Monatshefte für Chemie 116, 417—429 (1985)

**Monatshefte für Chemie**
*Chemical Monthly*


# Description of Structures in Terms of Polyhedrapacking

**Kamal Girgis*** and **Pierre Villars**

Institut für Kristallographie und Petrographie, Eidgenössische Technische Hochschule Zürich, CH-8092 Zürich, Switzerland

*(Received 24 July 1984. Accepted 12 August 1984)*

The structures of alloys can be described in terms of polyhedrapacking. We studied *all* structure types found in the binary systems $T^5$ or $T^6$ with $B^3$ or $B^4$ ($T^5$: V, Nb, Ta; $T^6$: Cr, Mo, W; $B^3$: Al, Ga, In, Tl; $B^4$: Si, Ge, Sn, Pb) elements. Most of the structures examined until now could be built up with one or two polyhedra, only in a few cases more than two polyhedra are required. It is found that there are two types: a three-dimensional distribution of discrete polyhedra sharing corners, edges or faces and a layer-like distribution. This model proved valid for all structure types studied. Classification of the structures according to their polyhedrapacking criteria is introduced (Table 1). Table 2 includes the coordination numbers of all atoms in the studied structures.

*(Keywords: Coordination polyhedra; Polyhedrapacking model; Classification of structures; Systematics of crystal structures)*

*Beschreibung von Strukturen mittels des Polyederpackungs-Modells*

Die Strukturen von Legierungen können mit dem Polyederpackungsmodell beschrieben werden, dessen Gültigkeit bewiesen wurde. Wir haben *alle* Strukturtypen, die in den binären Systemen $T^5$ oder $T^6$ mit $B^3$ oder $B^4$ Elementen auftreten, beschrieben. Es zeigt sich, daß die meisten Strukturen mit einer oder zwei Polyedersorten aufgebaut werden können. Eine Klassifizierung der Strukturen gemäß ihrer Polyederpackungstypen wurde eingeführt (Tabelle 1). Zwei Typen von Polyederaufbau wurden festgestellt: entweder ein 3-dimensionales Gerüst aus einzelnen Polyedern, die Ecken, Kanten oder Flächen miteinander gemeinsam haben oder Polyederschichten. Tabelle 2 enthält die Koordinationszahlen aller Atome der behandelten Strukturtypen.

## Introduction

A fruitful approach to understand the crystal chemistry of alloy structures is to consider the coordination spheres. Further the search for a model to describe these "sometimes" complicated structures led us to the polyhedrapacking principle. The aim is to present a simple description of the complex alloy structures and to systematize the different known structure types.

## Coordination Polyhedra

To define a coordination polyhedron, we first limit the coordination sphere. *Girgis*[1] introduced the $\sum(r_A + r_B)/d_{AB}$-method for this purpose. $\sum(r_A + r_B)$ is the sum of the radii of the atoms concerned (*Teatum, Gschneidner, Waber*[2]) and $d_{AB}$ is the interatomic distance between these atoms A and B. The $(r_A + r_B)/d_{AB}$ versus the number of atoms are represented in a histogram. The widest range in which no atoms are present is called the "maximum gap" (*Brunner*[3]). 95% of the studied cases show such a "maximum gap" (*Bhandary, Girgis*[4,5]). The number of nearest neighbours before the "max. gap" is taken to be the conventional coordination number (CCN). These atoms (neighbours) constitute the coordination polyhedron for the corresponding (central) atom (*Girgis*[1]). An example is shown in Fig. 1.

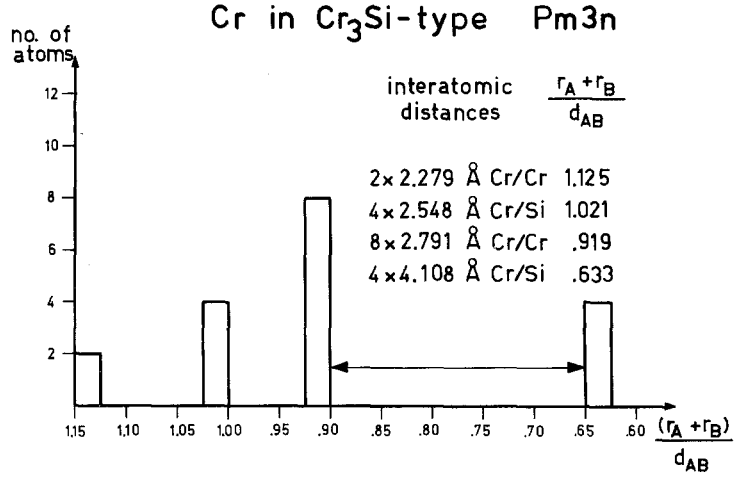



Fig. 1. Distribution of near neighbours as a function of their $(r_A + r_B)/d_{AB}$ for Cr in the $Cr_3Si$ structure type

## The Principle of Describing Structures with Coordination Polyhedra as Building Blocks

### *Procedure*

The coordination polyhedra of all the atomic positions of the structure will be determined with the help of the "max. gap" method as mentioned above.

The structure will be described by packing the least number of polyhedra types (one or two are in most cases sufficient). *All the atoms* in the unit cell *must be* included in the structure building polyhedra. The polyhedra should not penetrate each other.

If there is more than one possibility to describe the structure, the following priorities are considered:

1. The polyhedron (polyhedra) of the transition metals is considered first.

2. The least number of polyhedra types are considered.

2.1. Known polyhedra are considered first, e.g. *Kasper* polyhedra (CN 12, 14, 15, 16), cubooctahedron, tetrakishexahedron, rhombohedron, cube, trigonal prisms etc.

