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A Two-Correlations Model for Brass-Like Phases

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In order to find energetic rules for the stability of metallic phases it is advantageous to adapt the concepts for these rules in connexion with the density matrix. Four specializations of this matrix lead to the assumption of two lattice-like spatial correlations in a crystal, one for the valence electrons and the other for the outer core electrons. The commensurabilities of these two correlations to the crystal structure give an indication of the energetic preference of a structure of a given composition and valence electron concentration. Since displacive transformations may be understood as an ordering of the atoms with respect to the core-electron correlation, an analysis of the core-electron correlation is possible on the basis of solved displacive crystal structures. The binding is discussed for the Cu, Mg and W families of structures in brass-like phases.

Introduction

There is no doubt that the set of atomic radii has been very useful not only for analysing crystal structures but especially for assessing the energetic preference of a given structure in a given mixture of chemical elements. Although the atomic radii for 12-coordination are determined only to one Å/100, they have been reproducibly analysed from solved crystal structures and represent a part of our empirical knowledge on solid phases. The question therefore arises as to whether there are similar concepts which may help to assess the energy of a structure, and thus build up a natural system of structural types.

In order to find such concepts we must look for the basis of the concept of energetic preference. A material system is described by its energy matrix (also called energy operator) $U^{\text{op}}_{xx'}$, where $x=(x^i_1,x^i_2,\ldots,x^i_N)$ are the (spatial and spin) coordinates numbered by i for each of the N particles in the system; the state of this system is described by a density matrix (also called density operator) $D_{x'x}$; and the energy expectation is calculated as $\bar{U}=\int_{xx'}U^{\text{op}}_{xx'}D_{x'x}$. We consider the internal energy instead of the Gibbs energy, as it is the simpler concept, and both concepts are equivalent in the sense of thermodynamic transformation theory. Different states may have the same energy expectation, but if we compare states of the same volume, entropy and mole numbers, the realized state gives the lowest energy expectation, *i.e.* the highest energetic preference. From the realized density matrix the atomic radius of a component atom may be calculated by the reduction process $D^{\text{re}}_{x_1x_1}:=\int_{x_2x_3}\ldots D_{x_1x_2\ldots,x_1x_2\ldots}$ which gives the probability of finding the particle 1 in the unit volume; the probability of finding any particle (say electron) is given by $ND^{\text{re}}_{x_1x_1}$, because of symmetry. The atomic radius therefore gives information on the density matrix and is thus useful for energetic arguments. However the reduced density matrix $D^{\text{re}}_{x_1'x_1}$ is not sufficient for energy calculations as $U^{\text{op}}_{xx'}$ contains members like $1/|x^i_1-x^i_2|$ depending on two spatial coordinates. Therefore a first step in the specialization of D may be the use of the two particle reduced density matrix $D^{\text{re}}_{x_1'x_2'x_1x_2}=\int_{x_3x_4\ldots}D_{x_1'x_2'x_3\ldots,x_1x_2x_3\ldots}$ which is necessary and sufficient for energy calculations. Since the energy matrix does not essentially depend on spin, the reduction of D over spins may be complete; also the nuclear particles may be thought of as fixed.

A second specialization step is very common: to compare only structures of the same kinetic energy; in this case only the diagonal $D^{\text{re}}_{x_1x_2}$ of the matrix $D^{\text{re}}_{x_1'x_2'x_1x_2}$ needs to be considered; it may be called the *spatial correlation* of the electrons; this term recalls that the spatial density of the electrons is insufficient to calculate or assess the energy. The spatial correlation is no longer a matrix but a function, although a function in six-dimensional space; it is this property which has prevented crystallographers studying it as closely as the atomic radii have been studied in the past. Strictly speaking every crystal structure must be described by a six-dimensional spatial correlation, because of the gravitational field, but this effect is not considerable.

It is therefore reasonable to assume, as a third step of specialization of the density matrix, that the spatial correlation of the electrons has nearly the form $D(x^i_1-x^i_2)$ so that it may be approximately described by a three-dimensional function, which may be called the *electron place lattice*; it is clear that this neither implies nor forbids that electrons have more or less fixed places in a crystal structure. The electron place lattice is a function having a periodicity radius of 50 to 100 Å (Schubert, 1964, p. 100). It should not be confused with a lattice having an infinite periodicity radius.

