forsyth & d'Alte da Veiga, 1962), and the δ phase (Shoemaker & Shoemaker, 1963). The coordination numbers are 16, 15, 14 and 12; all coordination shells are triangulated and all the interstices are tetrahedral. No C.N.13 polyhedra such as are found in the χ phase (α-Mn) occur. The symmetries of the coordination polyhedra have been described by Kasper (1956), by Frank & Kasper (1958, 1959) and by Shoemaker, Shoemaker & Wilson (1957). These structures represent close packings of atoms of different sizes.

The percentage of atoms with a particular coordination type is the same for the *M* phase as for the μ phase: it is 15·4% for each of the coordination types C.N.16, C.N.15, and C.N.14 and 53·8% for C.N.12.

An analysis of the structure of the *M* phase in terms of pentagon-strips and triangle-strips (see bottom of Fig. 1) shows that it is included among the structures predicted by Frank & Kasper (1959) in their analysis of complex alloy structures of this kind. This was at first not recognized since this structure is listed as entry 9 of their Table 3, ostensibly describing structures containing two *different* kinds of layer. This entry, and one other (the third), both with numerical symbol (2,2), are, however, special cases and actually contain *equivalent* layers resulting in symmetry higher than the stated *P*2. The number of atoms per unit cell for the predicted *M* phase is correctly given as 52, but the number of atoms with coordinations 14 and 15 is 8 in each case rather than the given 9 and 7.

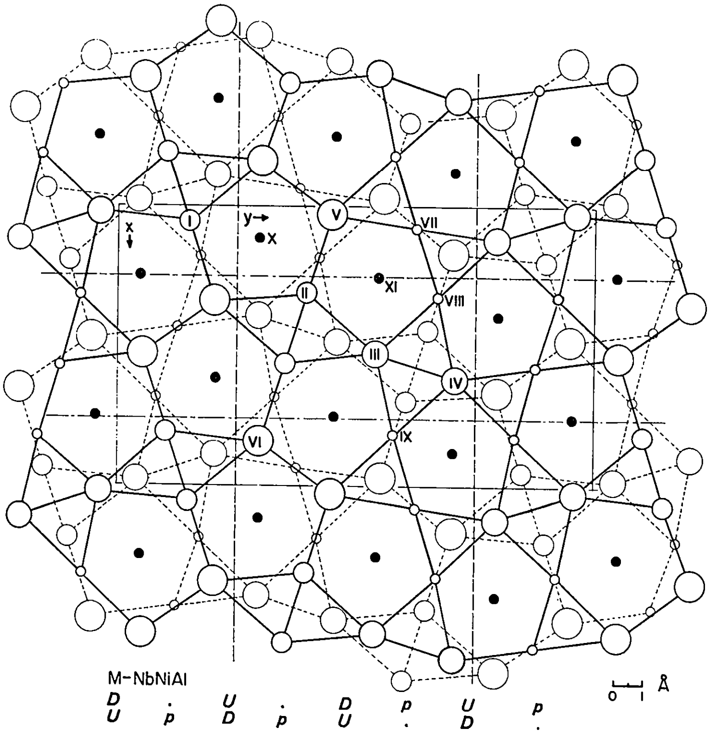

Fig. 1. The crystal structure of the *M* phase, Nb–Ni–Al, in projection on (001). Light circles joined by dashed lines are atoms on one main layer at $z=\frac{3}{4}$, heavy circles joined by solid lines are atoms on the other main layer at $z=\frac{1}{4}$. Each solid black circle represents two atoms in superposition on secondary layers at about $z=0$ and $z=\frac{1}{2}$. Increasing size of circles indicates increase in C.N. from 12 to 16.

Table 3. *Observed and calculated structure factors for the M phase,* Nb–Ni–Al
* Non-observed, value listed under FOBS is $F_{\min}$.

