Fig. 3. Ball-and-stick drawings of the coordination polyhedra for (a) Ga(1), (b) Ga(2), and (c) Mg. The site symmetries for these atoms are 4mm, m and mm, respectively. In all cases, the c axis is vertical. Numerals indicate the type of Ga atoms. The central atom is stippled.

Just as gallium possesses a unique structure among the elements, it appears that Ga_5Mg_2 may also have a unique structure. A search of standard references such as Pearson's (1967) book reveals no A_5B_2 compounds isotypic with Ga_5Mg_2. Nor does Mg, in fact, form an A_5Mg_2 phase with any of the other Group IIIA elements.

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The Crystal Structure of Zr4Co4Ge7 (V-Phase)

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The crystal structure of the V-phase $Zr_4Co_4Ge_7$ has been determined by single-crystal X-ray diffraction analysis. The structure is of a new type with four formula units in a tetragonal unit cell of space group $I4/mmm$ (D_{4h}^{17}), having the dimensions $a = 13\cdot228 \pm 0\cdot004$, $c = 5\cdot229 \pm 0\cdot003$ Å and $c/a = 0\cdot3952 \pm 0\cdot0002$. The structure was refined by the least-squares method, giving a final R value of $0\cdot092$ for the 392 independent structure factors observed. It may be characterized as intermediate between the tetrahedrally close packed structures (σ-phase related structures, Laves phases) and the structures of the $CuAl_2$-type family.

Introduction

In their study of the ternary system titanium–nickel–silicon, Westbrook, DiCerbo & Peat (1958) reported the occurrence of a ternary phase of the composition $Ti_4Ni_4Si_7$ to which they ascribed the name 'V-phase'. Subsequently Jordan (1963) found thirteen isotypic compounds in which the large titanium atoms were replaced by zirconium, niobium or tantalum, the smaller transition metal component nickel by cobalt and iron, and germanium could substitute silicon. The phases were reported to be nearly homogeneous at the composition 4:4:7, with the possible exemption of two phases, where the exact composition has not been determined. While investigating similar ternary systems (including hafnium as the larger transition metal component) Markiv, Gladyševskij & Fedoruk (1966), Markiv, Gladyševskij, Kripjakevič & Fedoruk (1966) and Markiv (1966) independently discovered a number of isotypic phases at the approximate composition 1:1:2, having a body-centered tetragonal unit cell. This unit cell could be used to index the powder patterns of the V-

phases and it appears therefore that the compounds found by the Ukraine–Russian authors are isotypic with the V-phases. This conclusion is also supported by the similar lists of representatives given by Jordan (1963) and Markiv (1966) (Table 1.) The present investigation was undertaken to establish the crystal structure of these phases.

Table 1. V-*phases found by Jordan* (1963), +, *and Markiv* (1966), *

	Silicides			Germanides		
	Fe	Co	Ni	Fe	Co	Ni
Ti		+*	+*		+	+*
Zr	+	+*		+	+*	
Hf		*	*			*
Nb	+*	+*	+*			
Ta	+	+*				

Experimental

Specimens and powder patterns of the V-phases were made available to the author through the kindness of Professor P.A. Beck and Mr A.G. Jordan of this laboratory. From the pronounced graininess of the powder photograph of Zr₄Co₄Ge₇ it could be concluded that the sample had large grains and therefore was favorable for the isolation of single crystals. The sample which had been prepared from the components of purity greater than 99·9 wt.%, and annealed at 1100 °C for four days, was found upon metallographic examination to contain $\sim 3\%$ of a second phase. The presence of the second phase was probably caused by a 0·5% weight loss of mainly germanium (the most volatile component) during the arc melting, thus shifting the overall composition of the sample slightly towards a higher transition metal content. This explains also the somewhat higher experimental density of $8·13 \pm 0·08$ g.cm^{-3} *versus* the value of 8·05 g.cm^{-3} deduced from the structure determination.

Several single crystals, isolated from the crushed sample, were examined with a Buerger precession camera (Mo $K\alpha$ radiation) and a Weissenberg goniometer (Cr $K\alpha$ and Mo $K\alpha$ radiation). The body-centered tetragonal unit cell as reported by Markiv (1966) ($a = 13·20$, $c = 5·23$ Å) was confirmed and the following lattice constants were obtained by the least-squares refinement of data taken with a 114·6 mm diameter Debye–Scherrer camera and Cr $K\alpha$ radiation ($\lambda_{K\alpha_1} = 2·28962$ Å):

$$a = 13·228 \pm 0·004, \qquad c = 5·229 \pm 0·003 \text{ Å}$$
$$c/a = 0·3953 \pm 0·0002. \qquad V = 915·0 \pm 1·1 \text{ Å}^3.$$

To facilitate the identification of V-phases, the observed and calculated intensities (using the positional parameters from the refined structure and a computer program by Jeitschko & Parthé, 1966) for a Debye–Scherrer diagram are listed in Table 2.

For the structure determination and refinement, intensity data were collected with a Weissenberg camera, with Mo $K\alpha$ radiation and the multiple film technique (five films interleaved with Cu foils). Intensities were estimated visually with the aid of an intensity strip, which was logarithmically scaled in steps of 10%. The reciprocal lattice planes ($hk0$), ($hk1$), ($hk2$), (hhl) and ($h, h-1, l$) were evaluated. The two single crystals selected for these photographs were both of elongated prismatic shape with rectangular cross-sections and

Table 2. *Calculated and observed intensities of the V-phase* Zr₄Co₄Ge₇

Debye–Scherrer camera, Cr $K\alpha$ radiation.