Two essential properties should be allotted to a spatial correlation (Schubert, 1964):

(1) The lattice-like property reducing the potential energy between the electrons.

(2) The commensurability with the crystal structure reducing the energy between electrons and ions.

This simple model may be named the one-correlation model; examples of its application to metallic structures will be given below.

A correlation may be a product of two correlations when the population is divided into two subpopulations which interact less strongly than the members of one and the same population. Our fourth specialization is the assumption that this possibility is realized in crystals with the valence electrons and the outer core electrons; therefore another model which may be called the two-correlations model seems to be useful; examples for its application to the explanation of structures of metallic phases will be given below. A proposal for two electron spatial correlations in a structure may be called a *binding* in it. The binding has a similarity to the set of atomic radii; it leads to a set of electron distances and correlation types (Schubert, 1964) which may be used during the analysis of a structure and for assessing the energetic preference of a structure.

Every spatial correlation causes an electrostatic field in the crystal structure. This field is well known in the ionic structures, where each cation has a positive charge and each anion a negative charge. But besides these monopole charges, dipole and higher charges also have an influence on the structure. However they have not been considered until now, as the spatial correlations of the electrons were not available. The crystal structure (as already mentioned) tends to minimize the energy of the electrostatic field, if the volume, entropy, and mole numbers are held constant.

The method of finding the binding is a natural extension of the method of finding atomic radii. From the structures of the elements a system of electron distances may be derived (Schubert, 1964, 1974). Then we seek commensurabilities between an electron lattice and the crystal lattice, making use of the occupancy rules and the rule that the electron distances form smooth functions of the composition in a mixture. Many interesting relations revealed by spatial correlations indicate that the correlations model expresses real features of the density matrix. A direct proof of the reality of the correlations has yet to be worked out; to seek it one should study variations of the tails of crystal reflexions, as the correlations are commensurable to the crystal and have a periodicity radius of 50 to 100 Å; since the outer core electrons per atom are more numerous than the valence electrons per atom the core-electron correlation should be sought first.

In order to describe a lattice-like correlation S it is useful to collect the three basal vectors of the lattice a_1^i,a_2^i,a_3^i (i=direction index of an orthogonal coordinate system) into the *basal matrix* a_s^i. A commensurability of an $A1$ correlation cell a_{A1}^i to a crystal cell a_C^i is then given by the matrix product $\mathbf{a}_C=\mathbf{a}_{A1}K$, where K is the *commensurability matrix* and a^i has been replaced by $\mathbf{a}$;K may be written in the form $(K_{11},K_{12},K_{13};\ K_{21},K_{22},K_{23};\ K_{31},K_{32},K_{33})$. Sometimes K is a number; for instance, in Cu may be assumed an $A1$ correlation of the valence electrons, which is $\mathbf{a}_{\mathrm{Cu}}=\mathbf{a}_{\mathrm{A1}}1$; in such a case we speak of a 1-*factorial commensurability* between the two lattices. In a commensurability equation, $\mathbf{a}_{A1}$ has generally to be distorted somewhat to give a whole-numbered K.

In order to have a simple special example we consider the commensurability of the beta brass structure (lattice constants a,b,c) to the gamma brass structure (lattice constants A,B,C). The lattice matrices of both structures in an orthonormal coordinate system i contain the lattice vectors as columns and may be written (under the assumption that the lattice vectors are parallel to the coordinate basal vectors) as

$$\begin{pmatrix} A & 0 & 0 \\ 0 & B & 0 \\ 0 & 0 & C \end{pmatrix} =:\mathbf{a}_\gamma\,, \qquad \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix} =:\mathbf{a}_\beta\,.$$

The well-known commensurability of both structures then becomes:

$$\begin{pmatrix} A & 0 & 0 \\ 0 & B & 0 \\ 0 & 0 & C \end{pmatrix} = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix} \begin{pmatrix} 3 & 0 & 0 \\ 0 & 3 & 0 \\ 0 & 0 & 3 \end{pmatrix}$$

or $\mathbf{a}_\gamma=\sum_\beta \mathbf{a}_\beta K_\gamma^\beta$ or $\mathbf{a}_\gamma=\mathbf{a}_\beta K$.