H	K	FOBS	FCAL
L=0			
0	2	*14	21
0	4	*20	-26
0	6	*25	-32
0	8	398	-359
0	10	*32	-12
0	12	401	-409
0	14	*36	14
0	16	128	-126
0	18	*37	42
0	20	194	215
1	1	*22	6
1	2	*27	-9
1	3	*31	-4
1	4	36	43
1	5	25	22
1	6	66	-62
1	7	212	198
1	8	398	-344
1	9	134	-118
1	10	*34	-43
1	11	*36	-6
1	12	109	100
1	13	94	74
1	14	68	64
1	15	179	-176
1	16	156	130
1	17	77	-80
1	18	*43	-8
1	19	*43	12
1	20	44	28
1	21	62	64
2	0	*28	0
2	1	*29	19
2	2	*31	14
2	3	*35	-19
2	4	*38	4
2	5	70	68
2	6	130	117
2	7	170	-144
2	8	93	64
2	9	44	-17
2	10	169	-176
2	11	243	246
2	12	121	-111
2	13	*43	-44
2	14	80	65
2	15	77	-69
2	16	65	45
2	17	*50	-30
2	18	*50	-16
2	19	*51	2
2	20	*52	11
2	21	*52	9
3	1	*35	-10
3	2	*37	-33
3	3	*39	-7
3	4	*41	20
3	5	151	152
3	6	594	557
3	7	135	-91
3	8	*51	22
3	9	*53	31
3	10	57	40
3	11	58	-61
3	12	*59	7
3	13	*61	34
3	14	180	-175
3	15	107	115
3	16	*63	-31
3	17	173	-173
3	18	145	-148
3	19	*60	-53
3	20	*57	-8
3	21	*51	-20
4	0	*41	36
4	1	92	-91
4	2	634	542
4	3	124	96
4	4	*45	0
4	5	72	68
4	6	130	-99
4	7	52	49
4	8	*53	-20
4	9	63	50
4	10	366	-400
4	11	67	-66
4	12	*60	-12
4	13	70	43
4	14	212	-240
4	15	97	-106
4	16	*63	-1
4	17	71	65
4	18	95	89
4	19	106	116
4	20	*55	47
4	21	146	-162
5	1	101	78
5	2	156	-145
5	3	110	-71
5	4	50	-43
5	5	*50	-33
5	6	84	84
5	7	87	73
5	8	*55	-36
5	9	114	92
5	10	85	-61
5	11	*60	39
5	12	76	76
5	13	137	-142
5	14	*63	33
5	15	113	-119
5	16	*63	-47
5	17	*62	17
5	18	*60	33
5	19	*56	29
5	20	*50	22
6	0	*51	31
6	1	*51	-19
6	2	*51	17
6	3	*52	45
6	4	*53	42
6	5	*54	32
6	6	63	-55
6	7	109	-95
6	8	135	-129
6	9	*59	-18
6	10	61	48
6	11	161	160
6	12	121	113
6	13	72	67
6	14	*63	-16
6	15	85	-79
6	16	*62	-16
6	17	*60	-36
6	18	*57	22
6	19	*52	-17
7	1	98	-86
7	2	*55	7
7	3	57	46
7	4	613	513
7	5	*57	-16
7	6	*58	-1
7	7	68	54
7	8	165	152
7	9	*61	37
7	10	*62	-9
7	11	*62	8
7	12	*63	-30
7	13	*63	-30
7	14	*63	-8
7	15	*62	17
7	16	205	-205
7	17	58	66
7	18	*52	15
7	19	122	-110
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8	2	*59	40
8	3	116	-100
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8	5	93	100
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8	8	201	-187
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8	10	*63	-34
8	11	119	90
8	12	229	-234
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8	14	*62	-15
8	15	*60	19
8	16	*56	7
9	1	*62	14
9	2	*62	-7
9	3	72	50
9	4	79	-69
9	5	*63	-42
9	6	*63	3
9	7	98	-93
9	8	110	96
9	9	133	119
9	10	*64	44
9	11	*63	8
9	12	*62	-36
9	13	82	-68
9	14	*58	-48
9	15	*53	21
10	0	*65	15
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10	2	*65	-25
10	3	*65	21
10	4	*65	-10
10	5	*65	-23
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10	8	*64	-19
10	9	*63	7
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10	11	104	-95
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10	13	87	85
11	1	94	-82
11	2	300	293
11	3	*65	-19
11	4	*64	-5
11	5	*64	10
11	6	210	187
11	7	63	49
11	8	*61	-7
11	9	*59	28
11	10	107	101
12	0	*61	46
12	1	*61	-27
12	2	*61	58
12	3	*60	31
12	4	*59	13
12	5	*57	-5
L=1			
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0	3	*20	-9
0	5	51	48
0	7	78	70
0	9	*31	2
0	11	34	26
0	13	40	27
0	15	54	-55
0	17	90	81
0	19	94	97
0	21	144	-166
1	1	*15	5
1	2	21	-15
1	3	22	16
1	4	55	56
1	5	190	-216
1	6	494	506
1	7	184	189
1	8	46	27
1	9	*33	3
1	10	*35	12
1	11	86	85
1	12	*38	16
1	13	70	-58
1	14	145	-136
1	15	172	-170
1	16	84	-74
1	17	159	151
1	18	112	-110
1	19	*43	4
1	20	*43	10
1	21	39	24
2	4	*17	1
2	5	48	56
2	6	77	-86
2	7	112	-118
2	8	107	-96
2	9	*35	-10
2	10	131	123
2	11	268	271
2	12	165	155
2	13	*44	30
2	14	61	-47
2	15	75	-67
2	16	*49	-24
2	17	53	-48