h k l	d_c (Å)	I_c	I_o	h k l	d_c (Å)	I_c	I_o
1 1 0	9.3536	2	–	8 4 0	1.4789	4	vw
2 0 0	6.6140	1	–	9 1 0	1.4608	0	–
1 0 1	4.8628	0	–	5 0 3	1.4555	14	} s
2 2 0	4.6768	0	–	4 3 3	1.4555	14	
3 1 0	4.1831	0	–	7 3 2	1.4468	9	w
2 1 1	3.9179	0	–	5 2 3	1.4215	1	–
3 0 1	3.3709	0	–	9 0 1	1.4149	2	vvw
4 0 1	3.3070	0	–	8 0 2	1.3975	0	–
3 3 0	3.1179	1	–	9 3 0	1.3944	2	vvw
3 2 1	3.0033	1	–	9 2 1	1.3836	0	} vw
4 2 0	2.9579	0	–	7 6 1	1.3836	5	
4 1 1	2.7346	1	–	8 2 2	1.3673	5	vw
0 0 2	2.6145	14	w	6 1 3	1.3601	1	–
5 1 0	2.5942	4	vw	8 5 1	1.3543	2	vvw
1 1 2	2.5180	0	–	6 6 2	1.3390	2	vvw
2 0 2	2.4314	0	–	7 7 0	1.3362	2	vvw
4 3 1	2.3607	51	} vvs	5 4 3	1.3322	3	vvw
5 0 1	2.3607	49		7 5 2	1.3255	2	vvw
4 4 0	2.3384	17	w	8 6 0	1.3228	0	} vvw
2 2 2	2.2821	6	vw	10 0 0	1.3228	2	
5 3 0	2.2686	1	–	0 0 4	1.3072	16	} m
5 2 1	2.2233	4	} vs	6 3 3	1.3060	1	
3 1 2	2.2171	46		9 4 1	1.3009	0	–
6 0 0	2.2047	23	m	10 2 0	1.2971	1	–
6 2 0	2.0915	2	vvw	1 1 4	1.2947	0	–
4 0 2	2.0510	8	vw	8 4 2	1.2873	9	} w
6 1 1	2.0079	2	} w	9 5 0	1.2848	2	
3 3 2	2.0034	11		2 0 4	1.2824	0	} vw
4 2 2	1.9589	13	w	7 0 3	1.2812	6	
5 4 1	1.9214	5	vw	10 1 1	1.2764	5	} w
7 1 0	1.8707	0	} w	9 1 2	1.2752	7	
5 5 0	1.8707	7		2 2 4	1.2590	0	–
6 3 1	1.8451	1	–	7 2 3	1.2578	1	–
5 1 2	1.8415	0	–	3 1 4	1.2477	0	–
6 4 0	1.8344	3	vw	10 3 1	1.2314	8	} w
7 0 1	1.7772	7	w	9 3 2	1.2303	2	
4 4 2	1.7430	0	–	10 4 0	1.2282	32	s
7 3 0	1.7369	5	vw	4 0 4	1.2157	0	–
1 0 3	1.7281	0	–	6 5 3	1.2147	9	w
7 2 1	1.7163	1	–	8 7 1	1.2106	6	vw
5 3 2	1.7135	0	–	3 3 4	1.2056	0	–
6 0 2	1.6854	0	–	11 1 0	1.1976	0	–
2 1 3	1.6719	0	–	4 2 4	1.1957	0	–
8 0 0	1.6535	3	vw	7 4 3	1.1947	1	} vw
6 2 2	1.6332	4	vw	8 1 3	1.1947	5	
3 0 3	1.6209	0	–	9 6 1	1.1908	0	–
6 5 1	1.6113	7	w	7 7 2	1.1898	27	s
8 2 0	1.6041	1	–	8 6 2	1.1803	11	} vs
3 2 3	1.5744	0	–	10 0 2	1.1803	37	
8 1 1	1.5655	3	} vw	11 0 1	1.1720	5	vw
7 4 1	1.5655	0		8 8 0	1.1692	0	–
6 6 0	1.5589	1	–	5 1 4	1.1674	4	vw
7 5 0	1.5377	0	–	10 2 2	1.1620	4	vvw
4 1 3	1.5316	0	–	9 7 0	1.1602	1	–
5 5 2	1.5214	4	} w	11 3 0	1.1602	1	–
7 1 2	1.5214	2		8 3 3	1.1575	0	–
6 4 2	1.5016	0	–	10 5 1	1.1540	66	} vvs
8 3 1	1.4845	0	–	11 2 1	1.1540	0	

both were mounted with the needle axis perpendicular to the primary X-ray beam. The one, rotating around the [001] axis, had the dimensions $0.03 \times 0.05 \times 0.20$ mm the other, with dimensions $0.03 \times 0.03 \times 0.15$ mm, was rotating around the [110] direction. Absorption corrections were made, assuming cylindrical shapes for the crystals (*International Tables for X-ray Crystallography*, 1959). After applying the proper Lorentz–polarization corrections, the structure factors were brought to a common scale by deriving average scale factors using those data present on corresponding films.

Derivation of the approximate structure

From the value of the experimental density mentioned above, the number of formula units per cell was calculated to be $4.04 \simeq 4$. The only systematic extinctions observed were those of the body-centered unit cell, and, since the values of $|F(hkl)|$ and $|F(\bar{h}kl)|$ were equal within the limits of error, the structure is of high Laue symmetry, thus reducing the choice to five possible space groups with the general diffraction symbol $I4/***$ (Donnay & Kennard, 1964).

It was noticed that the reciprocal lattice layers with $\Delta l = \pm 4$ were equal except for the normal decline with higher l-values. The quantitative evaluation of the two Weissenberg photographs (h,h,l) and $(h,h-1,l)$ showed that this relation held up to $l = 12$, which was the limit of the Mo $K\alpha$-sphere. Thus the structure is layered with atoms arranged in planes which are $\Delta z = \frac{1}{4}$ apart. This made it possible to compute three-dimensional Patterson functions with the data $(hk0)$, $(hk1)$ and $(hk2)$ only. In order to do this, unitary structure factors were calculated by dividing the observed structure factors by the average atomic scattering coefficient and the average temperature factor, which was obtained from a Wilson plot (Wilson, 1942). The unitary structure factors of the reciprocal planes $l > 2$ were then set equal to the corresponding planes $l \leq 2$. The evaluation of the three-dimensional sharpened Patterson function calculated with these data, using a computer program by Sly, Shoemaker & van den Hende (1962), turned out to be difficult, since even on

Fig. 1. Unitary structure factors in the reciprocal lattice plane $(hk0)$ of $Zr_4Co_4Ge_7$, showing pseudo-octagonal symmetry.

the basis of the Patterson function no unambigous decision could be made among the five possible space groups. Since, however, the z-projection symmetry for the five space groups is the same, it was attempted to gain as much information as possible from the $(hk0)$ data first.

A number of considerations were helpful for the tentative placement of atoms in the z axis projection:

(*a*) The unitary structure factor $U_{10\,10\,0}$ has a value very close to unity. Thus one can draw a sublattice which offers 21 possible locations for the placement of the $3\frac{3}{4}$ atoms within the asymmetric unit.