Instead of the characters β,γ the systematic designations of the phases may be used so that the equation is written as $\mathbf{a}_{\mathrm{Cu5Zn8}}=\mathbf{a}_{\mathrm{CuZn}}3$, where use has been made of the fact that $K=(3,0,0;\ 0,3,0;\ 0,0,3)$ is a multiplier and may be written simply as 3. The well-known fact is that the coefficients combining the $\mathbf{a}_\beta$ column vectors with one $\mathbf{a}_\gamma$ column vector are contained in one column of K. The above example gives a 3-factorial commensurability between the lattices of two different phases; in the following paragraphs factorial commensurabilities are mainly considered between two different electron spatial correlations of one and the same thermodynamic phase.

Structures of the Cu family

The above-mentioned simple concepts permit an explanation of many different crystal structures. Let us first consider the normal shear variants S of the Cu_3Au structure near the valence electron concentration $N_V/A\approx 1$ which may be interpreted as follows: $\mathbf{a}_S=\mathbf{a}_{\mathrm{Cu}}(1,0,0;\ 0,1,0;\ 0,0,L)=\mathbf{a}_{A1}(1,0,0;\ 0,1,0;\ 0,0,L+1)$, where L is called the shear length. The energy is minimized by the structure type (Schubert, 1964). The dependence of L^{-1} on the valence electron concentration N_V/A, which follows from the above equation, has been found experimentally (Schubert, 1964, 1973; Sato, 1965). Further normal shear variants are found at a valence electron concentration $N_V/A\approx 3$, *e.g.* $TiAl_3$ (described in *Structure Reports* [SR] 2, p.

762)* and $ZrAl_3$ (SR 7, p. 100); they correspond to the next higher whole-numbered commensurability of the valence electrons to the substructure in the basal plane: $\mathbf{a}_{TiAl3}=\mathbf{a}_{Cu}(1,0,0;\ 0,1,0;\ 0,0,2)=(3{\cdot}85,0,0;\ 0,3{\cdot}85,0;\ 0,0,8{\cdot}60)\text{Å}=\mathbf{a}_{A1}(1,-1,0;\ 1,1,0;\ 0,0,3{\cdot}5)$; $\mathbf{a}_{ZrAl3}=\mathbf{a}_{Cu}(1,0,0;\ 0,1,0;\ 0,0,4)=(4{\cdot}01,0,0;\ 0,4{\cdot}01,0;\ 0,0,17{\cdot}31)\ \text{Å}=\mathbf{a}_{A1}(1,-1,0;\ 1,1,0;\ 0,0,6{\cdot}5)$. The numbers of electron places per cell are $N_P/C=28$ and 52 while the numbers of valence electrons per cell are $N_V/C=26$ and 52. This finding conforms to the rule (Schubert, 1974) that in heavier compounds the electron lattice tends to full occupancy, while in less heavy compounds partial occupancy is more probable. The possibility of partial occupation of the electron correlation accounts for the difference in crystal structure at the same valence electron concentration. The electrostatic field in $TiAl_3$ and $ZrAl_3$ is indicated in Fig. 1 by dipole vectors; only the dipole vectors at the minority component need to be considered; the observed crystal structure thus minimizes the electrostatic energy.

A structure of the $ZrAl_3$ type is also found in the brass-like phase $Au_3Zn.h$ (SR 19, p. 160) but at 270 °C the phase $Au_3Zn.h$ transforms further into a room-temperature phase $Au_3Zn.r$ (SR 22, p. 107) which has, besides the component ordering of $Au_3Zn.h$, a displacive ordering of the atoms, which leads to a cell $\mathbf{a}_{Au3Zn.r}=\mathbf{a}_{Cu}(1,-1,0;\ 1,1,0;\ 0,0,4)$. From the atomic positions in the r phase which are shown in Fig. 2 it may be concluded that the transformation $h\rightarrow r$ is caused by the correlation of the outer core electrons (simply called core-electron correlation) and from the transformation temperatures it follows that the influence of the core electrons is comparable to that of the valence electrons. Since the core of Zn is smaller than the core of Au, certain Au atoms move towards the Zn atoms, and this leads to the displacive transformation. The correlation of the core electrons was first found in the interpretation of the crystal structure of In and may be described by $\mathbf{a}_{In}=(4{\cdot}598,0,0;\ 0,4{\cdot}598,0;\ 0,0,4{\cdot}947)\ \text{Å}=\mathbf{a}_{A1}(1,-1,0;\ 1,1,0;\ 0,0,1{\cdot}5)=\mathbf{a}'_{A2}(2,-2,0;\ 2,2,0;\ 0,0,3)$; the prime on $\mathbf{a}'_{A2}$ indicates a core-electron correlation; it is in this case occupied to only ~83/100 by the outer core electrons (here d electrons). Applying this correlation to $Au_3Zn.r$ we