2	18	*49	15
2	19	47	-39
2	20	43	-33
2	21	*32	-16
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3	5	136	-118
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3	7	39	23
3	8	38	39
3	9	*40	12
3	10	*42	-28
3	11	*44	2
3	12	*46	-1
3	13	*47	-30
3	14	*49	-7
3	15	67	52
3	16	129	-135
3	17	131	137
3	18	*48	-6
3	19	93	-101
3	20	94	-93
3	21	36	-56
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4	1	104	-97
4	2	*27	4
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4	4	167	203
4	5	*33	14
4	6	*35	8
4	7	*38	26
4	8	64	47
4	9	64	56
4	10	*44	-5
4	11	*45	19
4	12	66	56
4	13	60	32
4	14	*49	-7
4	15	*49	11
4	16	84	68
4	17	*48	10
4	18	*47	-17
4	19	*43	-35
4	20	58	-48
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5	2	*34	31
5	3	*35	-27
5	4	*36	21
5	5	*38	10
5	6	78	78
5	7	198	-198
5	8	243	268
5	9	177	177
5	10	46	44
5	11	*47	19
5	12	89	-90
5	13	91	-75
5	14	95	-93
5	15	149	140
5	16	124	-105
5	17	*47	8
5	18	*44	18
5	19	*38	3
6	0	*38	-13
6	1	55	-55
6	2	80	-90
6	3	57	44
6	4	*40	-20
6	5	73	-57
6	6	101	-103
6	7	81	79
6	8	*45	-18
6	9	52	57
6	10	210	231
6	11	173	-182
6	12	91	78
6	13	125	124
6	14	*49	5
6	15	66	63
6	16	*47	-23
6	17	*44	-8
6	18	*39	2
6	19	*10	-13
7	1	*42	-30
7	2	245	292
7	3	73	-61
7	4	*43	18
7	5	*44	12
7	6	*45	29
7	7	*46	0
7	8	*47	-5
7	9	*48	31
7	10	82	75
7	11	61	61
7	12	*49	-12
7	13	50	-34
7	14	86	-65
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7	17	75	72
8	0	*45	-4
8	1	57	58
8	2	164	-182
8	3	85	-77
8	4	*46	1
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8	6	77	54
8	7	*48	-6
8	8	*48	-7
8	9	*49	1
8	10	130	113
8	11	87	79
8	12	*48	5
8	13	*47	-10
8	14	110	94
8	15	91	91
8	16	*34	27
9	1	77	-75
9	2	89	85
9	3	69	56
9	4	65	56
9	5	*48	-1
9	6	*49	-4
9	7	*49	-15
9	8	*49	44
9	9	101	-83
9	10	49	37
9	11	*47	6
9	12	91	-88
9	13	119	111
9	14	53	-41
10	0	163	-163
10	1	71	56
10	2	*49	-18
10	3	94	-87
10	4	101	-109
10	5	*40	-34
10	6	*48	20
10	7	82	63
10	8	172	177
10	9	*46	-6
10	10	*44	-2
10	11	*41	-18
10	12	65	39
11	1	*47	11
11	2	*47	11
11	3	*47	-26
11	4	63	-60
11	5	*46	-36
11	6	*44	10
11	7	*43	-11
11	8	87	85
11	9	*35	1
11	10	*18	-7
12	0	*39	27
12	1	*38	0
12	2	*37	-23
12	3	78	81
12	4	133	-142
12	5	80	-76
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0	4	254	252
0	6	*28	24
0	8	*31	14
0	10	*24	-9
0	12	*35	4
0	14	*36	-25
0	16	45	61
0	18	37	-35
0	20	37	-13
1	1	65	-56
1	2	67	-59
1	3	166	160
1	4	430	-436
1	5	212	-201
1	6	69	-56
1	7	*32	-13
1	8	*33	8
1	9	*35	10
1	10	*26	0
1	11	*34	3
1	12	*39	-13
1	13	*40	-6
1	14	*41	-6
1	15	57	57
1	16	119	117
1	17	154	173
1	18	59	61
1	19	85	-78
1	20	84	84
1	21	*42	-31
2	0	245	-245
2	1	264	-265
2	2	285	-285
2	3	175	164
2	4	105	-101
2	5	113	-109
2	6	73	-63
2	7	*34	24
2	8	74	67
2	9	140	169
2	10	260	383
2	11	286	-396
2	12	193	256
2	13	155	181
2	14	70	73
2	15	*48	9
2	16	*49	-17
2	17	*50	23
2	18	57	-40
2	19	83	72
2	20	87	-90
2	21	89	-98
3	8	*12	18
3	9	46	45
3	10	64	74
3	11	63	71
3	12	*43	-15
3	13	67	-59
3	14	70	-53
3	15	*51	-34
3	16	*53	-3
3	17	88	94
3	18	75	-76
3	19	91	86
3	20	*56	-7
3	21	*55	-7
4	7	43	-44
4	8	*30	0
4	9	*35	19
4	10	*39	18
4	11	*42	6
4	12	*45	-12
4	13	*48	-6
4	14	*50	20
4	15	53	61
4	16	*54	-2
4	17	85	-80
4	18	*56	3
4	19	86	-98
4	20	*56	-32
4	21	105	117
5	4	87	-94
5	5	164	214
5	6	247	-347
5	7	178	-233
5	8	66	-68
5	9	*40	-18
5	10	*43	-17
5	11	61	-65
5	12	49	-42
5	13	51	41
5	14	107	111
5	15	154	205
5	16	105	131
5	17	111	-120
5	18	100	114
5	19	63	57
5	20	*55	20
5	21	*53	-20
6	0	219	-325
6	1	142	166
6	2	99	-113
6	3	147	-177
6	4	129	-158
6	5	*36	-41
6	6	62	62
6	7	104	112
6	8	205	280
6	9	115	-117
6	10	*46	44
6	11	*48	-19
