group ($P2_1/a$) and very similar distortions. In contrast to $K_xP_2W_4O_{16}$, the P and W or Mo atoms in these compounds are not located at the levels $y = \frac{1}{4}$ and $y = \frac{3}{4}$, but are slightly displaced from these planes. These displacements take place in opposite directions along [010] for two successive ReO_3-type slabs, with the result that the adjacent strings of octahedra belonging to a same slab are tilted with respect to one another. Thus, the structures of these sodium bronzes, as well as that of η-Mo_4O_{11}, are characterized by puckered ReO_3-type slabs.

The distribution of the sodium ions in the structure is worthy of note. In spite of their small size they are located in the distorted hexagonal tunnels while the 'perovskite' cages formed by eight octahedra or by seven octahedra and one tetrahedron are unoccupied. Moreover, the sodium ions which have four closest oxygen neighbors, with Na–O distances ranging from 2·45 (4) to 2·64 (5) Å, are more off-centered inside the tunnels than the K^+ ions in $K_xP_2W_4O_{16}$. The sodium ions are indeed shifted by 1·06 (4) and 1·04 (5) Å for $m = 4$ and $m = 6$ respectively from the center of gravity of the 'O_{18}' cage compared to 0·95 (4) Å for the K^+ ion in $K_xP_2W_4O_{16}$. In the same way, the 'O_{18}' cages of these bronzes are more distorted than those of $K_xP_2W_4O_{16}$ owing to the tilting of the strings of octahedra around their own direction, the angle of the tilt being close to 5° in both oxides.

This structural study shows that several members of the phosphate tungsten bronze family $A_xP_4O_8(WO_3)_{2m}$ of monoclinic symmetry can be stabilized by the presence of sodium in the distorted hexagonal tunnels. It is now established that this family can be synthesized for ions of the same size or smaller than potassium, the monoclinic pyrophosphate tungsten bronzes being obtained for ions of the same size or bigger than potassium. This is to be compared with the results previously obtained by Magnéli (1949, 1953) for the alkali tungsten bronzes A_xWO_3, the hexagonal tungsten bronzes being obtained in normal conditions only for K^+ and ions bigger than K^+, whereas the tetragonal tungsten bronzes were synthesized for K^+ and smaller ions. Studies are being carried out in order to isolate other members of this series, and especially odd-*m* members, which should differ from even members by a translation of the successive 'phosphate planes' with respect to each other. The influence of the distortion on the electron transport of these oxides will also be studied.

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The Structure of the κ Phase, Mn_5Ge_2

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Abstract. $M_r = 419·87$, orthorhombic, *Ibam*, $a = 11·781$ (8), $b = 6·136$ (6), $c = 5·368$ (2) Å, $V = 388·0$ Å^3, $D_m = 7·19$ (4), $D_x = 7·19$ Mg m^{-3}, $Z = 4$, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 31·6 mm^{-1}, $F(000) = 756$, room temperature. The structure was found to be a modification of Mg_5Ga_2 or Cu_5As_2 and was refined by full-matrix least squares to a final $R_w(F)$ value of 0·0402, based on 198 independent reflections. The unit cell is made up of four-by-two-by-two body-centered subcells with four atoms removed and the rest shifted somewhat in position. There are three kinds of coordination polyhedra in the structure, CN12, CN11 and two CN10. Ge atoms are surrounded solely by Mn atoms. The structure is described as a packing of CN10 polyhedra around Ge atoms.

Introduction. In the Mn–Ge system, four intermetallic compounds, $Mn_{3.25}Ge$, Mn_5Ge_2, Mn_5Ge_3 and Mn_3Ge_2, were reported by Elliot (1965). Wachtel & Henig (1969) examined magnetic properties for this system