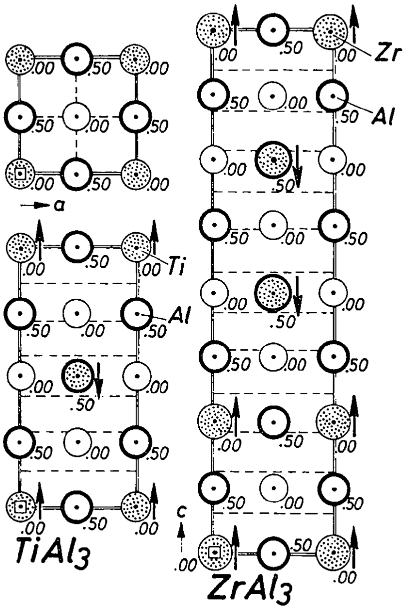
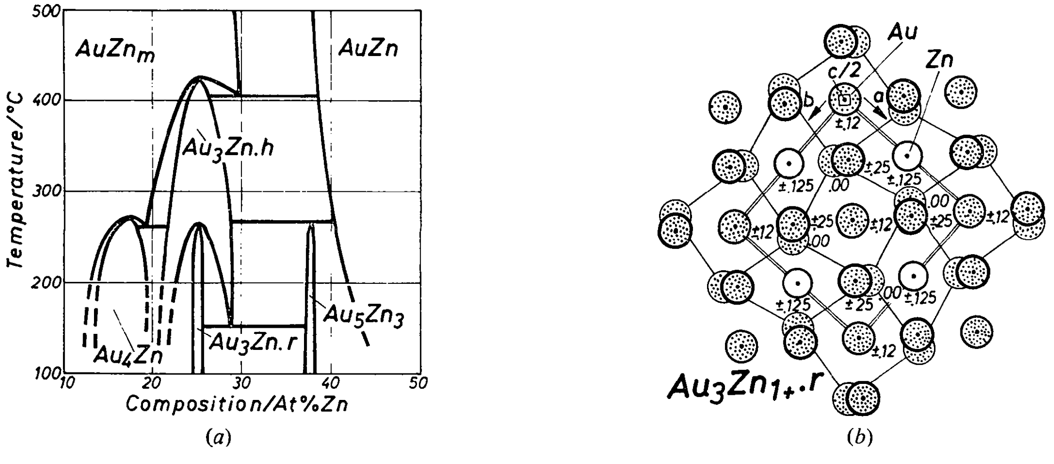


Fig. 1. Crystal structure of $TiAl_3$ and $ZrAl_3$. $\mathbf{a}(TiAl_3)=(3{\cdot}84,0,0;\ 0,3{\cdot}84,0;\ 0,0,8{\cdot}59)\text{Å}=\mathbf{a}_{A1}(1,-1,0;\ 1,1,0;\ 0,0,3{\cdot}5)$, $N_P/C=28$, $N_V/C=26$. $\mathbf{a}(ZrAl_3)=(4{\cdot}01,0,0;\ 0,4{\cdot}01,0;\ 0,0,17{\cdot}31)\text{Å}=\mathbf{a}_{A1}(1,-1,0;\ 1,1,0;\ 0,0,6{\cdot}5)$, $N_P/C=52$, $N_V/C=52$.