6	12	100	106
6	13	132	-147
6	14	61	68
6	15	123	142
6	16	*55	49
6	17	57	66
6	18	*56	-42
6	19	*55	-20
6	20	82	-80
6	21	80	82
7	1	*38	26
7	2	*39	2
7	3	*40	-42
7	4	116	-148
7	5	*42	-25
7	6	*43	17
7	7	*45	-4
7	8	98	103
7	9	*48	-20
7	10	*49	13
7	11	*51	26
7	12	53	-39
7	13	67	67
7	14	*54	0
7	15	*55	-24
7	16	*56	-27
7	17	*55	-43
7	18	*55	-23
7	19	77	74
7	20	*50	22
7	21	63	64
8	0	195	280
8	1	75	90
8	2	*44	1
8	3	45	59
8	4	110	-144
8	5	*46	-36
8	6	*47	8
8	7	*48	-29
8	8	*49	7
8	9	*51	-41
8	10	*52	-4
8	11	*53	-4
8	12	*54	0
8	13	*55	0
8	14	*55	-8
8	15	*55	-14
8	16	*55	-40
8	17	*54	-14
8	18	*53	-4
8	19	*49	22
8	20	*43	26
9	1	*48	-10
9	2	70	-70
9	3	83	85
9	4	71	-72
9	5	89	-86
9	6	126	-137
9	7	142	187
9	8	150	-194
9	9	155	-208
9	10	78	-78
9	11	*54	-39
9	12	74	63
9	13	94	89
9	14	114	120
9	15	124	-118
9	16	91	104
9	17	87	93
9	18	48	44
9	19	40	-21
10	0	*51	-54
10	1	88	-98
10	2	129	-166
10	3	*52	2
10	4	*52	-7
10	5	*53	-32
10	6	103	109
10	7	107	-113
10	8	*54	40
10	9	*55	33
10	10	*55	42
10	11	*55	17
10	12	*55	6
10	13	*55	-6
10	14	96	111
10	15	65	-59
10	16	*49	2
10	17	44	43
10	18	55	-53
11	1	*54	31
11	2	122	-148
11	3	*54	0
11	4	*54	9
11	5	*54	-29
11	6	*55	43
11	7	*55	-17
11	8	*55	10
11	9	*55	-2
11	10	*55	-33
11	11	*54	-26
11	12	*53	-6
11	13	*51	39
11	14	*48	-4
11	15	44	52
12	0	*55	7
12	1	56	-44
12	2	84	78
12	3	63	56
12	4	*55	8
12	5	*55	31
12	6	*55	-33
12	7	*54	-15
12	8	*54	10
12	9	*53	-2
12	10	52	-39
12	11	56	-57
12	12	*46	-18
12	13	*40	10
L=3			
0	1	*29	-6
0	3	*30	8
0	5	50	-48
0	7	79	-67
0	9	*34	4
0	11	44	-31
0	13	*37	-8
0	15	57	48
0	17	71	-64
0	19	67	-76
1	1	*30	-11
1	2	*30	18
1	3	35	-21
1	4	54	-47
1	5	147	161
1	6	329	-363
1	7	150	-145
1	8	49	-27
1	9	*37	5
1	10	*38	-6
1	11	64	-61
1	12	*40	-13
1	13	56	52
1	14	116	105
1	15	151	149
1	16	70	68
1	17	134	-132
1	18	100	87
1	19	*43	-4
1	20	*41	-6
1	21	*39	-25
2	0	*32	4
2	1	*32	-12
2	2	*33	8
2	3	*33	5
2	4	*34	-6
2	5	36	-35
2	6	73	64
2	7	109	97
2	8	101	82
2	9	*41	12
2	10	113	-105
2	11	215	-219
2	12	135	-119
2	13	*47	-25
2	14	*48	35
2	15	*49	52
2	16	*50	22
2	17	*51	36
2	18	*51	-11
2	19	*51	30
2	20	*51	24
2	21	*50	12
L=4			
0	0	865	783
0	2	*34	11
0	4	*34	-19
0	6	*35	-18
0	8	214	-216
0	10	*37	-8
0	12	239	-270
0	14	*37	7
0	16	87	-90
1	1	*35	7
1	2	*36	-3
1	3	*36	-2
1	4	*36	20
1	5	*37	13
1	6	38	-34
1	7	113	116
1	8	214	-218
1	9	80	-78
1	10	*41	-27
1	11	*41	-6
1	12	68	68
1	13	58	50
1	14	49	44
1	15	128	-123
1	16	105	97
1	17	62	-57
1	18	*42	-7
1	19	*40	12
1	20	*37	22
1	21	45	50
2	0	*38	-3
2	1	*38	5
2	2	*30	1
2	3	*30	-6
2	4	*40	1
2	5	55	38
2	6	77	72
2	7	104	-91
2	8	59	45
2	9	*45	-6
2	10	124	-109
2	11	159	161
2	12	82	-74
2	13	*49	-27
2	14	57	48
2	15	63	-52
2	16	*51	32
2	17	*51	-21
2	18	*51	-14
2	19	*51	3
2	20	*50	7
2	21	*48	5
L=5			
0	1	*37	-11
0	3	*37	-2
0	5	*38	20
0	7	51	31
0	9	*38	1
0	11	*37	8
0	13	*34	18
0	15	*27	-34
1	1	*40	0
1	2	*40	-10
1	3	*40	-5
1	4	*41	17
1	5	100	-95
1	6	233	250
1	7	97	91
1	8	*42	9
1	9	*43	12
1	10	*43	6
1	11	54	53
1	12	*43	13
1	13	*43	-35
1	14	102	-79
1	15	100	-97
1	16	42	-41
1	17	99	90
1	18	85	-70
2	0	*44	-21
2	1	*44	7
2	2	*44	10
2	3	*45	10
2	4	*45	-3
2	5	47	36
2	6	63	-46
2	7	68	-57
2	8	49	-47
2	9	*48	0
2	10	71	59
2	11	176	152
2	12	120	100
2	13	*51	15
2	14	*51	-35
2	15	*51	-49
2	16	*51	-14
2	17	*50	-36
2	18	*49	12
2	19	*47	-26
2	20	*44	-26
L=6			
0	0	226	-247
0	2	*38	3
0	4	108	119
0	6	*36	9
0	8	*34	-3
0	10	*29	-5
1	1	*44	-27
1	2	*44	-27
1	3	78	69
1	4	180	-190
1	5	90	-92
1	6	*44	-29
1	7	*44	-1
1	8	*44	7
1	9	*43	8
1	10	*43	3
1	11	*42	4
2	0	112	-101
2	1	159	-108
2	2	159	-117
2	3	89	67
2	4	57	-44
2	5	57	-48
2	6	*50	-31
2	7	*51	14
2	8	52	28

