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## The Crystal Structure of the Intermetallic Compound $Mg_3Cr_2Al_{18}$ \*

BY STEN SAMSON

*Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California, U.S.A.*

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A complete determination of the crystal structure of the ternary phase (*E* phase) in the magnesium–aluminum–chromium system with composition  $Mg_3Cr_2Al_{18}$  has been carried out with use of intensity data obtained from single crystal Weissenberg photographs. The refinement of the structure was carried out by application of the method of least squares. The space group is  $O_h^1-Fd3m$  with 184 atoms per unit cube. The lattice constant determined with use of powder samples was  $a_0 = 14.53 \pm 0.01$  Å. The truncated tetrahedron, the icosahedron and the hexagonal prism are prominent coordination polyhedra in this structure. An analysis of these polyhedra reveals that in places where interaction between the atoms of the transition element (chromium) and those of the hypoelectronic elements aluminum and magnesium are to be expected, the packing of the atoms is very efficient, whereas in places where such interactions are less likely the packing of atoms appears to be normal or rather loose.

### Introduction

In his examination of the magnesium–chromium–aluminum system Erdmann-Jesnitz (1940) observed a ternary intermetallic compound, the *E*-phase, with the approximate composition  $MgCrAl_3$ . Little, Axon & Hume-Rothery (1948) found that the composition of the *E* phase is not sharply defined but varies over a certain range and that, furthermore, zinc is soluble in the phase to some extent. Crystals extracted from two ternary alloys were found on analysis to have the compositions  $Mg_2Cr_{1.3}Al_{16.1}$  and  $Mg_2Cr_{1.3}Al_{17.6}$  and those from a sample containing some zinc were found to have the composition  $Mg_2Cr_{1.01}Zn_{0.04}Al_{10.9}$ . In their phase diagram the point corresponding to the formula  $Mg_2CrAl_{13}$  is approximately at the center of the single-phase field of *E*.

Little *et al.* (1948) reported that the crystal structure of *E* is cubic with a lattice spacing  $a_0 = 14.65$  kX. (= 14.68 Å) but that  $a_0$  is not constant but varies over a certain range. They suggested that the unit cell contains sixteen formula units of  $Mg_2CrAl_{12}$  but they did not determine the positions of the atoms.

In a previous paper (Samson, 1954) the crystal structure of the *E* phase was briefly described. The atomic positions with the positional parameters in an

early stage of the refinement were given. A more detailed description of the structure determination and the final results of the refinement will be given below.

### Experimental work

#### *Preparation of single crystals*

Ternary alloys containing magnesium, chromium and aluminum and quaternary alloys containing in addition some zinc were prepared by melting pieces of the pure metals together in aluminum crucibles by induction heating. During the preparation the alloys were kept in argon gas at atmospheric pressure. The melts were allowed to solidify at varying cooling rates. Some alloys were subsequently annealed for about a month at 460 °C. in evacuated and sealed pyrex tubes. At the time the previous paper (Samson, 1954) was published attempts to prepare single crystals of a size convenient for single-crystal X-ray photography from ternary magnesium–chromium–aluminum alloys had not been successful. For that reason crystals had to be isolated from a quaternary alloy containing some zinc. However, during subsequent preparative work some single crystals were obtained from a ternary alloy (approximate composition: Mg, 15%; Cr, 3%; Al, 82%) and in a slowly cooled and subsequently annealed quaternary alloy (approximate composition: Mg, 15%; Cr, 3%; Zn, 3%; Al, 79%) many well developed octahedral crystals comparatively large in size were found and isolated.

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Alloys containing more than approximately four percent of chromium (by weight) formed, when slowly cooled, segregates containing chiefly big crystals of  $CrAl_7$ .  $E$ -phase crystals could not be found in them. When the chromium content was lower than four percent the matrix was malleable and although  $E$ -phase crystals formed they were very tiny and hard to isolate.

#### Density, space group, unit-cell dimension.

The density of the octahedral crystals referred to above was found to be  $2.87 \text{ g.cm.}^{-3}$  by use of the flotation method while the very tiny crystal fragment used in the previous work gave a smaller value ( $2.80 \text{ g.cm.}^{-3}$ ), probably caused by some very small gas bubbles attached to the crystal surface.

The octahedral crystals gave X-ray diffraction patterns identical to those obtained by using the smaller crystal fragments isolated from the ternary alloy. Laue photographs indicated the Laue symmetry  $O_h-3m$ . Rotation and Weissenberg photographs (rotation about  $[001]$ ) were indexed on the basis of a face-centered cubic lattice with a cell constant approximately equal to  $14.55 \text{ \AA}$ . On the zero-layer Weissenberg photographs only reflexions with  $h = 2n$ ,  $k = 2n$ , and  $h+k = 4n$  could be observed. Only  $hhl$ -reflexions of the kind  $h+l = 2n$  were present. The only probable space group is thus  $O_h^7-Fd\bar{3}m$ .