(a) (b)

Fig. 2. (a) Part of the phase diagram Au–Zn. (b) Crystal structure of $Au_3Zn_{1+}.r$ $D^{18}_{2h}Acam$, $a=5{\cdot}585$, $b=5{\cdot}594$, $c=16{\cdot}648$ Å, $\sqrt{2}c/4a=1{\cdot}055$. 8Au(d).0.0.119, 8Au(e).25.25.25, 8Au(f).190.310.0, 8Zn(d).0.0.367. $\mathbf{a}_{Au3Zn}=\mathbf{a}_{Cu3Au}(1,-1,0;\ 1,1,0;\ 0,0,4)=\mathbf{a}_{A1}(1,-1,0;\ 1,1,0;\ 0,0,5)=\mathbf{a}'_{A2}(4,0,0;\ 0,4,0;\ 0,0,12)$. $\mathbf{a}_{Au5Zn2Ga}=\mathbf{a}_{Cu3Au}(2,-1,0;\ 2,1,0;\ 0,0,2)=\mathbf{a}_{A2}(4,0,0;\ 0,2,0;\ 0,0,3)=\mathbf{a}'_{A2}(8,0,0;\ 0,4,0;\ 0,0,6)$.

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* *Structure Reports* are cited throughout by the letters SR followed by the volume number and page number. Full references are contained in *Strukturbericht*, Leipzig: Akademische Verlags (for volumes 1–7) and *Structure Reports*, Utrecht: Oosthoek (for volume 8 onwards).

find $\mathbf{a}_{\mathrm{Au3Zn}.r} = {}_1(1\mathbf{a}_A, -1,0;\ 1,1,0;\ 0,0,5) = \mathbf{a}'_{A2}(4,0,0;\ 0,4,0;\ 0,0,12)$. The valence electron correlation of this proposal is heavily compressed in the direction of the long axis of the crystal, so that it could also be described by a somewhat strained *A*2 correlation $\mathbf{a}_{\mathrm{Au3Zn}.r} = \mathbf{a}_{A2}(2,0,0;\ 0,2,0;\ 0,0,5)$; if the last commensurability element were 6 instead of 5, we would have a 2-factorial commensurability between the two correlations which must be considered as energetically favourable. It could be attained if the valence electron concentration were higher. In fact in the mixtures Au–Zn and Au–Zn–Ga the phases Au_5Zn_3 (SR 22, p. 107) and Au_5Zn_2Ga (SR 22, p. 108) have been found, which may be interpreted as follows: $\mathbf{a}_{\mathrm{Au5Zn3}} = (11{\cdot}02,0,0;\ 0,5{\cdot}51,0;\ 0,0,33{\cdot}61)\,\text{Å} = \mathbf{a}_{\mathrm{Cu}}(2,-1,0;\ 2,1,0;\ 0,0,8) = \mathbf{a}_{A1}(2,-1,0;\ 2,1,0;\ 0,0,11) = \mathbf{a}'_{A2}(8,0,0;\ 0,4,0;\ 0,0,24)$ and $\mathbf{a}_{\mathrm{Au5Zn2Ga}} = (10{\cdot}946,0,0;\ 0,5{\cdot}473,0;\ 0,0,8{\cdot}084)\,\text{Å} = \mathbf{a}_{\mathrm{Cu}}(2,-1,0;\ 2,1,0;\ 0,0,2) = \mathbf{a}_{A1}(2,-1,0;\ 2,1,0;0,0,3) = \mathbf{a}'_{A2}(8,0,0;\ 0,4,0;\ 0,0,6)$. The latter structure is factorially commensurable because taking distortion into account $\mathbf{a}_{A1}(2,-1,0;\ 2,1,0;\ 0,0,3) = \mathbf{a}_{A2}(4,0,0;\ 0,2,0;\ 0,0,3)$; the structure is therefore especially stable; it is interesting that the phases approximating to factorial commensurability like Au_5Zn_3 are stabilized. Also Ti_3Pt_5 (SR 33, p. 126) is isotypic with Au_5Zn_2Ga; the outer core electrons of Ti take part in the *A*2 correlation, contrary to the observation that these electrons are often in an *A*0 correlation (cubic primitive correlation).