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and found a compound χ-Mn_2Ge. X-ray powder diffraction data of χ-Mn_2Ge, which has the Ni_2In ($B8_2$) structure type, were obtained by Ellner (1980). The compound $Mn_{3.25}Ge$ has a high- and a low-temperature phase, whose structure types are Ni_3Sn ($D0_{19}$) (Zwicker, Jahn & Schubert, 1949) and Al_3Ti ($D0_{22}$) (Kádár & Krén, 1971), respectively. The compound Mn_5Ge_2 also has a high- (ζ) and a low-temperature (κ) phase, which were reported to have a hexagonal (Ohoyama, 1961) and an orthorhombic lattice (Laridjani, Bigare & Guinier, 1970), respectively. The structure of the high-temperature Mn_5Ge_2 ζ phase was proposed first by Komura & Hirayama (1981). The Mn_5Ge_3 η phase has the Mn_5Si_3 ($D8_8$) type structure (Castelliz, 1953). According to Völlenkle, Wittmann & Nowotny (1964) Mn_3Ge_2 should be described more properly as $Mn_{11}Ge_8$. Israiloff, Völlenkle & Wittmann (1974) compared the powder diffraction pattern of $Mn_{11}Ge_8$ with that of $Cr_{11}Ge_8$, and concluded that $Mn_{11}Ge_8$ is isotypic with $Cr_{11}Ge_8$.

Ohoyama (1961) reported the powder diffraction pattern of the low-temperature Mn_5Ge_2 κ phase, but the indexing of the pattern was unsuccessful. Laridjani *et al.* (1970) also obtained powder diffraction data and tried to index the reflections by assuming an orthorhombic unit cell of dimensions $a = 9{\cdot}656$, $b = 10{\cdot}149$, $c = 10{\cdot}854$ Å. However, discrepancies were found among the two sets of data; for example, strong reflections such as $d = 2{\cdot}3641$, $2{\cdot}3354$ and $2{\cdot}0820$ Å in the data obtained by Laridjani *et al.* are not found in Ohoyama's paper. Their data are listed in Table 1 together with our observed data. In order to clarify the inconsistency between these papers, we tried to determine the structure of the Mn_5Ge_2 κ phase more accurately by single-crystal X-ray diffraction.

Experimental. Alloys were prepared by melting 99·99% Mn flakes and 99·999% Ge in an alumina crucible placed in an evacuated quartz tube. The mother alloy of Mn_5Ge_3 was made first in an electric furnace at 1420 K. After necessary amounts of Mn were added for Mn_5Ge_2, the alloy ingot was melted again at 1420 K and annealed at 870 K for 123 h for homogenization. A chemical analysis has not yet been made.

The powder diffraction pattern (Table 1) was obtained with an X-ray diffractometer with Zr-filtered Mo $K\alpha_1$ radiation ($\lambda = 0{\cdot}70926$ Å). Our data show good agreement with Ohoyama's.

A tiny plate-like fragment, 30 x 30 x 5 μm, was picked out from the ingot for single-crystal work. Laue and oscillation photographs indicated orthorhombic symmetry.

Table 1. *Comparison of the observed powder data with those estimated from the single-crystal work and other authors' data*

* Indicates extra reflections from the Mn_5Ge_3 η phase and † from the Mn_5Ge_2 ζ phase