A powder specimen of the pure  $E$  phase was prepared by grinding isolated octahedral crystals. A powder photograph was taken with nickel-filtered  $Cu K\alpha$  radiation in a Straumanis type camera of  $5 \text{ cm}$ . radius. The more accurate lattice parameter derived from the diffraction maxima of this photograph by the method of Nelson & Riley (1945) was found to be  $a_0 = 14.526 \text{ \AA}$  ( $Cu K\alpha$ ,  $\lambda = 1.5418 \text{ \AA}$ ). Another powder photograph was taken from filings of a rapidly quenched and subsequently annealed ternary alloy of the type  $\alpha_{Al}+E$  which on chemical analysis was found to have the composition: Mg, 7.6%; Cr, 10.7%; Al, by difference. The Nelson-Riley plot gave for this photograph nearly the same lattice constant  $a_0 = 14.527 \text{ \AA}$ . Since the ambient temperature during photography is not precisely known the lattice spacing for the  $E$  phase at room temperature (about  $25 \text{ }^\circ\text{C}$ .) may be taken as  $a_0 = 14.53 \pm 0.01 \text{ \AA}$ . This accuracy is sufficient for the purpose of this work.

#### Intensity data

Intensity data for both  $hk0$ - and  $hkl$ -reflexions were used for the final refinement. These data were collected from Weissenberg photographs (nickel-filtered  $Cu K\alpha$  radiation) with application of the multiple-film technique of de Lange *et al.* (1939) and Robertson (1943). The single crystal used was isolated from a ternary alloy (not containing zinc). It was a plate of the dimensions  $0.03 \times 0.06 \times 0.12$  millimeter. Absorption correction was not made.

The octahedral crystals referred to above, although of a size more convenient for single-crystal X-ray photography, were not used for obtaining intensity data for the final refinement because of the uncertainty regarding the amount of zinc present in these crystals.

#### Derivation of the trial structure

The trial structure was derived by exploring the different types of point positions in space group  $O_h^7$  beginning with those of highest multiplicity. The  $96g$ -position was quickly recognized to have necessary properties for incorporation in the structure of roughly the correct composition with respect to the number of large atoms (magnesium atoms) and small atoms (aluminum and chromium atoms). By using this point position as a starting point, the atomic arrangement given in Table 1 was derived.

Packing considerations indicate that the magnesium and aluminum atoms are in the positions given in Table 1. In view of the short nearest neighbour distances around position  $16c$  it seems likely that these positions are occupied exclusively or at least predominantly by chromium atoms.

The atomic arrangement given in Table 1 corresponds to the composition  $Mg_3Cr_2Al_{18}$ , which is in fairly good agreement with that, found by Little *et al.* (1948) ( $1\frac{1}{2} \times Mg_2CrAl_{12} = Mg_3Cr_{15}Al_{18}$ ). The calculated density ( $\rho_{\text{calc.}} = 2.87 \text{ g.cm.}^{-3}$ ) also agrees very well with the measured one.

Approximate positional parameters were obtained by assuming the radius of the magnesium atoms to be about  $1.60 \text{ \AA}$  and the radii of the aluminum and chromium atoms to be about  $1.40 \text{ \AA}$  and  $1.25 \text{ \AA}$  respectively. The structure factors calculated for the trial structure were in excellent agreement with those obtained from the observed intensities.

Table 1. Preliminary and final positional parameters

Kind of atom	No. of atoms	Point position	Parameter		Ligancy
			approximate	refined	
$Al_f$	96	$g X, X, Z$ etc.	$X = 0.067$ $Z = 0.298$	$X = 0.0666 \pm 0.0003$ $Z = 0.2998 \pm 0.0004$	12
$Al_f$	48	$f X, 0, 0$ etc.	$X = 0.134$	$X = 0.1407 \pm 0.0006$	12
$Mg_d$	16	$d \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ etc.			14
$Mg_b$	8	$b \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ etc.			16
Cr	16	$c \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ etc.			12

Origin of coordinates at  $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$  from center ( $\bar{3}m$ )