The phenomenon of factorial commensurability is good support for the assumption that the *A*2 correlation of the outer core electrons of In also occurs in brass-like phases; however, a further indication of the *A*2 correlation is the existence of structures which show, besides a displacive superstructure of the Cu_3Au type, a monoclinic distortion: $Pt_3Ge.r$ (SR 24, p. 116) and $Pt_3Si.r$ (SR 29, p. 129), Fig. 3: $\mathbf{a}_{\mathrm{Pt3Si}.r} = (7{\cdot}701,0,0;\ 0,7{\cdot}758,0;\ [-0{\cdot}252],0,7{\cdot}754)\,\text{Å} = \mathbf{a}'_{A2}(0,4,-4;\ 0,4,4;\ 5{\cdot}5,0,0)$; $\mathbf{a}_{\mathrm{Pt3Ge}.r} = (7{\cdot}922,0,0;\ 0,\ 7{\cdot}768,0;\ [-0{\cdot}085],0,7{\cdot}768)\,\text{Å} = \mathbf{a}'_{A2}(0,4,-4;\ 0,4,4;\ 5{\cdot}75,0,0)$. The bracketed matrix elements should be neglected for calculating the commensurability matrix. The shorter $\mathbf{a}_1$ axis of $Pt_3Si.r$ is caused by the smaller number of core electrons (as compared with $Pt_3Ge.r$), which leads to a smaller number $N_{P'}/C$ of core electron places per cell and therefore to the smaller commensurability element 5·5. Both corresponding elements favour a monoclinic distortion, as they are half integer (the element 5·75 only when it is doubled), so that commensurability of the core electrons is improved by the distortion. The valence electron correlation in Pt_3Ge and Pt_3Si may be considered as 1-factorially commensurable to the crystal substructure. If this is no longer the case, as in $Pt_3Ga.r$ (Chattopadhyay & Schubert, 1975), the core-electron correlation is more disturbed so that the mono-

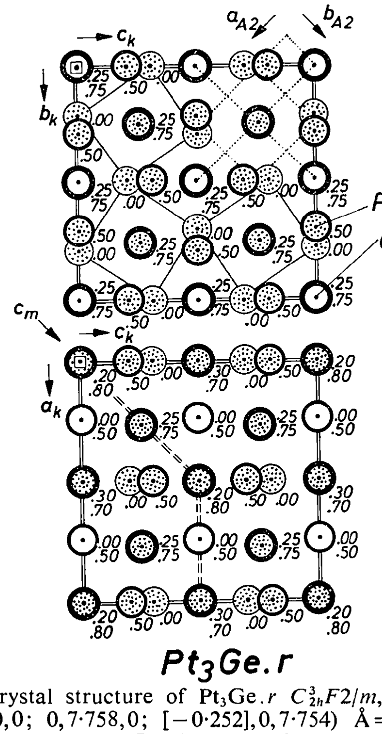

Fig. 3. Crystal structure of $Pt_3Ge.r$ $C^3_{2h}F2/m$, $\mathbf{a}(Pt_3Si.r) = (7{\cdot}701,0,0;\ 0,7{\cdot}758,0;\ [-0{\cdot}252],0,7{\cdot}754)\,\text{Å} = \mathbf{a}'_{A2}(0,4,-4;\ 0,4,4;\ 5{\cdot}5,0,0)$. $\mathbf{a}(Pt_3Ge.r) = (7{\cdot}922,0,0;\ 0,7{\cdot}768,0;\ [-0{\cdot}085],0,7{\cdot}768)\,\text{Å} = \mathbf{a}'_{A2}(0,4,-4;\ 0,4,4;\ 5{\cdot}75,0,0)$.