2.2. Polyhedra with higher symmetry (higher order).

2.3. Polyhedron with the clear "max. gap".

2.4. Polyhedron with the lower CN.

### *Validity of this Model*

The polyhedrapacking principle proved its validity for all structure types treated (a part of them in Table 1). More details are found in Refs.[5–8]. Therefore it is expected that this principle is valid for all intermetallic structures.

### *Some Examples*

We would like to show the steps to describe a structure with polyhedrapacking in the case of $V_5Al_8$ as a representative for the $\gamma$-brass structure type ($Cu_5Zn_8$) and of $CrAl_{6.6}$ as a representative for the $\alpha$-$V_7Al_{45}$ structure type.

#### $Cu_5Zn_8$ (D $8_2$) Structure Type: Representative: $V_5Al_8$

Crystallographic data:

$V_5Al_8$ $Cu_5Zn_8$ type c I 52 I $\bar{4}$3 m $a = 9.207$ Å $Z = 4$

There are two crystallographically independent V atoms, $V_1$ and $V_2$, in the asymmetric unit. $V_1$ has CN 12 and $V_2$ 13. The polyhedron around $V_1$ is an icosahedron having 3 m ($C_{3v}$) symmetry. The 13-verticon around $V_2$ has mm 2 ($C_{2v}$) symmetry and is bounded by 22 triangular faces, see Fig. 2.

The structure can be built up by packing $V_1$ polyhedra. Two $V_1$ polyhedra share a triangular face along [110].

Another two $V_1$ double icosahedra in a higher plane share with the lower two $V_1$ polyhedra 4 triangular faces which are shaded. These 4 icosahedra form a "tetrahedron". These tetrahedron units "centres" are in 000 and 1/2 1/2 1/2. Each tetrahedron unit shares with the next higher tetrahedron unit the shaded atoms in Fig. 3.

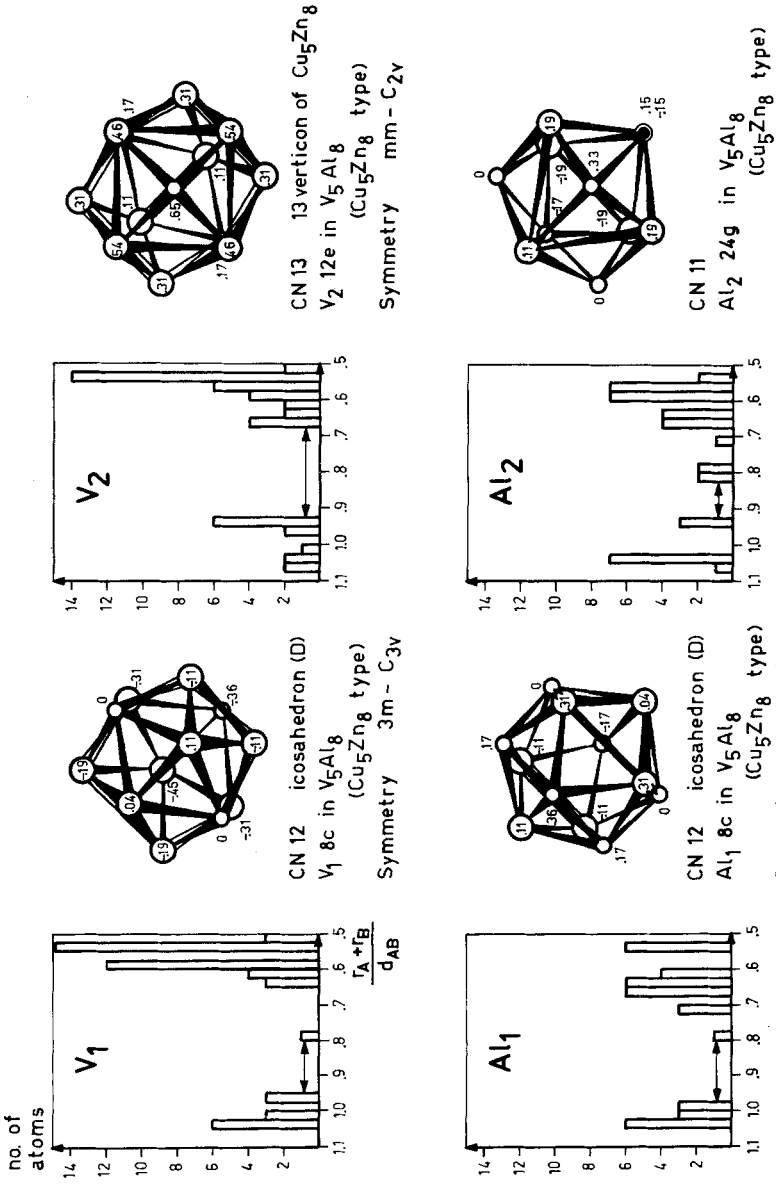



Fig. 2. Distribution of the near neighbours of equivalent points in the $V_5Al_8$ structure ($V_1$, $V_2$, $Al_1$, $Al_2$) and the corresponding polyhedra