In this structure there are pentagon-strips parallel to the *a* axis that have triangle-strips on both sides in the same layer. The pentagon-strips immediately above and below in the adjacent main layers do not have triangle-strips on either side. Therefore these pentagons are larger than the ones in the first layer. Fig. 1 shows that the atoms in the larger pentagons are indeed the ones with the larger coordination numbers.

The *M* phase is closely related to the μ phase, in which the atoms in the main layers normal to $[110]_{\mathrm{hex}}$ also form pentagons and triangles (Fig. 2). In fact, the *M* phase contains blocks of μ-phase structure. This also follows from comparison of the Frank–Kasper letter symbols of these structures given at the bottom of Figs. 1 and 2.

Frank & Kasper (1959) have derived many other known and unknown structures of hexagonal, trigonal, or cubic symmetry from the μ phase by different ways of stacking the hexagonal layers normal to $[001]_{\mathrm{hex}}$. Fig. 2 suggests an alternative way of representing this group of structures. It appears that in these structures the atoms are arranged in layers perpendicular to [110], consisting of only pentagons and triangles, with atoms between the layers forming continuous rows of C.N.12 atoms in the [110] direction. Fig. 3 shows the pentagon layers for Zr_4Al_3 (Wilson, Thomas & Spooner, 1960) and for the Laves phases: $MgCu_2$ and $MgZn_2$. Other ways of stacking the hexagonal layers or joining up the pentagons (Fig. 4) lead to the Laves phase $MgNi_2$, the 5- and 9-layer structures described by Komura (1962) and other hypothetical structures.