(*b*) Because of the pseudo-octagonality of the $(hk0)$ reciprocal lattice net (Fig. 1) the arrangement of atoms around the [100] and [110] axes has to be similar in the z-projection.

(*c*) The length of the z axis makes a placement of two zirconium atoms above each other extremely unlikely.

(*d*) Additional information was obtained from an electron-density projection computed with about 15 structure factors, for which the signs had been determined with the aid of Harker–Kasper inequalities (Harker & Kasper, 1948).

The combined results of these considerations provided several positions which were likely to be occupied. These positions were then tried out systematically – by assuming distinct z parameters – as starting positions for the interpretation of the three-dimensional Patterson function with the superposition method (a detailed description of this method is given by Shoemaker, Barieau, Donohue & Lu, 1953). After several trials a self-consistent set of atomic positions was obtained. The distribution of the three kinds of atoms was then concluded from the interatomic distances, the weights of the Patterson peaks and from the atomic arrangements in related compounds. An intensity calculation with this trial structure gave an R value (defined throughout the paper as $R = \Sigma\,|F_o - F_c|/\Sigma\,F_o$) of 0.18 for the observed structure factors, indicating that the structure was essentially correct.

Structure refinement

The structure was refined on the University of Illinois IBM 7094 computer with a full-matrix least-squares program (Gantzel, Sparks & Trueblood, 1961) and the function minimized was $\Sigma\,w^2(\Delta F)^2$ with $w = 1/F_{obs}$. Although the structure may be described with all five space groups of $I4***$, the space group with the highest symmetry: $I4/mmm\,-D_{4h}^{17}$ was chosen for the refinement. This is the most probable space group, since the description of the structure in space groups $I\bar{4}2m$, $I\bar{4}m2$ and $I4mm$ would allow, besides an increase in the number of x and y parameters, three or six additional z parameters, which are not required because of the layered nature of the structure, as mentioned above. The fifth possible space group, $I422$, was not ruled out initially, since it requires only one additional parameter: the 16 cobalt atoms of position $16(k)$ in $I4/mmm$
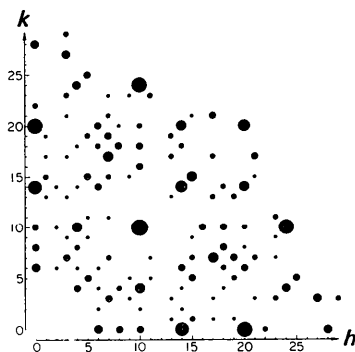
need to be placed in 8(j) of $I422$ with $x_1 \simeq 0{\cdot}15$ and $x_2 \simeq 0{\cdot}35$. This would allow for a staggering of the cobalt atoms rather than a straight alignment along the z axis as required by space group $I4/mmm$. However the least-squares refinement in $I422$ revealed a strong interaction of the two Co parameters and therefore the refinement was completed in the centrosymmetric space group. This decision was justified later by the Fourier synthesis along the z axis, which gave no indication of a staggering of the Co atoms.

The values of the atomic scattering factors were taken from *International Tables for* X-*ray Crystallography* (1962) and were corrected for the real part of the anomalous dispersion (Dauben & Templeton, 1955). Using the (hk0), (hk1), and (hk2) data a total of 14 parameters was refined: the six positional x parameters, the isotropic temperature parameters for the atomic positions and one general scale factor. The z parameter of Ge(4) was refined separately from the (hhl) and the ($h,h-1,l$) data. These are most sensitive to the z parameters and were also considered to be more reliable, since they were collected with a smaller crystal whose shape resembled more closely that of a cylinder, for which the absorption correction was made. The final value for this parameter was $z = 0{\cdot}252 \pm 0{\cdot}002$. Since this value deviates only insignificantly from $\frac{1}{4}$ it was preferred to fix it with the idealized value $z = 0{\cdot}250$ and to increase the limits of error correspondingly. Six additional least-squares cycles were then run using all the observed data. The refinement was considered to be complete when the shifts of all parameters in the last three cycles were within the standard deviations computed from the inverse matrix. Table 3 lists the final parameters. The residual value for the 392 observed structure factors (Table 4) is $R = 0{\cdot}092$.

Since the atomic scattering powers in $Zr_4Co_4Ge_7$ are not very different, it was considered worthwhile to perform a test for possible disorder. Using a least-squares program originally written by Busing, Martin & Levy (1962) and later revised by Stucky, two least-squares cycles were run whereby the occupancy factors only were refined. The resulting values for these factors varied between 0·96 (for the Co position) and 1·01 (Ge(4) position) with standard deviations of the order of 0·02. Thus it was concluded that the initial atomic distribution is essentially correct. As with most intermetallic compounds, however, a disorder in the range of some atomic per cent must be regarded as possible.