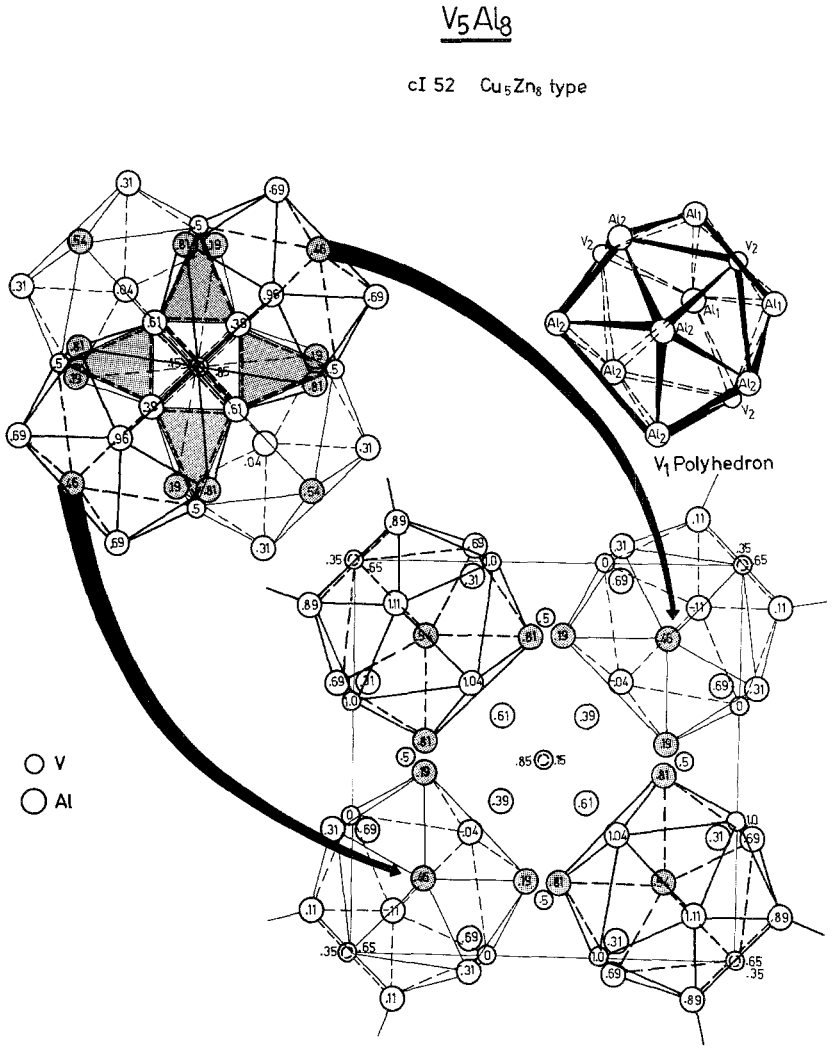
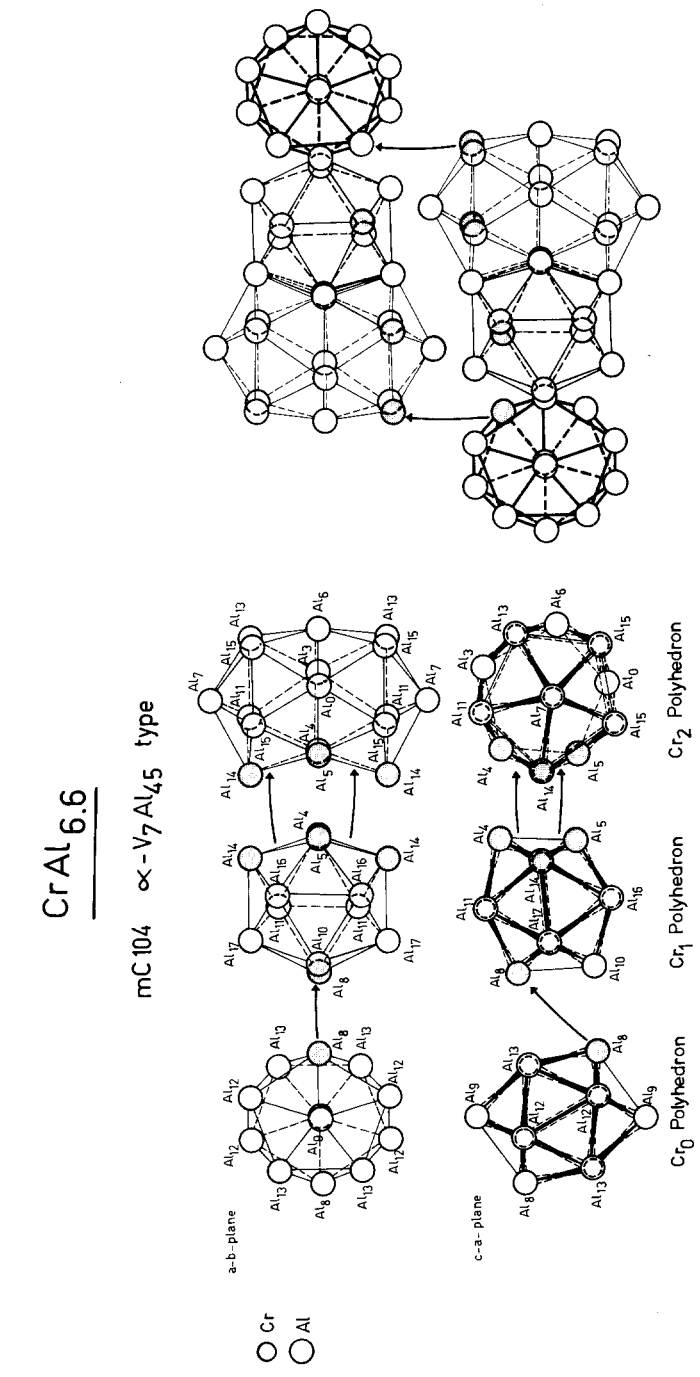



Fig. 3. Description of the $Cu_5Zn_8$ structure type (representative: $V_5Al_8$) in terms of polyhedrapacking. Shared atoms or faces are shaded. Numbers are the coordinates in the $z$-direction


CrAl6.6
mC104 α-V7Al45 type
Cr
Al
a-b-plane
c-a-plane
Cr0 Polyhedron
Cr1 Polyhedron
Cr2 Polyhedron