### Refinement of the structural parameters

The approximate atomic coordinates were first adjusted by visual comparison of observed intensities with those calculated for several sets of parameter values. In the course of this refinement evidence was found that the chromium atoms occupy at least predominantly the point position 16c. In order to obtain more accurate parameters three successive least-squares procedures as described by Hughes (1941) were subsequently carried out using the data obtained from all observable  $hk0$ - and  $hk1$ -Weissenberg reflexions. The scale and temperature factors were evaluated separately for the  $hk0$ - and  $hk1$ -reflexions from two semilogarithmic plots. One and the same temperature and absorption factor parameter  $B$  was used for both the  $hk0$ - and  $hk1$ -reflexions as it was found that the actual parameters differed from one another by an insignificant amount. In the subsequent refinement two separate scale factors were introduced as cross correlation leading to only one scale factor could not be established. The atomic form factors as listed in *Internationale Tabellen*, Bd. II (1935) were used and the values of the form factors for chromium were corrected for anomalous dispersion (James, 1948). The customary Lorentz and polarization factors were used. The  $F_{\text{obs}}$  values with weights proportional to  $F_{\text{obs}}^{-2}$  were taken as observational quantities. Forty-three observational equations were set up and reduced to nine normal equations which were solved for the three positional parameters, the temperature factor-absorption parameter  $B$ , the two scale factors and three compositional parameters, one of them expressing the fraction of aluminum atoms in the position 16c and two expressing the fraction of chromium atoms in the position 96g and 48f respectively. All off-diagonal matrix elements were included in the calculation and the nine normal equations were solved by the method of Crout (1941). A set of only three normal equations separately set up and solved for the three positional parameters alone (during each refinement step) gave shifts almost identical with those obtained by solving the set of nine equations. Thus there was very little coupling between the six non-positional parameters and the three positional ones. The calculation of the least-squares refinements were carried out by extensive use of IBM punched card machines.

The fraction of chromium atoms in the 48f and 96g positions came out to be 7% and 4% respectively, but confidence in these figures is shaken by the fact that the fraction of aluminum atoms in the 16c position came out to be minus 26%. This would imply that the scattering power of the atoms to be placed in this position is higher (approximately 12%) rather than lower than that of chromium. This result was interpreted as being caused by systematic errors introduced in the refinement process by deficiencies in the atomic form factors and perhaps also by errors in the observational quantities or by the fact that the

five crystallographically different atoms were assumed to have the same temperature factor.

Strong evidence is, however, produced by this result that the 16c position is occupied exclusively by chromium atoms. If this is true, the structure must be almost completely ordered with respect to the aluminum and chromium atoms, as otherwise the calculated density would not be consistent with the measured one.

Since X-ray diffraction data do not suffice for determining the distribution of the magnesium and aluminum atoms over the occupied atomic positions the possibility of disorder between these atoms cannot be excluded. However, in view of the difference in size of the magnesium atoms and aluminum atoms a possible disorder must be expected to be rather slight.

In Table 1 the final values of the positional parameters, accordingly changed to place the origin of coordinates at  $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$  from the center of symmetry are listed together with the probable errors as evaluated from the residuals (Whittaker & Robinson, 1937).

The calculated and observed structure factors are listed in Table 2. The reliability factor  $R$  is 0.116. The interatomic distances are given in Table 3. In calculating the probable errors also given in this table the functional dependence of the distances on the positional parameters was taken properly into account.

Table 2. *Calculated and observed structure factors*

$h$	$k$	$l$	$F_{\text{calc.}}$	$F_{\text{obs.}}$	$h$	$k$	$l$	$F_{\text{calc.}}$	$F_{\text{obs.}}$
0	0	0	2544	—	3	1	1	124	147
2	2	0	32	42	3	3	1	81	95
4	0	0	177	181	5	1	1	5.5	—
4	4	0	334	362	5	3	1	-264	228
6	2	0	331	302	5	5	1	-298	255
8	0	0	51	70	7	1	1	392	397
6	6	0	-336	371	7	3	1	34	66
8	4	0	192	210	7	5	1	-19	—
10	2	0	-200	188	9	1	1	-40	76
8	8	0	1008	871	9	3	1	86	88
10	6	0	6.4	—	7	7	1	-33	77
12	0	0	96	102	9	5	1	-68	83
12	4	0	277	260	11	1	1	-4.0	—
14	2	0	177	160	9	7	1	84	100
10	10	0	127	135	11	3	1	-126	119
12	8	0	36	—	11	5	1	61	65
14	6	0	-104	101	9	9	1	-161	104
16	0	0	593	550	11	7	1	49	—
16	4	0	118	116	13	1	1	-8.5	—
12	12	0	152	140	13	3	1	178	182
14	10	0	117	136	13	5	1	125	119
16	8	0	58	63	11	9	1	131	102
18	2	0	46	60	13	7	1	-81	89
					15	1	1	-21	—
					15	3	1	-3.3	—
					11	11	1	-22	—
					15	5	1	30	—
					13	9	1	11	—
					15	7	1	269	282
					13	11	1	-49	—
					17	1	1	-107	133
					17	3	1	89	97
					15	9	1	115	122
					17	5	1	-67	73
					13	13	1	-187	171