Table 4. *Observed and calculated structure factors of* $Zr_4Co_4Ge_7$

h	k	F_o	F_c
ℓ = 0			
0	0	-	1935
2	0	-	38
4	0	<41	19
6	0	536	720
8	0	344	369
10	0	297	293
12	0	<67	42
14	0	524	592
16	0	<69	41
18	0	<69	-58
20	0	338	365
22	0	97	102
24	0	78	68
26	0	<64	45
28	0	114	122
34	0	106	117
1	1	-	-67
3	1	68	50
5	1	160	158
7	1	<21	2
9	1	31	34
11	1	<26	-3
13	1	130	-122
15	1	146	133
17	1	78	81
19	1	80	-76
21	1	<40	13
23	1	<44	10
25	1	<46	17
27	1	<47	-13
29	1	<44	26
2	2	<28	8
4	2	<20	8
6	2	172	-171
8	2	136	-127
10	2	186	155
12	2	37	30
14	2	136	-121
16	2	<36	0
18	2	33	-28
20	2	<42	-10
22	2	<43	15
24	2	<44	-2
26	2	<43	-8
28	2	47	-50
3	3	73	71
5	3	121	108
7	3	346	371
9	3	199	-196
11	3	74	59
13	3	144	144
15	3	<37	-12
17	3	95	90
19	3	<41	28
21	3	84	88
23	3	112	-104
25	3	46	51
27	3	129	130
29	3	68	-68
4	4	471	572
6	4	217	-220
8	4	257	-286
10	4	530	618
12	4	<32	-16
14	4	121	-95
16	4	56	60
18	4	98	101
20	4	<41	31
22	4	44	-54
24	4	147	151
26	4	<42	-12
28	4	44	-54
5	5	434	481
7	5	43	39
9	5	164	151
11	5	158	140
13	5	<37	11
15	5	203	192
17	5	74	68
19	5	112	104
21	5	<43	31
23	5	<45	-7
25	5	108	101
27	5	<46	34
6	6	222	210
8	6	56	55
10	6	<34	21
12	6	<37	-36
14	6	236	210
16	6	70	-71
18	6	132	-116
20	6	168	164
22	6	<42	24
24	6	<44	-29
26	6	<45	6
7	7	286	260
9	7	68	66
11	7	116	111
13	7	<36	-16
15	7	145	118
17	7	247	246
19	7	139	-120
21	7	106	83
23	7	69	76
25	7	<45	15
27	7	<44	33
8	8	<68	24
10	8	75	-71
12	8	62	-48
14	8	78	79
16	8	65	-58
18	8	150	-139
20	8	69	68
22	8	<45	40
24	8	53	-61
26	8	<45	-20
9	9	100	-73
11	9	93	-78
13	9	<35	-12
15	9	106	90
17	9	61	-57
19	9	<41	11
21	9	<42	26
23	9	69	-78
25	9	<42	22
10	10	648	676
12	10	63	65
14	10	71	65
16	10	180	155
18	10	179	164
20	10	120	106
22	10	<46	8
24	10	240	215
26	10	<43	16
11	11	80	70
13	11	46	47
15	11	<39	9
17	11	45	58
19	11	47	45
21	11	<44	36
23	11	92	-77
25	11	46	60
12	12	<66	71
14	12	56	-56
16	12	<40	-21
18	12	<41	-9
20	12	<43	29
22	12	<43	10
24	12	<42	-20
13	13	111	-108
15	13	<40	21
17	13	127	129
19	13	108	-93
21	13	<43	-11
23	13	<42	17
14	14	259	259
16	14	38	-39
18	14	104	-98
20	14	156	185
22	14	<42	28
24	14	<41	5
15	15	209	179
17	15	<42	28
19	15	<43	19
21	15	54	62
23	15	<41	22
16	16	<62	33
18	16	<43	-10
20	16	<42	-5
22	16	<41	17
17	17	80	82
19	17	<43	31
21	17	105	102
23	17	<43	-47
18	18	<62	22
20	18	<42	-11
22	18	<42	-40
19	19	<57	7
21	19	47	-49
23	19	<37	-22
20	20	170	164
22	20	<37	23
ℓ = 1			
1	0	-	-2
3	0	21	-16
5	0	563	-680
7	0	372	362
9	0	217	-204
11	0	167	-148
13	0	131	117
15	0	181	-164
17	0	<41	10
19	0	191	-175
21	0	100	85
23	0	<46	29
25	0	119	-127
27	0	<45	19
29	0	<42	-31
2	1	<13	4
4	1	54	-47
6	1	136	124
8	1	173	171
10	1	177	-172
12	1	66	-64
14	1	147	123
16	1	<40	18
18	1	<42	15
20	1	44	-32
22	1	<42	17
24	1	<44	4
26	1	<46	-29
28	1	49	60
3	2	17	22
5	2	162	-158
7	2	110	-108
9	2	32	28
11	2	<33	23
13	2	<38	17
15	2	98	-92
17	2	48	-49
19	2	<42	21
21	2	<47	-24
23	2	<46	23
25	2	<46	-18
27	2	<45	-36
4	3	395	486
6	3	99	94
8	3	28	-25
10	3	206	220
12	3	<35	-12
14	3	119	108
16	3	<40	20
18	3	180	173
20	3	<45	34
22	3	85	-84
24	3	119	120
26	3	<46	19
28	3	46	47
5	4	177	-209
7	4	78	81
9	4	<30	7
11	4	228	237
13	4	119	119
15	4	196	-191
17	4	166	157
19	4	<42	24
21	4	<43	15
23	4	<45	43
25	4	<45	18
27	4	<46	35
6	5	234	-256
8	5	131	-147
10	5	338	-351
12	5	109	-105
14	5	202	-199
16	5	129	-115
18	5	<41	-16
20	5	175	-173
22	5	88	-87
24	5	59	-76
26	5	<46	-41
28	5	<43	-29
7	6	192	213
9	6	<32	5
11	6	<35	5
13	6	135	126
15	6	53	-56
17	6	<42	22
19	6	<44	-37
21	6	68	66
23	6	54	54
25	6	44	-49
27	6	<45	13
8	7	144	148
10	7	<31	13
12	7	160	-154
14	7	260	274
16	7	<41	27
18	7	<44	6
20	7	47	54
22	7	<46	0
24	7	87	71
26	7	56	-49
28	7	96	91
9	8	57	56
11	8	40	-35
13	8	104	104
15	8	<41	13
17	8	40	-37
19	8	<46	-8
21	8	<49	59
23	8	50	57
25	8	54	-44
27	8	<44	-8
10	9	146	-140
12	9	<37	-7
14	9	<39	-4
16	9	<41	-4
18	9	48	46
20	9	53	-63
22	9	<45	-13
24	9	<45	-7
26	9	<46	-7
11	10	76	74
13	10	<42	28
15	10	274	-250
17	10	89	87
19	10	63	-68
21	10	<48	-16
23	10	<48	-3
25	10	<47	-37
12	11	<40	14
14	11	<42	3
16	11	<44	-2
18	11	144	126
20	11	<45	-17
22	11	71	-69
24	11	61	64
13	12	<41	-28
15	12	103	-103
17	12	53	-50
19	12	<48	16
21	12	50	-52
23	12	<49	-1
14	13	146	145
16	13	<46	37
18	13	63	58
20	13	<48	28
22	13	<48	1