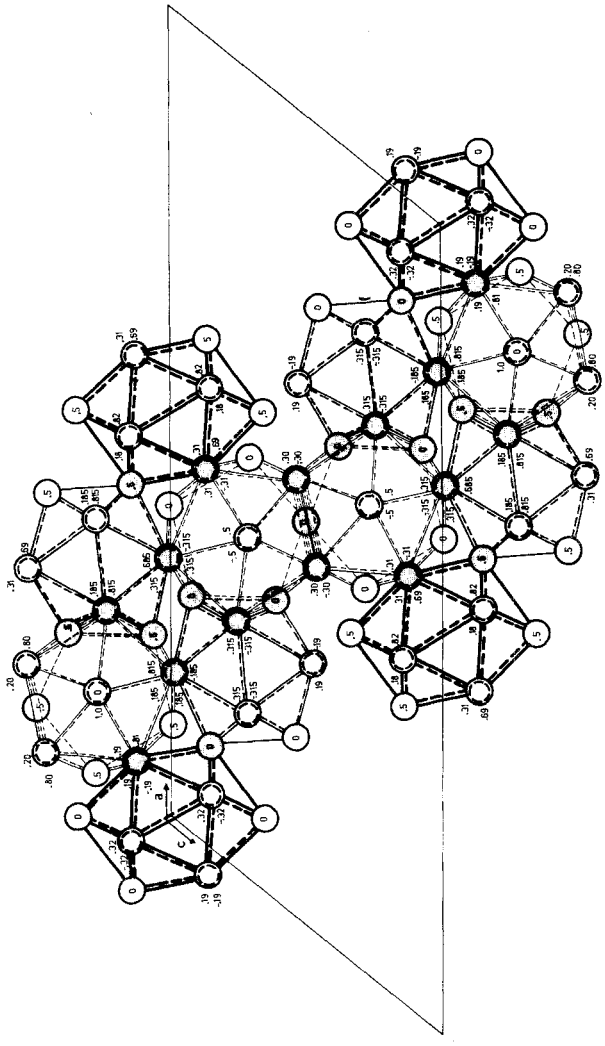


Fig. 4. Description of the $\alpha$-$V_7Al_{45}$ structure type (representative: $CrAl_{6,6}$) in terms of polyhedrapacking. Shared atoms or faces are shaded. Numbers are the coordinates in the $z$-direction

*Table 1*

A : STRUCTURES DESCRIBED BY PACKING OF ONE POLYHEDRON

| Structure type | Representative | Pearson symbol | Space group | Atom | CN | Polyhedra used & their symmetry (idealized) | Type of packing |
|---|---|---|---|---|---|---|---|
| β-$PtHg_4$ | $CrGa_4$ | cI10 | I432 | Cr | 8 | cube; 432-O | I |
| $Ni_3P$ | $Ta_3Ge$ | tI32 | $I\bar{4}$ | Ge | 9 | 14A-polyhedron; 1-$C_1$ | I |
| $Ti_3P$ | $Nb_3Si$ | tP32 | $P4_2/n$ | Si | 9 | 14A-polyhedron; 1-$C_1$ | I |
| $CuAl_2$ | $SiTa_2$ | tI12 | I4/mcm | Si | 10 | square antiprism (bicapped) ; 422-$D_4$ | II |
| $CuMg_2$ | $V_2Sn_3$ | oF48 | Fddd | V | 10 | bicapped dodecahedron; 2-$C_2$(222-$D_2$) | I |
| α-$Ti_6Sn_5$ | $V_6Ga_5$ | hP22 | $P6_3/mmc$ | V 1 | 11 | pentacapped trigonal prism;2mm-$C_{2v}$ | I |
| $VAl_{10}$ | $VAl_{10}$ | cF176 | Fd3m | V | 12 | icosahedron; $\bar{3}$m-$D_{3d}$($\bar{5}\bar{3}$(2/m)-$I_h$) | I |
| $Cu_5Zn_8$ | $V_5Al_8$ | cI52 | $I\bar{4}3m$ | V 1 | 12 | icosahedron; 3m-$C_{3v}$($\bar{5}\bar{3}$(2/m)-$I_h$) | I |
| $WAl_{12}$ | $WAl_{12}$ | cI26 | Im3 | W | 12 | icosahedron; 3m-$C_{3v}$($\bar{5}\bar{3}$(2/m)-$I_h$) | I |
| σ-CrFe | $Nb_2Al$ | tP30 | $P4_2/mnm$ | Al 2 | 12 | icosahedron; m-$C_s$($\bar{5}\bar{3}$(2/m)-$I_h$) | II |
| $WAl_4$ | $WAl_4$ | mC30 | Cm | W 2 | 12 | icosahedron; 1-$C_1$($\bar{5}\bar{3}$(2/m)-$I_h$) | I |
| $Mn_2Hg_5$ | $V_2Ga_5$ | tP14 | P4/mbm | V | 12 | bicapped pentagonal prism; | |
| | | | | | | mm2-$C_{2v}$($\bar{1}$0m2-$D_{5h}$) | II |
| $TiAl_3$ | $VAl_3$ | tI8 | I4/mmm | V | 12 | cubooctahedron; m3m-$O_h$ | II |
| $AuCu_3$ | $SiNb_3$ | cP4 | Pm3m | Nb | 12 | cubooctahedron; m3m-$O_h$ | II |
| $WAl_5$ | $WAl_5$ | hP12 | $P6_3$ | W | 12 | cubooctahedron; 3-$C_3$(m3m-$O_h$) | II |
| $Ni_3Sn$ | $Ta_3Si$ | hP8 | $P6_3/mmc$ | Si | 12 | (8A+6α)polyhedron; $\bar{6}$m2-$D_{3h}$ | I |
| FeSi | CrSi | cP8 | $P2_13$ | Cr | 13 | (10A+6α)polyhedron; 3-$C_3$ | I |
| $MoSi_2$ | $Cr_2Al$ | tI6 | I4/mmm | Cr | 14 | rhombic dodecahedron; 4mm-$C_{4v}$(m3m-$O_h$) | II |
| $U_3Si_2$ | $Nb_3Ga_2$ | tP10 | P4/mbm | Nb 1 | 14 | "tetrakishexahedron"; 4/mmm-$D_{4h}$ | I |
| $Cr_5B_3$ | $Nb_5Si_3$ | tI32 | I4/mcm | Nb 1 | 14 | "tetrakishexahedron"; 4/mmm-$D_{4h}$ | II |
| $CrSi_2$ | $VSi_2$ | hP9 | $P6_222$ | V | 14 | 14-verticon of $CrSi_2$type; 222-$D_2$ | |
| | | | | | | (6/mmm-$D6_h$) | I |
| $Cr_3Si$ | $V_3Ga$ | cP8 | Pm3n | V | 14 | Kasper (14) ;$\bar{4}$2m-$D_{2d}$(6m-$D_{6d}$) | II |
| $Mn_5Si_3$ | $V_5Si_3$ | hP16 | $P6_3/mcm$ | V 1 | 14 | Kasper like (14) ; 32-$D_3$ | II |
| α-Mn | $Al_{12}Ta_{17}$ | cI58 | $I\bar{4}3m$ | Ta 2 | 16 | Kasper (16) ; 3m-$C_{3v}$ | I |