Table 3. *Interatomic distances, bond numbers and calculated valences*

Kind of atom	Ligancy	Distance (Å)	Bond number $n$	Calculated valence	Coordination polyhedron
$Mg_b$	12 $Al_g$	$3.226 \pm 0.006$	0.095 } 0.201 }	1.944	Friauf polyhedron*
	4 $Mg_d$	$3.146 \pm < 0.001$			
16					
$Mg_d$	12 $Al_g$	$3.109 \pm 0.002$	0.145 } 0.201 }	2.142	Approx. hexagonal prism with two $Mg_b$ atoms at the approx. hexagonal axis
	2 $Mg_b$	$3.146 \pm < 0.001$			
14					
$Al_f$	2 $Al_g$	$2.745 \pm 0.004$	0.385 } 0.187 } 0.395 } 0.279 } 0.480 } 0.223 } 0.095 } 0.129 }	3.153	Approx. pentagonal prism with two atoms at the approx. pentagonal axis
	2 $Al_g$	$2.932 \pm 0.012$			
	1 $Al_g$	$2.738 \pm 0.011$			
	2 $Al_f$	$2.829 \pm 0.005$			
	1 $Al_f$	$2.687 \pm 0.010$			
	1 Cr	$2.811 \pm 0.006$			
	1 $Mg_b$	$3.226 \pm 0.006$			
	2 $Mg_d$	$3.146 \pm < 0.001$			
12					
$Al_f$	2 $Al_g$	$2.687 \pm 0.010$	0.480 } 0.279 } 0.220 } 0.545 }	4.046	Approx. pentagonal prism with two atoms at the approx. pentagonal axis
	4 $Al_g$	$2.829 \pm 0.005$			
	4 $Al_f$	$2.890 \pm 0.013$			
	2 Cr	$2.578 \pm 0.002$			
12					
Cr	6 $Al_f$	$2.578 \pm 0.002$	0.545 } 0.223 }	4.608	Icosahedron
	6 $Al_g$	$2.811 \pm 0.006$			
12					

\* Coordination polyhedron with sixteen vertices and twenty-eight triangular faces also occurring in  $A12$ ,  $C14$ ,  $C15$  and  $C36$  type structures.

### Description of the structure

$O_h^2$  is also the space group of diamond. The atomic arrangements around the points occupied by carbon atoms in the diamond structure are all the same, except for the change caused by the glide operation. The same is true for the points at  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$  etc. which form an equivalent set of points but shifted  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$  with respect to the first set. There are consequently eight points of one type  $A$  and eight points of a second type  $B$ .

The structure of the  $E$  phase may now be described as follows. At the points of the first type are magnesium atoms (position  $8b$ ). These are surrounded by twelve aluminum atoms (position  $96g$ ) at the vertices of a truncated tetrahedron, bounded by four six-sided faces and four equilateral triangles (Fig. 1(a), (b)). Out from the centers of the four six-sided faces of this shell there are four magnesium atoms (position  $16d$ ) located at the vertices of a regular tetrahedron (Fig. 1(c)). These magnesium atoms are shared by two such adjacent 17-atom complexes (Fig. 2).

The atomic arrangement around the points of type  $A$  just described leaves large holes with their centers at the points of type  $B$ . In these holes fit with good packing efficiency clusters of six aluminum atoms at the vertices of a regular octahedron (position  $48f$ ) which in its turn is surrounded by four chromium atoms at the vertices of a regular tetrahedron (Fig. 3(a), (b)).

These chromium atoms (position  $16c$ ) are shared between two such 10-atom complexes (Fig. 3(c)). This atomic arrangement is, as is easily recognized, identical with a cubic close-packed arrangement.

The structure can thus be described briefly as consisting of two different kinds of groups such as shown in Fig. 1(c) and Fig. 3(b) respectively, with each group surrounded by four groups of the same kind and four groups of the other kind (Fig. 4).

### Discussion of the structure

#### *Coordination polyhedra, packing of atoms*

In order to compare and correlate certain geometrical features of this structure with those observed in other metallic structures it is of interest to investigate the nature of the coordination polyhedra observed.

Eight of the twenty-four magnesium atoms ( $Mg_b$ ) have a coordination polyhedron with sixteen vertices and twenty-eight triangular faces (Fig. 1(c)), also occurring in the  $A12$ ,  $C14$ ,  $C15$ , and  $C36$  type structures and in the rather complex structure  $Mg_{32}(Al, Zn)_{49}$  (Bergman, Waugh & Pauling, 1957). For the sake of brevity this polyhedron will be referred to below as the Friauf polyhedron.\* Some of its interesting features will be pointed out here.

\* It was first observed in the  $MgCu_2$  and  $MgZn_2$  structures determined by Friauf (1927).