The secondary layers of the *M* phase consist of a net that is a combination of $4.3.4.3^2$ and $4^2.3^3$ tessellations, topologically the same as in the *P* phase. The triangles are approximately equilateral in the *P* phase, but in the *M* phase they deviate significantly from equilateral as in the μ and Laves phases.

Major networks

The 'major networks' of 6-coordinated bonds are given in Fig. 5. As in the *P* phase, there are two non-interconnected three-dimensional nets, but the additional rows of major ligands connecting C.N.14 atoms in the **c** direction are missing in the *M* phase. In the μ phase there is one three-dimensional network with additional non-interconnected planes of major ligands connecting C.N.15 atoms.

Analysis of the interatomic distances

The interatomic distances in the *M* phase are given in Table 4. They were analysed in the same way as was done before for the other σ-phase related phases. From the interatomic distances 5-coordinated (minor) and 6-coordinated (major) radii were derived for each kind of atom by a least-squares fit. There are 56 non-equivalent distances, and 17 radii were derived from these (one for each C.N.12 atom, and two for each C.N.14, C.N.15, and C.N.16 atom). The results are given in Table 5. The average value for each particular type of ligand is also given, and compared with the value (in parentheses) that was predicted for this radius from the average 12-coordinated radius of the atoms (Shoemaker & Shoemaker, 1964). In the calculation of the average radius the 12-coordinated radius of Al was taken to be 1·43 as derived from elementary Al. The agreement between the observed and predicted radii is very good for the minor radii; there are somewhat larger differences for the major radii, but none larger than 0·05 Å. As mentioned before, the *R* index for the structure arrived at by a least-squares fit of the distances to sums of these predicted radii was 0·24. The largest shift in atom position from this partially 'refined' structure to the final structure occurred for atom V (C.N.16) and is 0·13 Å. In Table 6 are given interatomic distance values calculated from the average least-square radii in Table 5; these may be compared

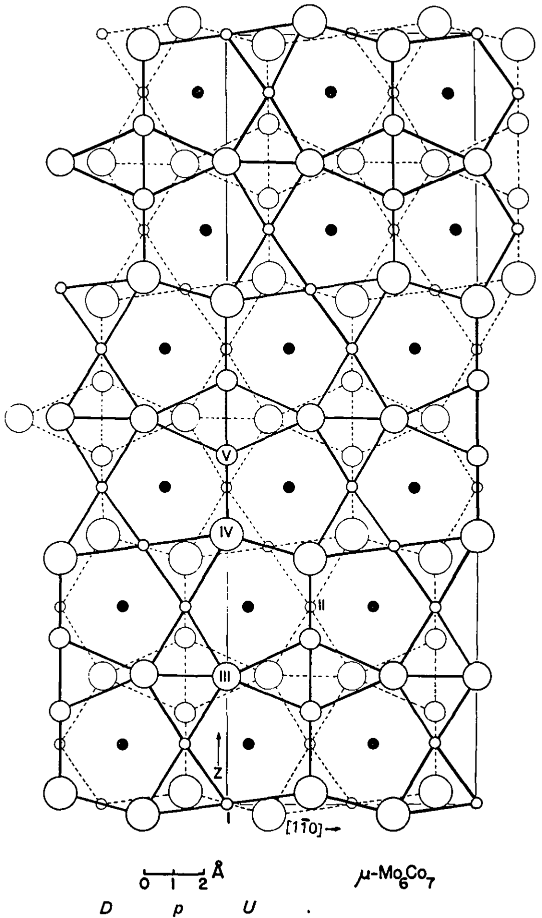

Fig. 2. The crystal structure of the μ phase, Mo_6Co_7, projected down [110]. Solid-line net and broken-line net represent the main layers separated by half of the short diagonal of the hexagonal cell. Each solid black circle represents two atoms in superposition on the secondary layers half way between the main layers. Size of circles as in Fig. 1.