Type of packing:

I : 3-dimensional arrangement of discrete polyhedra sharing corners, edges or faces

II : a layer like distribution of polyhedra (sheet polyhedrapacking)

Table 1 *(continued)*

B : STRUCTURES DESCRIBED BY PACKING OF TWO POLYHEDRA

| Structure type | Representative | Pearson symbol | Space group | Atom | CN | Polyhedra used & their symmetry (idealized) | Type of packing |
|---|---|---|---|---|---|---|---|
| $W_5Si_3$ | $V_5Si_3$ | tI32 | I4/mcm | V 1 | 14 | Kasper (14); $\bar{4}2m$-$D_{2d}$ ($\bar{6}m$-$D_{6d}$) | II |
| | | | | Si 1 | 10 | bicapped square antiprism; 422-$D_4$ | |
| $V_6Si_5$ | $V_6Si_5$ | oI44 | Ibam | V 3 | 14 | Kasper like; 2-$C_2$ | II |
| | | | | Si 3 | 10 | bicapped square antiprism;222-$D_2$ ($\bar{8}2m$-$D_{4d}$) | |
| $Cr_5Al_8$ | $Cr_5Al_8$ | hR26 | R3m | Cr 3 | 12 | icosahedron; m-$C_s$ ($\bar{5}\bar{3}$(2/m)-$I_h$) | I |
| | | | | Al 1 | 12 | icosahedron; 3m-$C_{3v}$ ($\bar{5}\bar{3}$(2/m)-$I_h$) | |
| $V_4Al_{23}$ | $V_4Al_{23}$ | hP54 | $P6_3/mmc$ | V 1 | 12 | icosahedron; $\bar{3}m$-$D_{3d}$ ($\bar{5}\bar{3}$(2/m)-$I_h$) | I |
| | | | | V 2 | 12 | complex unit; $\bar{6}m2$-$D_{3h}$ | |
| $Cr_{11}Ge_8$ | $V_{11}Ge_8$ | oP76 | Pnma | V 1 | 13 | 13-verticon of $Cr_{11}Ge_8$ type; 1-$C_1$ | II |
| | | | | V 2 | 14 | Kasper like (14); 1-$C_1$ | |
| β-$Ti_6Sn_5$ | $Nb_6Sn_5$ | oI44 | Immm | Nb 3 | 15 | Kasper (15); mm2-$C_{2v}$ | I |
| | | | | Nb 4 | 12 | ($16\triangle+2\square$)polyhedron; mm2-$C_{2v}$ | |
| $Ti_5Ga_4$ | $Nb_5Ga_4$ | hP18 | $P6_3/mcm$ | Nb 1 | 14 | Kasper (14); 32-$D_3$ | I |
| | | | | Ga 1 | 14 | 24△-polyhedron; $\bar{3}m$-$D_{3d}$ | |

Type of packing:
I : 3-dimensional arrangement of discrete polyhedra sharing corners, edges of faces
II : a layer-like distribution of polyhedra (sheet polyhedrapacking)