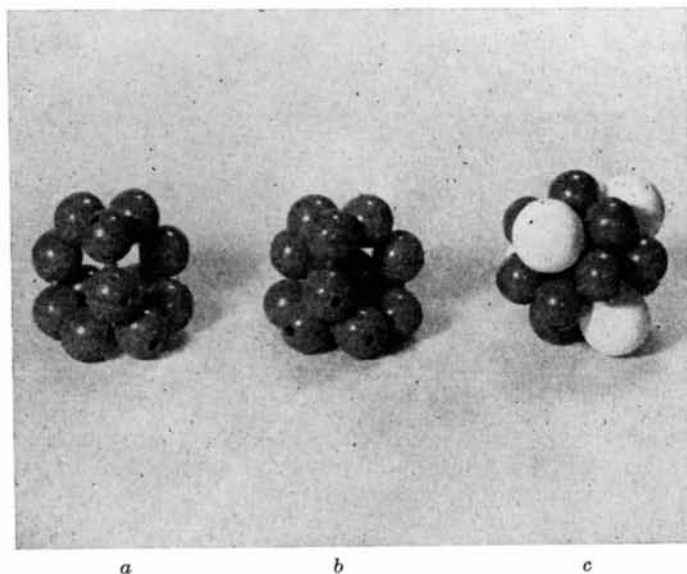


Fig. 1. The atomic arrangements produced by the point positions: (a)  $96g$ , (b)  $96g$  and  $8b$ , (c)  $96g$ ,  $8b$  and  $16d$  (Friauf polyhedron).

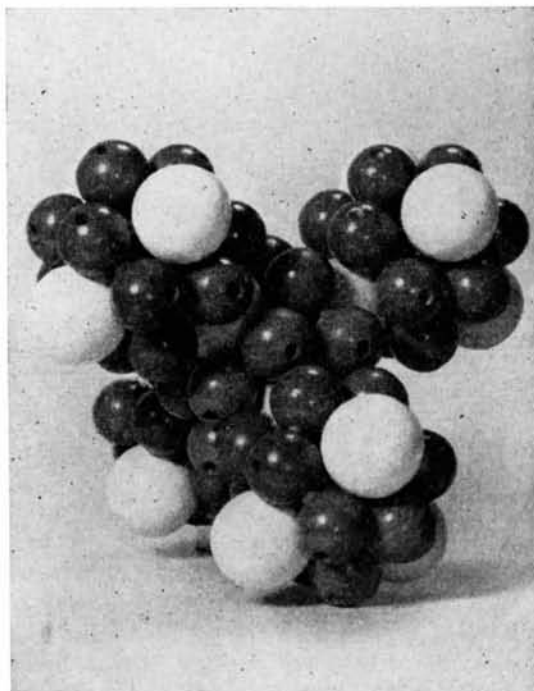


Fig. 2. Four 17-atom complexes as shown in Fig. 1(c) are tetrahedrally arranged around one such central group. The centers of these groups form the set of points of the type  $B$  (see text).

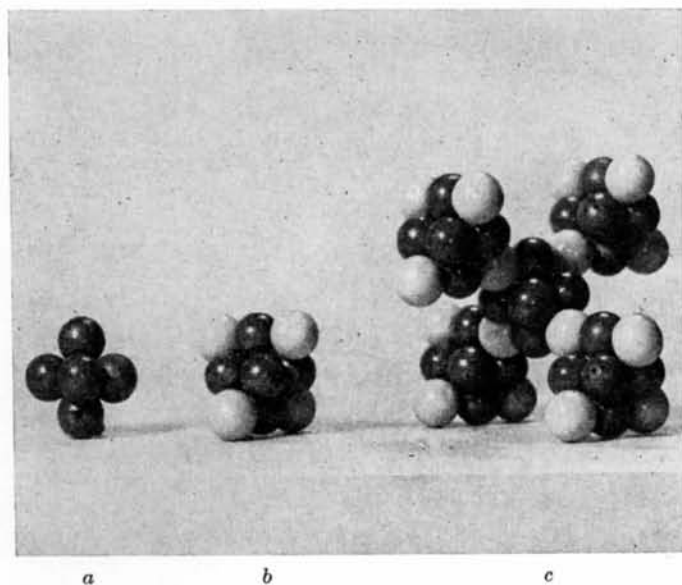


Fig. 3. The atomic arrangements produced by the point positions: (a)  $48f$ , (b)  $48f$  and  $16c$  and (c) the atomic arrangements around the points of the type  $A$  (see text).

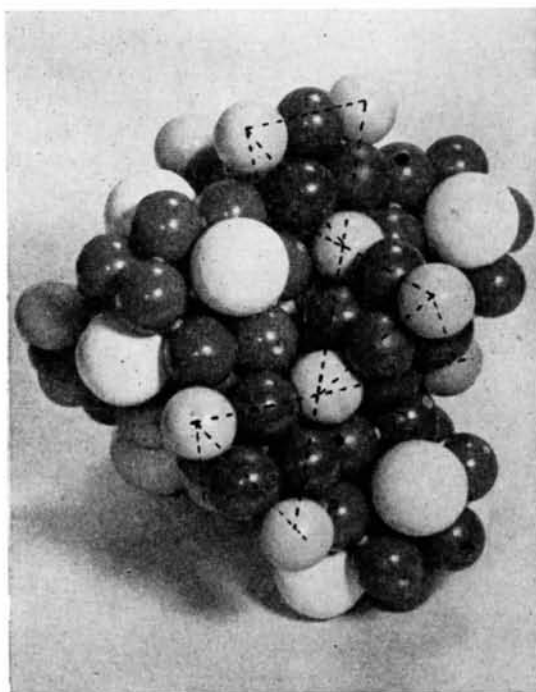


Fig. 4. The atomic arrangements around the two sets of points  $A$  and  $B$  forming the complete structure.