	Estimated value		Observed value		Ohoyama (1961)		Laridjani (1970)	
h k l	d_{cal}	I/I_0	d_{obs}	I/I_0	*d*	I/I_0	*d*	I/I_0
2 1 1	3·3318	12	3·330	13	3·330	*s*	3·3294	35
0 2 0	3·0680	3	3·069	8	3·063	*w*	3·0632	5
4 0 0	2·9452	7	2·945	9	2·946	*m*	2·9461	18
					2·814†	*w*	2·8144†	10
2 2 0	2·7210	11	2·721	14	2·723	*w*	2·7231	3
0 0 2	2·6840	6	2·683	7	2·678	*m*	2·6782	4
			2·517*	7				
2 0 2	2·4424	10	2·441	11	2·442	*w*		
1 1 2	2·4072	32	2·408	20	2·405	*s*	2·4050	18
4 1 1	2·3800	4					2·3641	39
							2·3354*	55
5 1 0	2·1996	28	2·200	25	2·199	*s*	2·1822	37
4 2 0	2·1247	100	2·126	100	2·126	*vvs*	2·1152	100
			2·118*	55			2·0820*	90
0 2 2	2·0201	100	2·018	76	2·020	*vvs*	2·0207	77
1 3 0	2·0152	27						
4 0 2	1·9838	96	1·984	58	1·983	*vvs*	1·9832	50
2 3 1	1·8180	7	1·818	12	1·817	*s*	1·8181	10
3 3 0	1·8140	2						
6 1 1	1·7660	6	1·765	10	1·768	*s*	1·7672	12
5 1 2	1·7013	3	1·703	6	1·698	*vw*	1·6984	10
4 2 2	1·6659	2			1·669	*w*	1·6676	2
2 1 3	1·6491	2			1·650	*w*	1·6504	3
1 3 2	1·6115	3	1·614	6	1·612	*vw*	1·6122	4
6 0 2	1·5847	2			1·585	*vw*	1·5815	31
0 4 0	1·5340	11	1·536	15	1·536	*s*	1·5352	10
3 3 2	1·5030	4	1·503	6	1·503	*w*	1·5032	5
8 0 0	1·4726	11	1·474	12	1·473	*s*	1·4732	11
6 2 2	1·4080	5	1·410	5	1·410	*w*	1·4095	3
6 3 1	1·3696	4			1·370	*m*	1·3727	5
0 0 4	1·3420	15	1·340	18	1·341	*vs*	1·3411	26
5 3 2	1·3387	25						
8 2 0	1·3276	1			1·331	*vw*	1·3312	21
2 3 3	1·3128	3	1·315	5	1·313	*w*	1·3134	5
6 1 3	1·2929	2			1·294	*m*	1·2942	4
4 0 4	1·2212	1			1·222	*vw*	1·2224	45
1 5 0	1·2206	1						
4 4 2	1·2135	17	1·215	18	1·217	*s*	1·2174	25
8 2 2	1·1900	16	1·192	13	1·192	*s*	1·1921	32
10 0 0	1·1781	2			1·175	*w*	1·1752	25
2 5 1	1·1724	4	1·174	8				
3 5 0	1·1713	1						
9 1 2	1·1555	8	1·157	8	1·157	*m*	1·1572	35
5 1 4	1·1456	5	1·146	7				
4 2 4	1·1346	22	1·136	15				
1 3 4	1·1170	6	1·117	8				
1 5 2	1·1111	8	1·112	11				
6 3 3	1·1106	2						
9 3 0	1·1025	6	1·104	9				
5 5 0	1·0884	7	1·090	9				
10 0 2	1·0788	1						
8 4 0	1·0623	4	1·063	6				
6 2 4	1·0421	1						
6 5 1	1·0216	2						
10 2 2	1·0177	2						
0 4 4	1·0100	4	1·012					
10 3 1	1·0029	2						
2 5 3	0·9974	2						
8 0 4	0·9919	4	0·991					

Lattice constants from a least-squares fit to 20 interplanar spacings measured on the X-ray diffractometer. Density measured with a pycnometer. Rigaku automated four-circle diffractometer (AFC-5), graphite-monochromated Mo $K\alpha$ radiation, $0 \le h \le 14$, $0 \le k \le 7$, $0 \le l \le 6$, $2\theta_{max} = 50°$, θ–2θ scan, scan range $(1{\cdot}2 + 0{\cdot}5\tan\theta)°$, scan rate 2° min^{-1} in θ. Backgrounds measured at the beginning and end of each scan range for 5 s. Monitor counting method used to avoid the effect of the incident-beam fluctuation. Each reflection measured up to three times, until the condition $\sigma(|F_o|)/|F_o| \le 0{\cdot}05$ was satisfied. Lp correction made at each scan. Absorption and extinction corrections not applied, since the effects were found to be small. Systematic absences hkl $h+k+l = 2n+1$, $0kl$ $k = 2n+1$ and $l = 2n+1$, $h0l$ $h = 2n+1$ and $l = 2n+1$ indicate space groups *Ibam* or *Iba*2, as with Mg_5Ga_2 (Schubert, Gauzzi & Frank, 1963) or Cu_5As_2 (Liebisch & Schubert, 1971) which have similar lattice dimensions. The structure was assumed to be isotypic with

Table 2. *Refined parameters for the* Mn_5Ge_2 *κ phase (Ibam)*

$U_{eq} = \frac{1}{3}$trace **U**.