15	14	<45	-25
17	14	58	61
19	14	46	-54
21	14	107	103
16	15	46	-54
18	15	72	-65
20	15	105	-95
17	16	<47	-11
19	16	<47	-14
18	17	84	73
ℓ = 2			
0	0	476	628
2	0	34	-37
4	0	327	353
6	0	49	32
8	0	27	-16
10	0	501	552
12	0	163	-144
14	0	220	177
16	0	153	132
18	0	<48	-18
20	0	99	94
22	0	62	53
24	0	153	157
26	0	74	-76
28	0	<51	15
30	0	116	117
1	1	19	-19
3	1	406	-509
5	1	74	-63
7	1	139	144
9	1	253	-250
11	1	301	-287
13	1	47	-46
15	1	55	58
17	1	154	-146
19	1	103	-91
21	1	<53	35
23	1	116	-120
25	1	50	-50
27	1	<50	22
29	1	<48	-27
2	2	203	-238
4	2	254	-324
6	2	177	-200
8	2	208	-211
10	2	105	-111
12	2	79	-72
14	2	154	-136
16	2	147	-138
18	2	125	-132
20	2	<50	-19
22	2	52	-43
24	2	86	-88
26	2	<51	-25
28	2	66	-64
3	3	335	423
5	3	50	-49
7	3	245	-283
9	3	107	-111
11	3	153	174
13	3	251	-246
15	3	154	-148
17	3	214	226
19	3	121	-119
21	3	102	-101
23	3	<49	-26
25	3	<55	42
27	3	<55	-25
29	3	56	-69
4	4	73	-73
6	4	32	-25
8	4	216	-254
10	4	118	109
12	4	72	-77
14	4	49	31
16	4	168	-171
18	4	53	-66
20	4	124	121
22	4	128	-113
24	4	<56	-14
26	4	<55	13
28	4	<52	-31
5	5	247	268
7	5	127	-139
9	5	<31	17
11	5	<37	26
13	5	100	-108
15	5	102	89
17	5	<45	1
19	5	<50	29
21	5	53	-34
23	5	52	-49
25	5	64	57
27	5	<53	-11
29	5	<49	1
6	6	229	-240
8	6	185	-214
10	6	163	180
12	6	171	-183
14	6	88	-85
16	6	<48	-19
18	6	102	-100
20	6	<52	-39
22	6	<48	-21
24	6	<48	29
26	6	98	-91
28	6	59	-56
7	7	431	504
9	7	236	-247
11	7	223	-226
13	7	131	139
15	7	79	69
17	7	55	-49
19	7	104	-102
21	7	158	149
23	7	90	-94
25	7	55	-61
27	7	107	108
29	7	<48	-33
8	8	146	-161
10	8	61	-45
12	8	178	-164
14	8	106	-103
16	8	53	-69
18	8	165	-159
20	8	53	-58
22	8	<46	-7
24	8	62	-51
26	8	85	-85
28	8	56	-57
9	9	94	-94
11	9	85	-70
13	9	224	-219
15	9	<42	-12
17	9	<43	-19
19	9	82	-84
21	9	104	-87
23	9	56	-60
25	9	<54	-1
27	9	60	-59
29	9	<45	-23
10	10	236	231
12	10	<50	18
14	10	196	193
16	10	65	-67
18	10	<47	4
20	10	220	208
22	10	48	-49
24	10	57	45
26	10	55	48
28	10	<47	26
11	11	110	102
13	11	195	-184
15	11	75	-88
17	11	124	122
19	11	55	-58
21	11	96	-92
23	11	<55	-39
25	11	<55	43
27	11	<53	-28
12	12	<45	-22
14	12	178	-160
16	12	56	-60
18	12	65	-50
20	12	54	-48
22	12	<54	-32
24	12	<52	37
26	12	<49	20
28	12	82	69
13	13	<48	0
15	13	<53	15
17	13	103	90
19	13	88	83
21	13	54	41
23	13	136	118
25	13	<55	49
27	13	<52	49
14	14	<51	26
16	14	<53	14
18	14	75	74
20	14	<54	7
22	14	<55	7
24	14	61	66
26	14	99	88
15	15	123	118
17	15	54	52
19	15	<53	18
21	15	<54	35
23	15	<55	33
25	15	<52	3
16	16	91	-97
18	16	124	-106
20	16	<55	43
22	16	<55	-27
24	16	75	-64
17	17	180	177
19	17	67	-66
21	17	<54	-32
23	17	<51	13
25	17	<49	37
18	18	53	-54
20	18	<54	10
22	18	99	-77
24	18	<48	-36
19	19	<55	-12
21	19	52	-48
23	19	89	-87
20	20	<53	17
22	20	<49	-2
24	20	86	85
21	21	55	63
23	21	56	-54
22	22	<46	22
ℓ = 3			
1	0	<40	-1
2	1	<40	1
3	2	<41	9
4	3	393	381
5	4	186	-169
6	5	222	-210
7	6	185	178
8	7	155	126
9	8	<68	48
10	9	116	-121
11	10	68	65
12	11	<73	12
13	12	<76	-24
14	13	129	131
15	14	<81	-23
ℓ = 4			
0	0	870	1059
1	1	<51	-41
2	2	<51	11
3	3	62	64
4	4	391	364
5	5	355	325
6	6	173	142
7	7	194	195
8	8	<68	17
9	9	<68	-55
10	10	482	519
11	11	<77	56
12	12	<83	55
13	13	89	-88
14	14	234	215
15	15	157	148
16	16	<87	28
17	17	<86	69
18	18	<85	20
19	19	<83	5
20	20	145	144
ℓ = 5			
1	0	<55	0
2	1	<55	0
3	2	<56	5
4	3	285	271
5	4	129	-122
6	5	174	-155
7	6	126	134
8	7	105	98
9	8	<78	37
10	9	94	-95
11	10	<80	52
12	11	<82	10
13	12	<85	-20
14	13	106	108
15	14	<86	-19
ℓ = 6			
0	0	343	311
1	1	<65	-18
2	2	114	-116
3	3	202	203
4	4	<73	-30
5	5	150	141
6	6	135	-127
7	7	285	284
8	8	88	-96
9	9	<83	-57
10	10	137	144
11	11	85	69
12	12	<85	-16
13	13	<86	3
14	14	<87	16
15	15	<87	81
ℓ = 7			
1	0	<68	0
2	1	<68	-1
3	2	<69	5
4	3	196	185
5	4	77	-84
6	5	112	-108
7	6	94	94
8	7	70	71
9	8	<72	26
10	9	<76	-69
11	10	<78	39
ℓ = 8			
0	0	446	471
1	1	<73	-16
2	2	<74	1
3	3	<75	30
4	4	180	173
5	5	172	154
6	6	78	73
7	7	80	96
8	8	<76	8
9	9	<76	-31
10	10	286	293
11	11	<75	30
ℓ = 9			
1	0	<73	1
2	1	<73	-1
3	2	<74	4
4	3	109	124
5	4	<74	-57
6	5	<75	-74
7	6	<75	66
8	7	<75	49
9	8	<75	17
ℓ = 10			
0	0	138	133
1	1	<76	-6
2	2	<76	-54
3	3	100	97
4	4	<75	-17
5	5	<75	62
6	6	<74	-64
7	7	125	145
8	8	<73	-49
9	9	<72	-30
10	10	<71	70
ℓ = 12			
0	0	198	218
10	10	147	153