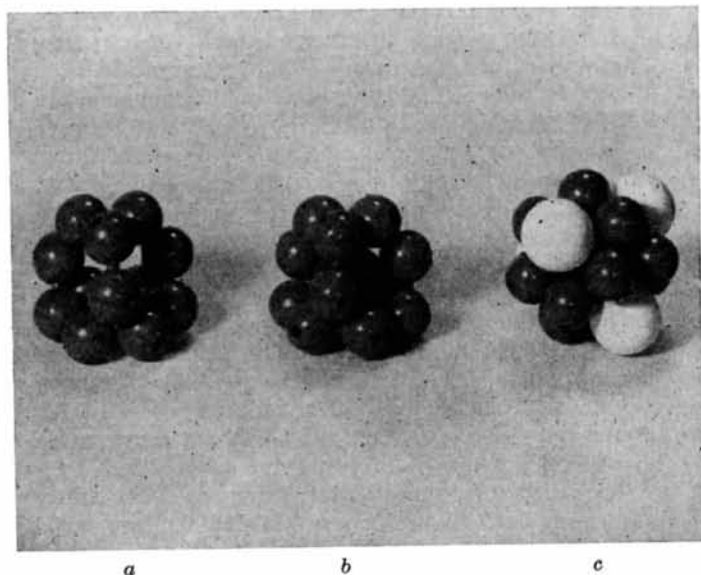


Fig. 1. The atomic arrangements produced by the point positions: (a) 96g, (b) 96g and 8b, (c) 96g, 8b and 16d (Friauf polyhedron).

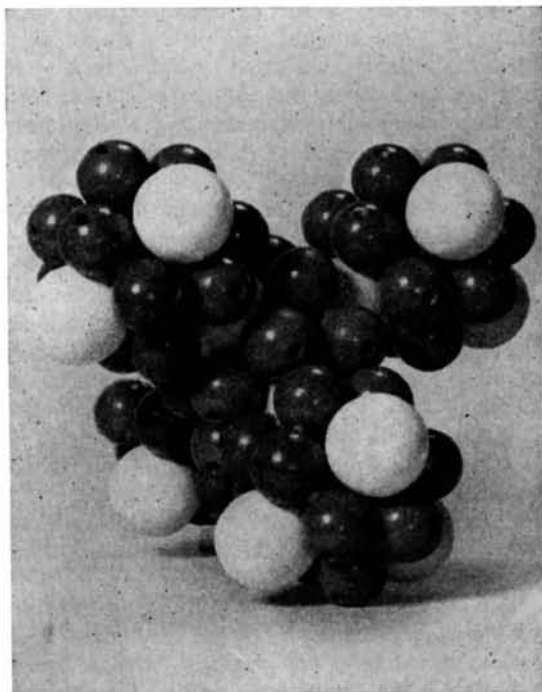


Fig. 2. Four 17-atom complexes as shown in Fig. 1(c) are tetrahedrally arranged around one such central group. The centers of these groups form the set of points of the type B (see text).

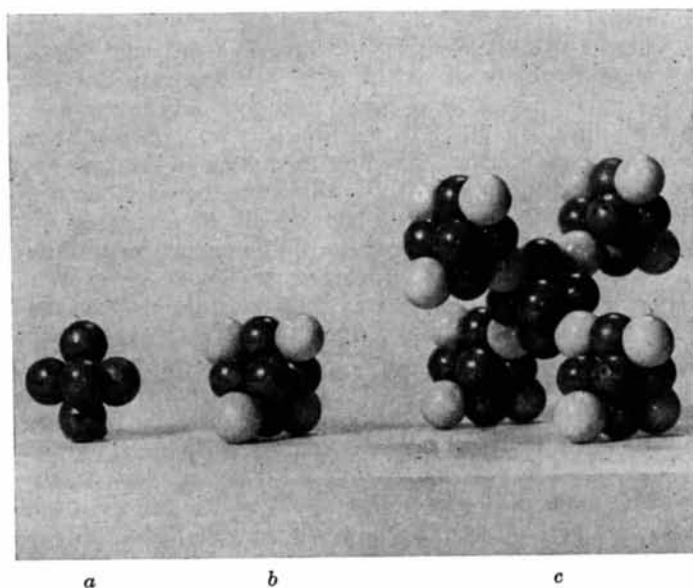


Fig. 3. The atomic arrangements produced by the point positions: (a) 48f, (b) 48f and 16c and (c) the atomic arrangements around the points of the type A (see text).