C : STRUCTURES DESCRIBED BY PACKING OF MORE THAN TWO POLYHEDRA

| Structure type | Representative | Pearson symbol | Space group | Atom | CN | Polyhedra used & their symmetry (idealized) | Type of packing |
|---|---|---|---|---|---|---|---|
| $V_8Ga_{41}$ | $V_8Ga_{41}$ | hR49 | $R\bar{3}$ | V 1 | 10 | 1/2 cube+1/2 icosahedron; 3-$C_3$ | I |
| | | | | V 2 | 10 | 1/2 cube+1/2 icosahedron; 1-$C_1$(3-$C_3$) | |
| | | | | Ga 1 | 12 | cubooctahedron;$\bar{3}$-$S_6$ (m3m-$O_h$) | |
| α-$V_7Al_{45}$ | $CrAl_{6.6}$ | mcl04 | C2/m | Cr 0 | 12 | icosahedron; 2/m-$C_{2h}$ ($\bar{5}\bar{3}$(2/m)-$I_h$) | I |
| | | | | Cr 1 | 12 | icosahedron; m-$C_s$ ($\bar{5}\bar{3}$(2/m)-$I_h$) | |
| | | | | Cr 2 | 12 | icosahedron; 1-$C_1$ ($\bar{5}\bar{3}$(2/m)-$I_h$) | |
| $Cr_{11}Ge_{19}$ | $Cr_{11}Ge_{19}$ | tP120 | $P\bar{4}n2$ | Cr 1 | 12 | icosahedron; $\bar{4}$-$S_4$ ($\bar{5}\bar{3}$(2/m)-$I_h$) | II |
| | | | | Cr 3 | 14 | rhombic dodecahedron (vD);2-$C_2$(m3m-$O_h$) | |
| | | | | Cr 4 | 12 | icosahedron; 2-$C_2$($\bar{5}\bar{3}$(2/m)-$I_h$) | |
| | | | | Cr 5 | 14 | rhombic dodecahedron (see Cr 3);2-$C_2$ | |
| | | | | Cr 6 | 12 | icosahedron (see Cr 1); 2-$C_2$ | |
| | | | | Cr 7 | 14 | rhombic dodecahedron (see Cr 3);2-$C_2$ | |

Type of packing:
I : 3-dimensional arrangement of discrete polyhedra sharing corners, edges or faces
II : a layer-like distribution of polyhedra (sheet polyhedrapacking)

Table 2. *Summary of coordination numbers of individual atoms in the treated structures**

| Str. Type | Representative | Atom | Eq.Pts. | C.N. |
|---|---|---|---|---|
| β-$PtHg_4$ | $CrGa_4$ | Cr | 2a | 8 |
| | | Ga | 8c | 8 |
| $Ni_3P$ | $Ta_3Ge$ | Ta 1 | 8g | 14 |
| | | Ta 2 | 8g | 14 |
| | | Ta 3 | 8g | 13 |
| | | Ge | 8g | 9 |
| $Ti_3P$ | $Nb_3Si$ | Nb 1 | 8g | 15 |
| | | Nb 2 | 8g | 15 |
| | | Nb 3 | 8g | 14 |
| | | Si | 8g | 9 |
| $CuAl_2$ | $SiTa_2$ | Ta | 8h | 15 |
| | | Si | 4a | 10 |
| $CuMg_2$ | $V_2Sn_3$ | V | 16g | 10 |
| | | Sn 1 | 16g | 15 |
| | | Sn 2 | 16c | 15 |
| α-$Ti_6Sn_5$ | $V_6Ga_5$ | V 1 | 6h | 11 |
| | | V 2 | 6g | 12 |
| | | Ga 1 | 6h | 14 |
| | | Ga 2 | 2b | 14 |
| | | Ga 3 | 2c | 15 |
| $VAl_{10}$ | $VAl_{10}$(a) | V | 16c | 12 |
| | | Al 1 | 96g | 19 |
| | | Al 2 | 48f | 12 |
| | | Al 3 | 16d | 12 |
| | $VAl_{10}$(b) | V | 16c | 12 |
| | | Al 1 | 96g | 12 |
| | | Al 2 | 48f | 12 |
| | | Al 3 | 16d | 14 |
| | | Al 4 | 8b | 16 |
| $Ni_3Sn$ | "$Ta_3Si$" | Ta | 6h | 12 |
| | | Si | 2c | 12 |
| FeSi | CrSi | Cr | 4a | 13 |
| | | Si | 4a | 13 |
| $MoSi_2$ | $AlCr_2$ | Cr | 4e | 14 |
| | | Al | 2a | 14 |
| $U_3Si_2$ | $Nb_3Ga_2$ | Nb 1 | 2a | 14 |
| | | Nb 2 | 4h | 17 |
| | | Ga | 4g | 9 |
| $Cr_5B_3$ | $Nb_5Si_3$ | Nb 1 | 4c | 14 |
| | | Nb 2 | 16l | 16 |
| | | Si 1 | 4a | 10 |
| | | Si 2 | 8h | 9 |
| $CrSi_2$ | $VSi_2$ | V | 3d | 14 |
| | | Si | 6j | 12 |
| $Cr_3Si$ | $V_3Ga$ | V | 6c | 14 |
| | | Ga | 2a | 12 |
| $Mn_5Si_3$ | $V_5Si_3$ | V 1 | 4d | 14 |
| | | V 2 | 6g | 15 |
| | | Si | 6g | 11 |
| α-Mn | $Al_{12}Ta_{17}$ | Ta 1 | 2a | 16 |
| | | Ta 2 | 8c | 16 |
| | | Ta 3 | 24g | 15 |
| | | Al | 24g | 13 |
| $W_5Si_3$ | $V_5Si_3$ | V 1 | 4b | 14 |
| | | V 2 | 16k | 15 |
| | | Si 1 | 4a | 10 |
| | | Si 2 | 8h | 10 |
| β-$Ti_6Sn_5$ | $Nb_6Sn_5$ | Nb 1 | 8k | 12 |
| | | Nb 2 | 8l | 11 |
| | | Nb 3 | 4i | 15 |
| | | Nb 4 | 4e | 12 |
| | | Sn 1 | 8l | 7 |
| | | Sn 2 | 4f | 8 |
| | | Sn 3 | 4j | 8 |
| | | Sn 4 | 4i | 8 |
| $Ti_5Ga_4$ | $Nb_5Ga_4$ | Nb 1 | 4d | 14 |
| | | Nb 2 | 6g | 15 |
| | | Ga 1 | 2b | 8 |
| | | Ga 2 | 6g | 9 |
| $V_8Ga_{41}$ | $V_8Ga_{41}$ | V 1 | 6c | 10 |
| | | V 2 | 18f | 10 |
| | | Ga 1 | 3a | 12 |
| | | Ga 2 | 3b | 8 |
| | | Ga 3 | 9d | 10 |
| | | Ga 4 | 18f | 13 |
| | | Ga 5 | 18f | 13 |
| | | Ga 6 | 18f | 10 |
| | | Ga 7 | 18f | 10 |
| | | Ga 8 | 18f | 10 |
| | | Ga 9 | 18f | 9 |
| α-$V_7Al_{45}$ | $CrAl_{6.6}$ | Cr 0 | 2a | 12 |
| | | Cr 1 | 4i | 12 |
| | | Cr 2 | 8j | 12 |
| | | Al 0 | 2d | 12 |
| | | Al 3 | 4i | 12 |
| | | Al 4 | 4i | 13 |
| | | Al 5 | 4i | 12 |
| | | Al 6 | 4i | 13 |
| | | Al 7 | 4i | 12 |
| | | Al 8 | 4i | 12 |
| | | Al 9 | 4i | 11 |