Table 3. *Atomic parameters of* $Zr_4Co_4Ge_7$ *and their standard deviations*

	Position	x	$\sigma(x) \times 10^4$	y	$\sigma(y) \times 10^4$	z	$\sigma(z)$	B[Å^2]	$\sigma(B)$
8Zr(1)	$8h$	0·1390	3	0·1390	3	0	–	0·52	0·03
8Zr(2)	$8j$	0·6962	2	$\frac{1}{2}$	–	0	–	0·52	0·03
16Co	$16k$	0·1482	2	0·6482	2	$\frac{1}{4}$	–	0·54	0·03
8Ge(1)	$8h$	0·2934	3	0·2934	3	0	–	0·49	0·04
8Ge(2)	$8i$	0·2918	2	0	–	0	–	0·42	0·04
8Ge(3)	$8j$	0·9069	2	$\frac{1}{2}$	–	0	–	0·53	0·04
4Ge(4)	$4e$	0	–	0	–	0·250	0·004	0·47	0·04

Discussion

The V-phase structure (Fig. 2) may be described as intermediate between two structure families: the tetrahedrally close packed structures and the CuAl₂-type family. The tetrahedrally close packed structures are characterized by the predominance of fairly regular coordination polyhedra of coordination numbers (C.N.) 12, 14, 15 and 16 (Frank & Kasper, 1958, 1959). Shoemaker & Shoemaker (1968a) have proposed the name 'tetrahedrally close packed structures' for these phases, since they have slightly distorted tetrahedral voids only. They have typically metallic character, *i.e.* their occurrence and varying compositions are governed by valence electron rules (Greenfield & Beck, 1956; Das & Beck, 1960; Bardos & Beck, 1966; Laves & Witte, 1936; Klee & Witte 1954; Nevitt, 1963; Wernick, 1967). This group of compounds may be divided into two subgroups. The one, commonly called the σ-phase related structures (for references see Shoemaker & Shoemaker, 1968a, b) is formed by metals of not more than 15% difference in atomic radii (C.N. 12). The structures of the other subgroup, the Laves phases (MgNi₂-, MgCu₂- and MgZn₂-type, for references see Nevitt, 1963) are formed by elements differing about 10 to 60% in atomic radii. These structures are distinguished from the σ-phase related structures in so far as they have C.N. 12 and C.N. 16 polyhedra only. The lack of intermediate coordination polyhedra is probably responsible for the occurrence of the Laves phases in ternary systems along the pseudobinary sections $A(B,C)_2$ only, in contrast to the σ-phase related structures where the C.N. 14 and C.N. 15 sites can accomodate both small and large atoms (Shoe-maker & Shoemaker, 1965).

The CuAl₂ family comprises a number of structures (CuAl₂-, U₃Si₂-, C₅B₃-type sructures) which may be described as stacking variants of the tessellation net $3^2.4.3.4$, formed by the larger atoms only (Aronsson, 1961). The structure types W₅Si₃, Mn₅Si₃ and Ti₅Ga₄ (for references see Schubert, 1964) with a transition metal/meta metal ratio similar to that of the V-phase may be regarded, like the V-phase structure, as intermediate between the tetrahedrally close packed structures and the structures of the CuAl₂ family (Aronsson, 1961). The structural relationships among these various silicide structure types have been discussed by Parthé, Lux & Nowotny (1955) and Nowotny (1963).

Like most of the tetrahedrally close packed structures and the structures of the CuAl₂ family, the V-phase is a layered structure. It has two identical main layers at $z = 0$ and $\frac{1}{2}$, translated, relative to each othe₁
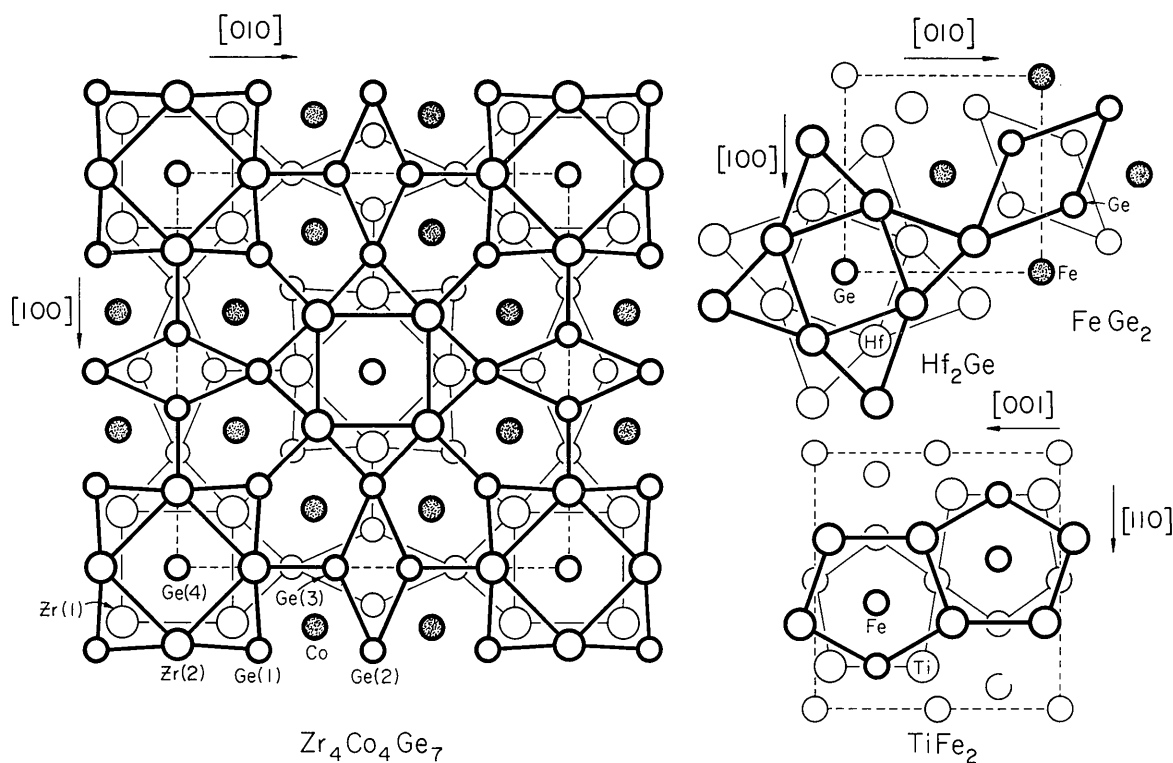