	Ge	Mn (1)	Mn (2)	Mn (3)
	8 (*j*)	4 (*b*)	8 (*f*)	8 (*j*)
x	0·12005 (13)	0·0	0·23028 (16)	0·10063 (19)
y	0·77664 (27)	0·5	0·5	0·19017 (39)
z	0·0	0·25	0·25	0·0
U_{eq}(Å^2)	0·00717 (79)	0·00660 (142)	0·00820 (106)	0·00924 (117)

Table 3. *Interatomic distances* (Å) *for the* Mn_5Ge_2 *κ phase*

	Ge	Mn (1)	Mn (2)	Mn (3)
Ge		2·585 (2)†	2·524 (2)* 2·605 (2)*	2·548 (4) 2·608 (3) 2·701 (1)*
Mn (1)	2·585 (2)*	2·684 (1)*	2·713 (3)	2·612 (2)*
Mn (2)	2·524 (2)* 2·605 (2)*	2·713 (3)*	2·684 (1)*	2·670 (3)* 2·784 (3)*
Mn (3)	2·548 (4) 2·608 (3) 2·701 (1)*	2·612 (2)†	2·670 (3)* 2·784 (3)*	
CN	10	12	11	10

* Distances occurring twice.
† Distances occurring four times.

Mg_5Ga_2 having the space group *Ibam* as a starting model. Refinement on *F* with 198 independent reflections (from 1290 observed reflections) and isotropic temperature factors reduced $R_w(F)$ to 0·0476, $w = 1/\sigma^2(|F_o|)$. With anisotropic temperature factors (21 variables) final $R_w(F) = 0{\cdot}0402$, $R(F) = 0{\cdot}0375$, $S = 1{\cdot}6662$, $(\Delta/\sigma)_{max} = 0{\cdot}35$, final $\Delta\rho$ excursions $\leq 1{\cdot}7$ e Å^{-3}. Scattering factors for Mn and Ge atoms from *International Tables for X-ray Crystallography* (1974). Full-matrix least-squares program *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979) on HITAC M-180 and M-200H computers at the Information Processing Center of Hiroshima University.

Another possible space group, *Iba*2, was excluded because with refinement in this space group, some additional parameters required had large standard deviations and the correlation coefficients became large.

Discussion. The final parameters for the Mn_5Ge_2 κ phase are listed in Table 2.* A perspective view of the structure is shown in Fig. 1 (*ORTEP*; Johnson, 1976). The structure is considered as built of four-by-two-by-two body-centered subcells along the *a*, *b* and *c* axes, respectively, with four atoms at $00\frac{1}{4}$, $00\frac{3}{4}$, $\frac{1}{2}\frac{1}{2}\frac{1}{4}$ and $\frac{1}{2}\frac{1}{2}\frac{3}{4}$ removed and the rest shifted somewhat in position, the *z* parameters being unchanged. It may then be considered as a stacking of four layers as follows: on the planes $z = \frac{1}{4}$ and $\frac{3}{4}$, only Mn atoms are placed, the rest of the Mn and Ge atoms being placed alternately along *a* and *b* axes on $z = 0$ and $\frac{1}{2}$ planes. Mn and Ge atoms around the removed atoms are shifted close to each other and form two tetrahedra of different sizes, both of which consist of like atoms. Similar arrangements of tetrahedra around removed atoms are found in the γ-brass structure.

Interatomic distances are listed in Table 3. Four kinds of coordination polyhedra in the structure are shown in Fig. 2. Fig. 2(*a*) shows a polyhedron around

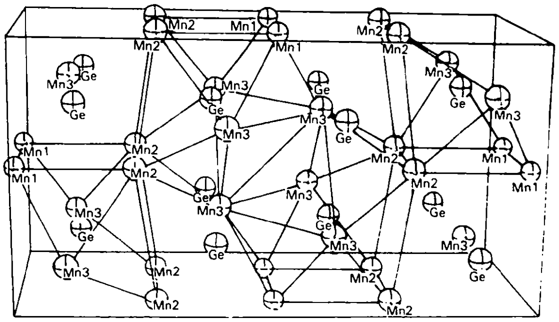

Fig. 1. Perspective view of the Mn_5Ge_2 κ phase in the **c** direction. The origin is at the lower left corner, **b** is vertical, **a** is horizontal. Polyhedra around the Ge atoms are connected by solid lines.