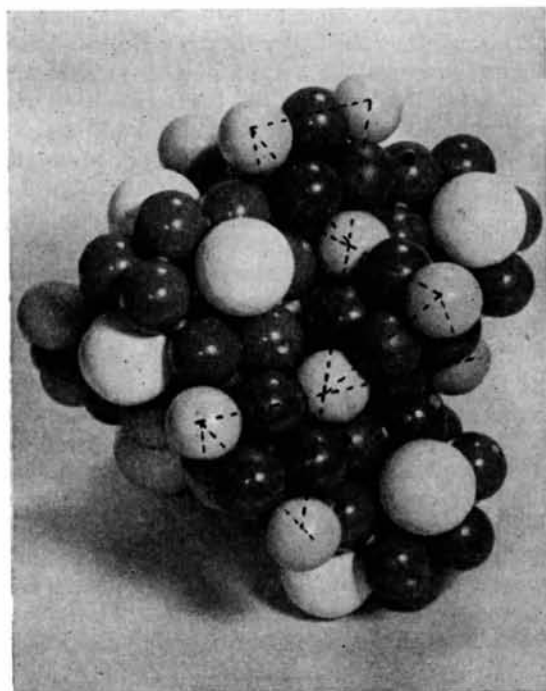


Fig. 4. The atomic arrangements around the two sets of points A and B forming the complete structure.

The metrical nature of the truncated tetrahedron (Fig. 1(a)) (an integral part of the Friauf polyhedron) is such that if the six-sided faces are regular hexagons the distances from the center to the twelve vertices of the truncated tetrahedron is 17.3% larger than those between neighboring vertices. With twelve equal spheres in contact with one another at the vertices of such a truncated tetrahedron it is possible to accommodate a sphere 34.5% larger in radius at the center of the truncated tetrahedron ( $\frac{1}{2} \cdot \sqrt{22} - 1 = 1.345$ ). In the present structure the assumed central sphere would be 35% larger than the assumed spheres at the vertices of the truncated tetrahedron if the average of all the distances between the eighteen vertices is taken ( $\frac{2}{3} \cdot 2.745 + \frac{1}{3} \cdot 2.738$ ). The magnesium atoms have a radius only approximately 15% larger in size than that of the aluminum atoms, to use as a basis for comparison the atomic radii of the pure metals corrected for the proper coordination numbers (Pauling, 1947). The apparent packing efficiency provided by the atomic arrangement of  $Mg_b$  and  $Al_g$  is thus rather small. An inspection of other known Friauf polyhedra with a magnesium atom at the center reveals that the radius ratio  $Mg/B$  ( $B$  = small atoms at the vertices) calculated for the atomic radii of the pure metals ('nominal' radius ratio) approaches the corresponding radius ratio calculated for the assumed spheres referred to above ('observed' radius ratio) in the succession of structures  $Mg_3Cr_2Al_{18}$ ,  $MgZn_2$ ,  $MgCu_2$  and  $MgNi_2$ , the difference between the 'observed' and 'nominal' radius ratio being 0.21, 0.16, 0.06, and 0.03 respectively. The average Mg-Mg distances in the same polyhedra are 3.15, 3.17, 3.03 and 2.96 Å. Hence, it seems, that the apparent overall size of the magnesium atom at the center of the Friauf polyhedron decreases gradually as the twelve aluminum atoms at the vertices of the truncated tetrahedron are replaced by twelve zinc atoms, twelve copper atoms or twelve nickel atoms respectively. The  $Mg_3Al_2$  phase with the  $\alpha$ -manganese type structure ( $A12$ ) (Laves *et al.*, 1934) although incorporating one Friauf polyhedron identical with that observed for the  $E$  phase cannot be included in this discussion because its structural parameters have not yet been refined.\*

The four magnesium atoms  $Mg_a$  located out from the centers of the four six-sided faces of the truncated tetrahedron (Fig. 1(c)) are next to be considered. In the different types of structures referred to above these magnesium atoms are in their turn surrounded by a Friauf polyhedron, while in this structure their coordination polyhedron is an approximate hexagonal prism with two magnesium atoms ( $Mg_b$ ) on the approximate hexagonal axis (Fig. 2). These prisms are formed by the six-sided faces of two adjacent truncated tetrahedra and have accordingly aluminum atoms ( $Al_g$ )

at their vertices. Around each Friauf polyhedron a set of four such prisms is arranged with their centers ( $Mg_a$  atoms) at the vertices of a regular tetrahedron. With the twelve equal spheres referred to above at the vertices of the truncated tetrahedron it would be possible to accommodate a sphere 28% larger in radius at the center of the approximate hexagonal prism. The packing around the  $Mg_a$  atoms, again, seems to be rather loose.

The coordination shell around the  $Al_f$  atoms may be described as approximating a pentagonal prism with ten aluminum atoms (6  $Al_g$  + 4  $Al_f$ ) at the vertices and two chromium atoms on the approximate pentagonal axis of this prism. The packing appears to be of normal efficiency. The same is true for the  $Al_g$  atoms but the prisms around them are much more distorted.