Fig. 2. Structure of the V-phase Zr₄Co₄Ge₇ as compared to the structures of Hf₂Ge and FeGe₂ (both crystallizing in the CuAl₂-type) and TiFe₂ (MgZn₂-type). The outlined building elements in the CuAl₂ and MgZn₂-type structures are very similar to those present in Zr₄Co₄Ge₇. In the drawing of the Zr₄Co₄Ge₇ structure the atoms at $z = \frac{1}{2}$ are connected with thick lines, atoms at $z = 0$ with thin lines and non connected atoms are superimposed with $z = \frac{1}{4}$ and $\frac{3}{4}$.

by half the base diagonal. These layers are formed by the Zr atoms and the Ge atoms (1), (2) and (3) which are in contact with each other, thus forming a tessellation of pentagons, squares and triangles (Fig. 2). The Co and Ge(4) atoms are situated at $z=\frac{1}{4}$ and $\frac{3}{4}$ and have no close neighbors within their layers. The structure exhibits a high degree of close packing.* However it should not be considered as a purely tetrahedrally close packed structure since some of the tetrahedra have edges differing by more than 40% in length; furthermore it does not contain Frank-Kasper polyhedra only. It is interesting to note that the tetrahedrally close packed structures and the structures of the $CuAl_2$ family occur most frequently in the binary systems of the components forming a V-phase. The structural relationship of the V-phase to these structure types can be demonstrated by comparison of the coordination polyhedra.

As can be seen from Fig. 3 the environments of the Zr atoms (1) and (2) are the same, if one disregards some minor differences in the interatomic distances (Table 5). This coordination polyhedron may be derived from the Frank–Kasper polyhedron C.N. 15 by replacing each of two atoms from the 'belt' by a pair of atoms at the same level, whereby the C.N. is increased to 17. A similar arrangement is also found around the Hf^I atom in $Hf_3^I Hf_2^{II} Sn_4$ (Ti_5Ga_4-type, Rossteutscher & Schubert, 1965) where the places of Zr are taken by Hf^I, those of Co by Hf^{II} and those of Ge by Sn. The coordination polyhedra for the Co and Ge(2) atoms are distorted icosahedra, which are present in all tetrahedrally close packed structures. The environment of Ge(1) is the same as that of Ge(2) except for the replacement of two neighboring Ge atoms by a Zr atom. This C.N. 11 polyhedron is also found for the Ge atoms in Zr_5Ge_3 (Mn_5Si_3-type, Parthé & Norton, 1958), where the places of both transition metals Zr and Co are occupied by Zr. The coordination around Ge(3) is the Frank-Kasper polyhedron C.N. 14. However, the distance of 2·46 Å to one of the crystallographically equivalent Ge atoms is very close to the covalent bonding distance of 2·45 Å in elemental germanium (diamond-type). Thus the Ge(3) atoms may be considered as forming pairs. The Ge atoms in Th_3Ge_2 (U_3Si_2-type, Tharp, Searcy & Nowotny, 1958) and $FeGe_2(CuAl_2$-type, Krén & Szabó, 1964) have similar environments with short Ge–Ge distances of $2·4_8$ and 2·62 respectively. The Ge(4) atoms are situated in a tetragonal antiprism of Zr atoms with two Ge atoms above and below the square faces. This C.N. 10 polyhedron is also found for the Ge atoms in Hf_2Ge ($CuAl_2$-type, Nowotny, Benesovsky & Schob, 1960) and the Si atoms of the fourfold positions in Nb_5Si_3

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* The term 'close packed' should be understood from a purely geometrical point of view, where atoms are considered as rigid spheres. The average atomic volume of intermetallic compounds in an alloy system is generally a smooth funtion of the composition, independent of the structure (for references see Schubert, 1964).

and $Ta_5Si_3(W_5Si_3$-type, Parthé, Nowotny & Schmid, 1955).

In Table 5 the interatomic distances in $Zr_4Co_4Ge_7$ are compared with the sum of the atomic radii for C.N. 12. There is a strong interaction of the transition metals with germanium (all distances Zr–Ge and Co–Ge are shorter than the corresponding sums of the C.N. 12 radii). The distances Zr–Zr, Zr–Co and Co–Co are all longer. The only short Ge–Ge distances are found for Ge(4), forming chains and Ge(3) forming pairs as already mentioned above.

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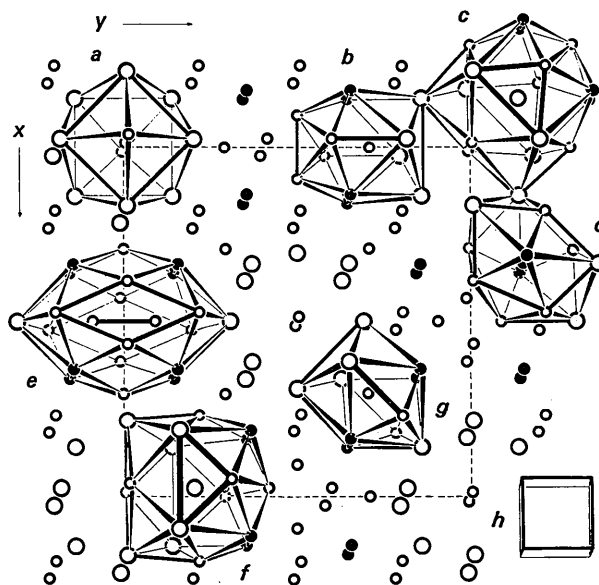

Fig. 3. Coordination polyhedra in $Zr_4Co_4Ge_7$. Co atoms are represented by black spheres, Zr and Ge atoms by large and small white spheres respectively. The environment of Zr (1) and Zr (2) is shown in *c* and *f*; *a*, *b* and *g* are the coordination polyhedra of Ge(4), Ge(2) and Ge(1) respectively; *d* shows the distorted icosahedron around the Co atoms and *e* is the coordination polyhedron around a pair of Ge(3) atoms. A cube with the cube edge $a=c/2$ as seen from the same viewpoint is drawn in *h*.