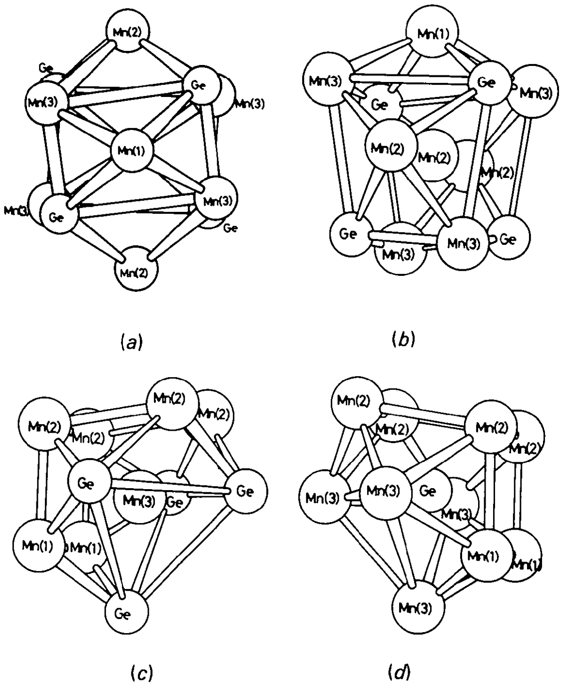

Fig. 2. Polyhedra in the Mn_5Ge_2 κ phase. (*a*) CN12, around Mn (1), (*b*) CN11, around Mn (2), (*c*) CN10, around Mn (3), (*d*) CN10, around Ge.

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* Lists of structure factors and anisotropic temperature factors for the κ phase Mn_5Ge_2 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39082 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Mn(1). It has 12 coordinated atoms; that is, four Ge, two Mn(1), two Mn(2) and four Mn(3) atoms forming a distorted cubo-octahedron. Figs. 2(*b*), 2(*c*) and 2(*d*) show coordination polyhedra of CN11, 10 and 10 around Mn(2), Mn(3) and Ge atoms, respectively. The Ge atom is surrounded solely by Mn atoms. The CN10 polyhedra around Mn(3) and Ge can be considered as heavily distorted bicapped dodecahedra (Bhandary & Girgis, 1977).

The structure of Mn_5Ge_2 thus obtained is not much different from that of Mg_5Ga_2 (Schubert *et al.*, 1963) or Cu_5As_2 (Liebisch & Schubert, 1971); however, both these structures were analyzed by the photographic method and the *R* values were rather high. The difference between the structures of Mn_5Ge_2 and Mg_5Ga_2 or Cu_5As_2 is in the coordination around the Mn(3) atoms on the 8(*j*) site [Fig. 2(*c*)]. Contrary to Mn_5Ge_2, the central Mg atom in Mg_5Ga_2 has nine coordinated atoms and the Cu atom in Cu_5As_2 has eleven coordinated atoms. In Mg_5Ga_2, two atoms (which would be placed at the upper left in the figure) are far from the central atom, and the Mg atom (which would be placed at the lower right, outside the figure) comes closer to the central atom. For the Cu_5As_2 structure, an extra Cu atom is placed close to the central atom in addition to the near neighbor, as in Fig. 2(*c*).

The packing of polyhedra around the minor component Ge in Mn_5Ge_2 is shown in Fig. 1. The polyhedra are arranged tetrahedrally, sharing the edge around the removed atoms.

From the structural point of view, there is considerable difference between the Mn–Ge and Mn–Si systems. The structure of Mn_5Si_2 is different from that obtained in the present paper. The CN11 and CN12 polyhedra found in Mn_5Si_2 have different shapes from those in Mn_5Ge_2 (Shoemaker & Shoemaker, 1976).

Observed powder data are compared with estimated values in Table 1 together with the data reported by Ohoyama and Laridjani *et al.* Several very weak reflections are omitted in the table. There are two extra reflections at $d = 2{\cdot}517$ and $2{\cdot}118$ Å, which are identified as reflections from the Mn_5Ge_3 η phase. Laridjani *et al.* (1970) concluded from powder data that Mn_5Ge_2 is orthorhombic, but their lattice constants differ from ours. In particular, reflections having $d = 2{\cdot}3354$ and $2{\cdot}0820$ Å in the Mn_5Ge_3 η phase were taken as the true reflections from κ-Mn_5Ge_2, so that a wrong unit cell was deduced. A reflection having $d = 2{\cdot}8144$ Å, which was observed by both Ohoyama and Laridjani *et al.*, belongs to the high-temperature Mn_5Ge_2 ζ phase.

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