The coordination polyhedron around each chromium atom may be described as a regular icosahedron, compressed in the direction of one of the three-fold axis. Six of the aluminum atoms ( $Al_f$ ) at the vertices of the distorted icosahedron are accordingly at a shorter distance (2.578 Å) and six at a longer distance (2.811 Å) from the central chromium atom. The mean value of these distances (2.695 Å) is incidentally very close to the sum of the metallic  $CN12$  radii of chromium and aluminum given by Pauling (1947) which is 2.696 Å. The weighted average of the distances between the twelve aluminum atoms at the vertices of the distorted icosahedron is 2.833 Å. Incidentally this distance is less than 1% smaller than twice the atomic  $CN12$  radius for aluminum given by Pauling (1947) which is 2.858 Å. The ratio between the two mean values referred to above is 0.951 and hence exactly the same as the corresponding ratio for the regular trigonal icosahedron (see section on manganese, Pauling, 1947). This coincidence is, however, not incidental because the metrical nature of the icosahedron is such that if the distances between several vertices, for instance, become all elongated or all shortened the distances between these vertices and the center of the icosahedron grow longer or shorter respectively in such a way that the ratio between the average distances (referred to above) retains very nearly a constant value. The average radius of the 'deformed central sphere' of a distorted icosahedron is thus very nearly 10% smaller than the average distance between the twelve vertices of the distorted icosahedron. To use, again, as a basis for comparison the ratio of the atomic ( $CN12$ ) radius for the pure metals (Pauling, 1947), which is 0.89 (for Cr/Al) it may be concluded that the packing efficiency around the chromium atoms is rather good. Similar icosahedral  $XAl_{12}$  atom complexes ( $X$  = transition element) have been observed in the structures  $\alpha(V-Al)$ , Brown (1957);  $V_4Al_{23}$ , Smith *et al.* (1957) and  $MoAl_{12}$ ,  $WAl_{12}$ , Adam & Rich (1954). The nominal  $CN12$  radius ratios are  $V/Al$ , 0.94;  $Mo/Al$ , 0.97 and  $W/Al$ , 0.98.

\* The same positional parameters as those observed for  $\alpha$ -Mn have been assumed in  $Mg_3Al_2$ .

*Bond distances and their interpretation*

The interatomic distances are listed in Table 3. The bond numbers as well as the calculated valences also given in Table 3 are those derived by application of the equation  $R_n = R_1 - 0.300 \log_{10} n$  using the single bond radii listed by Pauling (1947).

In terms of the valence bond theory of metals and intermetallic compounds (Pauling, 1949) the large apparent sizes of the magnesium atoms in this compound may be attributed to the fact that neither the Friauf polyhedron nor the approximate hexagonal prism incorporates any hyperelectronic (Pauling, 1950, 1956) atom and that, furthermore, the few chromium atoms present in this structure are well shielded by aluminum atoms and hence do not interact significantly, or at all, with the magnesium atoms. These may therefore be expected to have a valence of nearly two and the sixteen and fourteen bonds, respectively, formed around them must be rather weak. The long  $Mg_b-Al_f$  distances may be interpreted as unstrained approximate  $\frac{1}{10}$ -bonds, the somewhat shorter  $Mg_b-Mg_a$  distances as  $\frac{1}{5}$ -bonds and the  $Mg_a-Al_f$  distances as approximate  $\frac{2}{5}$ -bonds. The apparent large size of the magnesium atom at the center of the Friauf polyhedron in this structure thus supports the idea of electron transfer in the structures of  $MgZn_2$ ,  $MgCu_2$  and  $MgNi_2$  in which the packing of atoms become successively closer (Pauling, 1956).

The packing around the chromium atoms, which are hyperelectronic in character (Pauling, 1950, 1956) appears to be the closest observed in this structure. The six very short  $Cr-Al_f$  distances may be associated with a localized electron transfer. However, the geometry of the atomic arrangement is such that not even a large shift of the  $Al_f$ -position (only one degree of freedom) can alleviate the shortness of the  $Cr-Al_f$  bonds and as such a large shift would necessarily lead to excessively long and short  $Al-Al$  distances it seems inescapable that the  $Cr-Al_f$  bonds are under compressional strain. The small functional dependence of the short  $Cr-Al_f$  distances on the positional parameter for  $Al_f$  is also reflected in the small probable error for these distances (Table 3). Calculation of the bond numbers must therefore be interpreted with caution.

Summarizing the results it may be said that an analysis of the coordination polyhedra from which the *E* phase is constructed reveals that a possible interaction (electron transfer) between the atoms of the transition element and the hypoelectronic atoms mag-

nesium and aluminum is localized to a certain coordination polyhedron, the icosahedron, which provides a rather close packing of the atoms. In places, where such an interaction has been found less likely or unlikely, the apparent packing of atoms seems to be normal or rather loose.

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