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Table 5. Interatomic distances D and coordination numbers C.N. in the structure of $Zr_4Co_4Ge_7$

For comparison the sum of the atomic radii (CN 12) is listed too. All distances shorter than 3·8 Å are given.

		D [Å]	$r_A + r_B$ [Å]	Δ [Å]
Zr(1)	4 Zr(2)	3·285 ± 3	3·20	+0·09
C.N. 17	2 Zr(1)	3·677 ± 9	3·20	+0·48
	4 Co	3·106 ± 6	2·86	+0·25
	2 Ge(2)	2·732 ± 3	2·97	−0·24
	1 Ge(1)	2·888 ± 9	2·97	−0·08
	2 Ge(1)	2·904 ± 5	2·97	−0·07
	2 Ge(4)	2·910 ± 12	2·97	−0·06
Zr(2)	4 Zr(1)	3·285 ± 3	3·20	+0·09
C.N. 17	2 Zr(2)	3·670 ± 5	3·20	+0·47
	4 Co	3·129 ± 3	2·86	+0·27
	2 Ge(1)	2·736 ± 6	2·97	−0·23
	1 Ge(3)	2·787 ± 5	2·97	−0·18
	2 Ge(2)	2·904 ± 3	2·97	−0·07
	2 Ge(4)	2·906 ± 11	2·97	−0·06
Co	2 Zr(1)	3·106 ± 6	2·86	+0·25
C.N. 12	2 Zr(2)	3·129 ± 3	2·86	+0·27
	2 Co	2·615 ± 2	2·52	+0·10
	2 Ge(1)	2·448 ± 5	2·63	−0·18
	2 Ge(3)	2·466 ± 4	2·63	−0·16
	2 Ge(2)	2·486 ± 3	2·63	−0.14
Ge(1)	2 Zr(2)	2·736 ± 6	2·97	−0·23
C.N. 11	1 Zr(1)	2·888 ± 9	2·97	−0·08
	2 Zr(1)	2·904 ± 5	2·97	−0·07
	4 Co	2·448 ± 5	2·63	−0·18
	2 Ge(1)	3·078 ± 7	2·74	+0·34
Ge(2)	2 Zr(1)	2·732 ± 3	2·97	−0·24
C.N. 12	2 Zr(2)	2·904 ± 3	2·97	−0·07
	4 Co	2·486 ± 3	2·63	−0·14
	2 Ge(3)	3·017 ± 4	2·74	+0·23
	2 Ge(3)	3·026 ± 3	2·74	+0·29
Ge(3)	1 Zr(2)	2·787 ± 5	2·97	−0·18
C.N. 14	4 Co	2·466 ± 4	2·63	−0·16
	2 Ge(2)	3·017 ± 4	2·74	+0·28
	2 Ge(2)	3·026 ± 3	2·74	+0·29
	4 Ge(3)	3·141 ± 3	2·74	+0·40
	1 Ge(3)	2·463 ± 7	2·45*	+0·01
Ge(4)	4 Zr(2)	2·906 ± 11	2·97	−0·06
C.N. 10	4 Zr(1)	2·910 ± 12	2·97	−0·06
	2 Ge(4)	2·615 ± 43	2·74	−0·12

* Ge–Ge distance in elemental germanium (diamond type).

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The Crystal Structure of 3,5-Dinitro-4-methylbenzoic Acid

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3,5-Dinitro-4-methylbenzoic acid, $C_6H_2.CH_3.(NO_2)_2.COOH$, crystallizes in space group $P2_1/a$ with four molecules per unit cell. The structure comprises hydrogen-bonded dimers with the nitro groups twisted out of the ring plane by $47.5°$ and $38.9°$ respectively.

1. Introduction

3,5-Dinitro-4-methylbenzoic acid (Fig. 1) was synthesized during studies of Friedel–Crafts reactions by Leyshon (1952), who gives details of its preparation, but earlier references to this substance are given by Claus & Joachim (1891) and Wheeler & Harris (1927). It was selected for crystallographic study in 1954, the interest at that time being in the extent of the rotation of the nitro-groups out of the plane of the benzene ring, because of the methyl group between them, and also in the hydrogen bonding. Furthermore, the rather high density (1.62 g.cm^{-3}) indicated that the structure might well show interesting short non-bonded intermolecular distances.

Various early attempts at solving the structure were unsuccessful, including applications of the sign-determining procedure of Grant, Howells & Rogers (1957) which was then being developed. Later three-dimensional sign-determining approaches (Grant, Hine & Richards, 1960) also appeared to fail, and the structure has now been solved using the $I(\theta, \varphi)$ function of Tollin & Cochran (1964). In retrospect, a refined version of the three-dimensional sign-fixing method did produce a correct set of signs, but these were not recognized

as such at the time. It is intended to publish details of the sign-determining work later; the object of the present paper is to describe the structure and its solution.
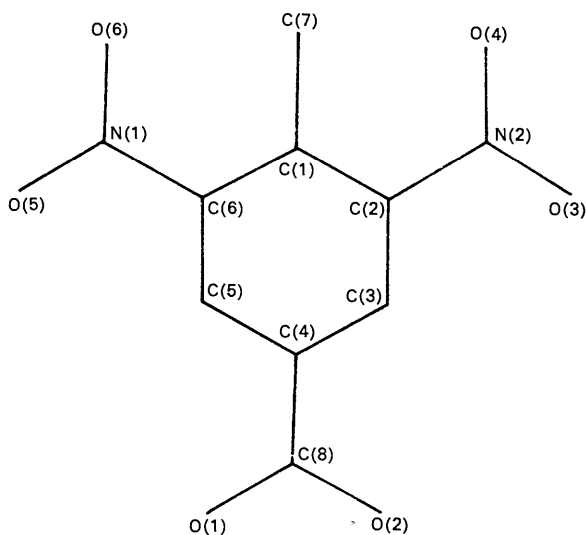

Fig. 1. The molecule of 3,5-dinitro-4-methylbenzoic acid showing the numbering scheme.