| | | | | |
|---|---|---|---|---|
| $Cu_5Zn_8$ | $V_5Al_8$ | V 1 | 8c | 12 |
| | | V 2 | 12e | 13 |
| | | Al 1 | 8c | 12 |
| | | Al 2 | 24g | 11 |
| $WAl_{12}$ | $WAl_{12}$ | W | 2a | 12 |
| | | Al | 24g | 11 |
| σ-CrFe | $Nb_2Al$ | Nb 1 | 8i | 14 |
| | | Nb 2 | 4g | 15 |
| | | Nb 3 | 8j | 14 |
| | | Al 1 | 2a | 12 |
| | | Al 2 | 8i | 12 |
| $WAl_4$ | $WAl_4$ | W 1 | 2a | 12 |
| | | W 2 | 4b | 12 |
| | | Al 1 | 2a | 15 |
| | | Al 2 | 2a | 15 |
| | | Al 3 | 4b | 12 |
| | | Al 4 | 4b | 11 |
| | | Al 5 | 4b | 15 |
| | | Al 6 | 4b | 10 |
| | | Al 7 | 4b | 12 |
| $Mn_2Hg_5$ | $V_2Ga_5$ | V | 4h | 12 |
| | | Ga 1 | 2d | 10 |
| | | Ga 2 | 8i | 10 |
| $TiAl_3$ | $VAl_3$ | V | 2a | 12 |
| | | Al 1 | 2b | 12 |
| | | Al 2 | 4d | 12 |
| $AuCu_3$ | $SiNb_3$ | Nb | 3c | 12 |
| | | Si | 1a | 12 |
| $WAl_5$ | $WAl_5$ | W | 2b | 12 |
| | | Al 1 | 2a | 12 |
| | | Al 2 | 2b | 12 |
| | | Al 3 | 6c | 12 |
| $V_6Si_5$ | $V_6Si_5$ | V 1 | 8j | 17 |
| | | V 2 | 8j | 15 |
| | | V 3 | 8f | 14 |
| | | Si 1 | 8j | 11 |
| | | Si 2 | 8j | 10 |
| | | Si 3 | 4a | 10 |
| $Cr_5Al_8$ | $Cr_5Al_8$ | Cr 1 | 1a | 12 |
| | | Cr 2 | 3b | 12 |
| | | Cr 3 | 3b | 12 |
| | | Cr 4 | 3b | 13 |
| | | Al 1 | 1a | 12 |
| | | Al 2 | 3b | 13 |
| | | Al 3 | 3b | 13 |
| | | Al 4 | 3b | 15 |
| | | Al 5 | 6c | 13 |
| $V_4Al_{23}$ | $V_4Al_{23}$ | V 1 | 2a | 12 |
| | | V 2 | 6h | 12 |
| | | Al 1 | 12k | 11 |
| | | Al 2 | 12k | 12 |
| | | Al 3 | 12k | 12 |
| | | Al 4 | 6h | 12 |
| | | Al 5 | 12k | 12 |
| $Cr_{11}Ge_8$ | $V_{11}Ge_8$ | V 1 | 8d | 13 |
| | | V 2 | 8d | 14 |
| | | V 3 | 4c | 16 |
| | | V 4 | 4c | 16 |
| | | V 5 | 4c | 14 |
| | | V 6 | 4c | 17 |
| | | V 7 | 4c | 15 |
| | | V 8 | 4c | 15 |
| | | V 9 | 4c | 15 |
| | | Ge 1 | 8d | 19 |
| | | Ge 2 | 4c | 13 |
| | | Ge 3 | 4c | 13 |
| | | Ge 4 | 4c | 11 |
| | | Ge 5 | 4c | 10 |
| | | Ge 6 | 4c | 11 |
| | | Ge 7 | 4c | 11 |
| | | Al 10 | 4i | 11 |
| | | Al 11 | 8j | 12 |
| | | Al 12 | 8j | 11 |
| | | Al 13 | 8j | 12 |
| | | Al 14 | 8j | 12 |
| | | Al 15 | 8j | 13 |
| | | Al 16 | 8j | 12 |
| | | Al 17 | 8j | 11 |
| $Cr_{11}Ge_{19}$ | $Cr_{11}Ge_{19}$ | Cr 1 | 2a | 12 |
| | | Cr 2 | 2c | 14 |
| | | Cr 3 | 4e | 14 |
| | | Cr 4 | 4e | 12 |
| | | Cr 5 | 4e | 14 |
| | | Cr 6 | 4e | 12 |
| | | Cr 7 | 4e | 14 |
| | | Cr 8 | 4h | 14 |
| | | Cr 9 | 4h | 8 |
| | | Cr 10 | 4h | 12 |
| | | Cr 11 | 4h | 14 |
| | | Cr 12 | 4h | 12 |
| | | Ge 1 | 8i | 10 |
| | | Ge 2 | 8i | 12 |
| | | Ge 3 | 8i | 14 |
| | | Ge 4 | 8i | 14 |
| | | Ge 5 | 8i | 14 |
| | | Ge 6 | 8i | 12 |
| | | Ge 7 | 8i | 10 |
| | | Ge 8 | 8i | 12 |
| | | Ge 9 | 8i | 14 |
| | | Ge 10 | 4g | 14 |

* The order of the structure types in this table is the same as in table 1.