with the actual distances in Table 4. The largest deviation is 0·122 Å; the mean deviation is 0·035 Å.

The presence of 13 at.% of aluminum causes all distances to be about 4% larger than the corresponding distances in the *P* phase ($Mo_{42}Cr_{18}Ni_{40}$). In the σ phase Nb_2Al the presence of 33 at.% of aluminum causes all distances to be 10 to 15% larger than those in other σ phases formed of transition elements only (Brown & Forsyth, 1961). Silicon in its ternary transition element phases (Bardos, Bardos & Beck, 1963) displays on the contrary a C.N.12 radius of about 1·20, slightly smaller than the C.N.12 radius for Fe, Co, and Ni.

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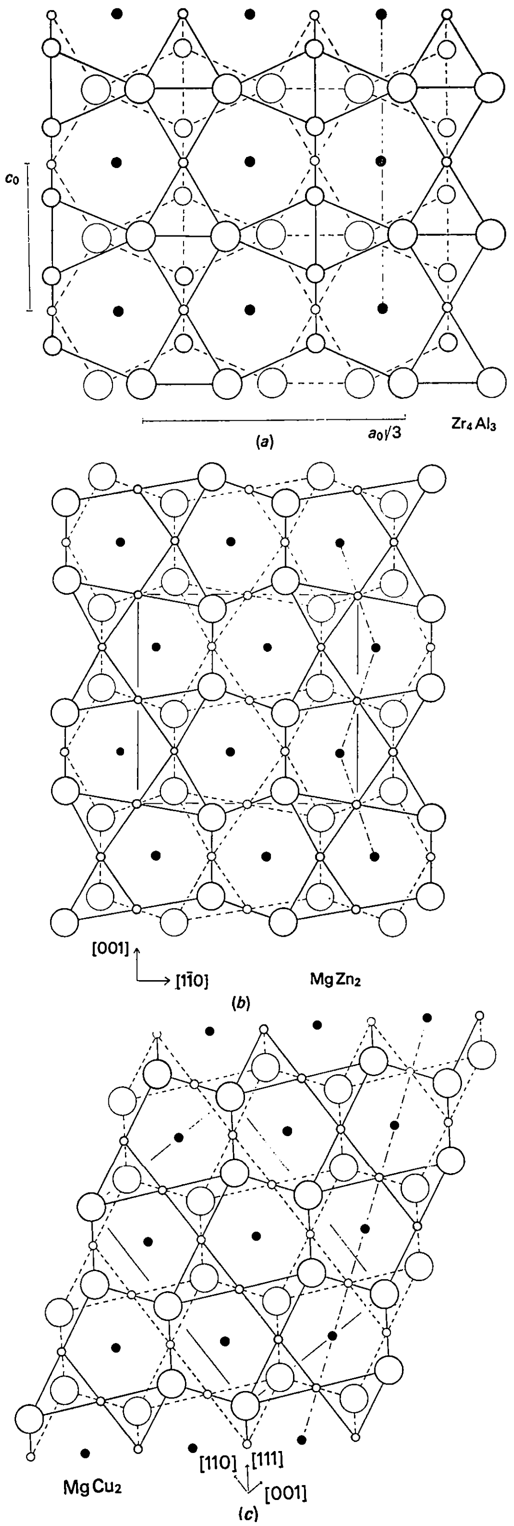

Fig. 3. Pentagon main layers and secondary layers in: (*a*) Zr_4Al_3, (*b*) $MgZn_2$, (*c*) $MgCu_2$. The main layers all contain the same basic unit consisting of two pentagons sharing one edge parallel to the *c* axis; these are stacked with triangles. The differences in stacking are indicated by the lines (alternating long and short dashes) joining the interlayer atoms (solid black circles) centering the pentagons in projection.

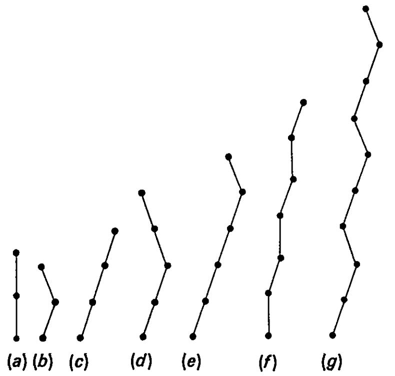

Fig. 4. Lines connecting interlayer atoms (see Fig. 3) in: (*a*) Zr_4Al_3, (*b*) $MgZn_2$, (*c*) $MgCu_2$, (*d*) $MgNi_2$, (*e*) 5-layer Laves phase (Komura), (*f*) μ phase. (*g*) 9-layer Laves phase (Komura).

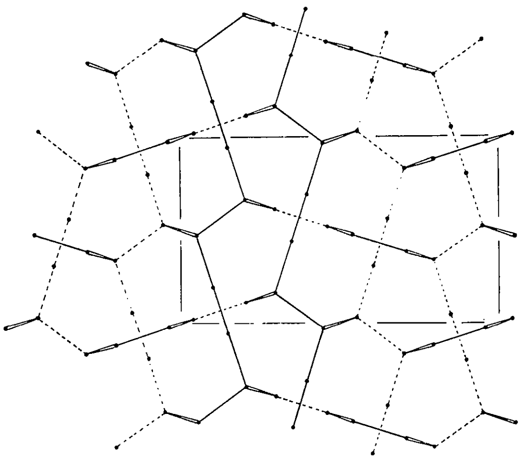

Fig. 5. Frameworks of six-coordinated ligands (major networks) in the *M* phase. Solid lines at $z=\frac{1}{4}$, broken lines at $z=\frac{3}{4}$. Tapered double lines indicate inclined ligands interconnecting nets on adjacent main layers and forming infinite vertical zigzag rows.

Table 4. *Observed interatomic distances for the M phase*

Roman numbers refer to atoms

Numbers in brackets represent number of ligands on a given atom having given distance value. For atoms X and XI the number of ligands should be divided by 2 if reading down. (This results from their higher multiplicity.)

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
C.N.	14	14	15	15	16	16	12	12	12	12	12
I		2·538*	3·115 3·130 [2]	3·103 [2]		3·118 2·760*		2·710 [2]		2·705 [2]	2·712 [2]
II			3·122 3·121 [2]	3·102 [2]	2·775*	3·148			2·722 [2]	2·710 [2]	2·723 [2]
III			2·841 [2]*	2·830*				2·793	2·787		2·799 [2] 2·768 [2]
IV						2·874 [2]*	2·806	2·774 2·795	2·808	2·854 [2] 2·824 [2]	
V					2·999 [2]*	2·996*	2·885 2·836 [2]		2·796 2·954 [2]	2·914 [2]	3·008 [2] 2·789 [2]
VI							2·938 [2]	2·962 [2]		2·813 [2] 2·831 [2]	3·020 [2]
VII								2·485	2·478	2·506 [2]	2·463 [2]
VIII										2·465 [2]	2·471 [2]
IX										2·509 [2]	2·433 [2]
X										2·514 [2] 2·419 [2]	
XI											2·436 [2] 2·497 [2]

Largest distance	3·148
Smallest distance	2·420
Average distance	2·782

Standard deviations are estimated to be about 0·015 Å, except for X–X and XI–XI which are estimated to be about 0·020 Å.

* Major ligand.

Table 5. *Summary of atomic radii for the M phase*

C.N.	Atom	*r*	*r**
12	VII	1·237	
	VIII	1·233	
	IX	1·232	
	X	1·228	
	XI	1·233	
		1·233 (1·24)†	
14	I	1·495	1·271
	II	1·501	1·270
		1·498 (1·50)	1·271 (1·22)
15	III	1·589	1·422
	IV	1·592	1·395
		1·591 (1·58)	1·408 (1·37)
16	V	1·657	1·501
	VI	1·673	1·485
		1·665 (1·66)	1·493 (1·52)

† In parentheses: values derived from average C.N.12 radius of the atoms and used in the preliminary refinement of the structure without intensity data.

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Table 6. *Interatomic distances in the M phase predicted from average least-squares radii of Table* 5

	C.N.12	C.N.14		C.N.15		C.N.16	
C.N.12	2·466						
C.N.14	2·731	2·996	2·541*				
C.N.15	2·824	3·089	2·679*	3·182	2·817*		
C.N.16	2·898	3·163	2·764*	3·256	2·902*	3·330	2·986*