C.N. : Coordination number
Eq.Pts. : Equivalent points

### $\alpha$-$V_7Al_{45}$ Structure Type: Representative $CrAl_{6.6}$

$CrAl_{6.6}$ crystallizes in the monoclinic space group C 2/m with 104 atoms per unit cell. The asymmetric unit contains 3 independent Cr atoms and 16 Al atoms. The Cr atoms ($Cr_0$, $Cr_1$ and $Cr_2$) have CN 12, forming distorted icosahedra. $Cr_0$ polyhedron possesses 2/m ($C_{2h}$) symmetry, $Cr_1$: m ($C_s$), $Cr_2$: 1 ($C_1$) respectively.

One can describe this structure in terms of packing these 3 Cr polyhedra, Fig. 4. $Cr_0$ polyhedron shares an $Al_8$ atom with $Cr_1$ polyhedron which shares two triangular faces with a complex unit of $Cr_2$ polyhedra (which is two icosahedra sharing a five membered ring of atoms). In the figure the polyhedra and their contacts are shown in the *ab* and *ca* planes. The structure is shown in *ca*-projection. These units of the three polyhedra repeat themselves in the unit cell, sharing the shaded atoms among each other as shown on the right hand side of the figure. The complex units of $Cr_2$ share two triangular faces with each other. Along the *b* axis the $Cr_2$ units share apices.

## Structure Classification According to Polyhedrapacking

A. We classify the structure types as follows (Table 1):

1. a. Structures described by packing of *one polyhedron.*

b. Structures described by packing of *2 polyhedra.*

c. Structures described by packing of *more than 2 polyhedra.*

2. a. 1. a to 1 c will be subdivided according to the *number of vertices of the polyhedron* (i.e. according to CN of the central atom around which the polyhedron considered is built up); beginning from lower coordination numbers going to higher ones.

b. Polyhedra having the *same number of vertices* will be subdivided according to their symmetry. We begin with cubic point group symmetries followed by hexagonal, trigonal, tetragonal, orthorhombic, monoclinic and triclinic point group symmetries.

B. Two types of polyhedrapacking were observed:

1. A three dimensional distribution of discrete polyhedra sharing corners, edges or faces.

2. A layer-like distribution of polyhedra (sheet polyhedrapacking). 2 is in fact a special case of 1.

This further feature is included in Table 1, "Type of Packing" column.

## Conclusions and Discussion

1. The polyhedrapacking principle *has proved* valid for all structures treated (Table 1). It is expected that this principle is *valid for all*

*intermetallic structure types.* Other concepts are valid just for some structures. At least it has not been studied, if any of these concepts is valid for all (most) structures available.

For example *Samsons* fascinating model[9] for giant molecules which describes the structures by packing *Friauf* polyhedra is limited by the fact that similar atoms in the structure should be surrounded by *Friauf* polyhedron.

Structures described by "*Kagomé* Nets" must exhibit these nets in the structure. For more details on structure description models see *Girgis*[10]

2. It delivers a simple, clear representation of the structures.

3. Different relationships are found:

$V_5Si_3$ and $V_6Si_5$ are both built up by similar polyhedra, although they belong to different structure types. $V_5Si_3$: $W_5Si_3$, t I 32, I 4/mcm; $V_6Si_5$, o I 44, Ibam. $V_5Si_3$ ($W_5Si_3$ type) and $V_5Ge_3$ ($Mn_5Si_3$ type) have both a *Kasper* polyhedron as a building unit. In the $V_5Ge_3$ it is very distorted, therefore we call it *Kasper*-like polyhedron.

4. Icosahedra, *Kasper*, *Kasper*-like 14 verticon and rhombic dodecahedron play a big role in the description of these structures, although they belong to different structure types.

## Acknowledgments

We thank *G. Hollinger* for assistance. This work was supported by the Swiss National Science Foundation.

## References

[1] *Girgis K.*, Collected Abstracts of the Fifth European Crystallographic Meeting, Copenhagen, Denmark, Aug. 1979, p. 86.
[2] *Teatum E., Gschneidner K. A., Weber J. T.*, LA-2345, U.S. Dept. of Commerce, Washington D.C., 1960.
[3] *Brunner G. O.*, Acta Crystallogr. **A 33**, 226 (1977).
[4] *Bhandary K. K., Girgis K.*, Monatsh. Chem. **108**, 341 (1977).
[5] *Bhandary K. K., Girgis K.*, Acta Crystallogr. **A 33**, 903 (1977).
[6] *Villars P., Girgis K., Niggli A.*, Monatsh. Chem. **114**, 1281 (1983).
[7] *Villars P., Girgis K., Niggli A.*, Acta Crystallogr. **B 39**, 603 (1983).
[8] *Girgis K.*, to be published.
[9] *Samson S.*, in: Structural Chemistry and Molecular Biology (*Rich A., Davidson N.*, eds.). San Francisco: Freeman. 1968.
[10] *Girgis K.*, Struktur, Kristallchemie und Eigenschaften intermetallischer Verbindungen, Lecture Notes, Ch. 4, ETH Zürich, 1984.