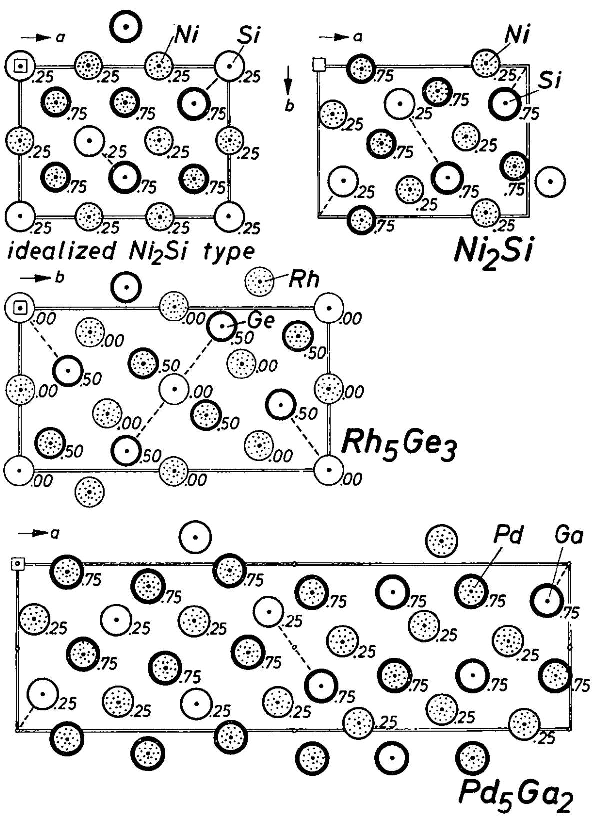

Fig. 4. Structures of the Ni_2Si family. $\mathbf{a}(Ni_2Si) = (7{\cdot}06,0,0;\ 0,4{\cdot}99,0;\ 0,0,3{\cdot}72)\,\text{Å} = \mathbf{a}'_{A2}(6,0,0;\ 0,4,0;\ 0,0,3)$, $N_V/A = 1{\cdot}33$. $\mathbf{a}(Rh_5Ge_3) = (5{\cdot}42,0,0;\ 0,10{\cdot}32,0;\ 0,0,3{\cdot}96)\,\text{Å} = \mathbf{a}'_{A2}(4,0,0;\ 0,8,0;\ 0,0,3)$, $N_V/A = 1{\cdot}5$. $\mathbf{a}(Pd_5Ga_2) = (18{\cdot}39,0,0;\ 0,5{\cdot}48,0;\ 0,0,4{\cdot}08)\,\text{Å} = \mathbf{a}'_{A2}(14,0,0;\ 0,4,0;\ 0,0,3) = \mathbf{a}_{A1}(6,2,0;\ 6,-2,0;\ 0,0,1)$. $N_V/A = 0{\cdot}9$.

clinic distortion is no longer realized but only the tetragonal distortion which belongs to the commensurability element 5·75. The monoclinic distortion may also be destroyed by a small substitution of Ga for Ge in Pt_3Ge.*r* (Khalaff & Schubert, 1974). An even stronger disturbance is the loss of 3:1 stoichiometry in $Pt_{3-}Ga_{1+}$, leading to the Cu_3Au type of structure, where even the displacive order is destroyed; the core-electron correlation must be assumed as twinned into three directions in this case.

A third indication for the *A*2 core-electron correlation is the structure of Ni_2Si (SR 16, p. 123) shown in Fig. 4, which occurs in several metallic mixtures on the valence electron rich side of phases like Pt_3Ge.*r*. It shows the commensurability: $\mathbf{a}_{Ni2Si}=(7{\cdot}06,0,0;\ 0,4{\cdot}99,0;\ 0,0,3{\cdot}72)$ Å$=\mathbf{a}_{Cu}(1{\cdot}5,-1,0;\ 1{\cdot}5,1,0;\ 0,0,1)=\mathbf{a}'_{A2}(6,0,0;\ 0,4,0;\ 0,0,3)$. The valence-electron commensurability is not given; it may be congruent to $\mathbf{a}_{Cu}$; but if the major component contributes some valence electrons, an *A*2 correlation factorial to the core electrons may be assumed. Structural types like Rh_5Ge_3, Pd_5Ga_2, Pt_2Ga.*r* and Ti_3Pt_5 belong to the Ni_2Si family. For Pd_5Ga_2 (Khalaff & Schubert, 1974) it is found that $\mathbf{a}_{Pd5Ga2}=\mathbf{a}_{Cu}(7,2,0;\ 7,-2,0;\ 0,0,1)=\mathbf{a}_{A1}(6,2,0;\ 6,-2,0;\ 0,0,1)=\mathbf{a}'_{A2}(14,0,0;\ 0,4,0;\ 0,0,3)$; this means that the valence-electron correlation spreads as compared with the core-electron correlation, similarly as in the series Au_5Zn_2Ga, Au_5Zn_3, Au_3Zn.*r*. The question arises why Ni_2Si or Pd_2Ga accepts the commensurability element 3 in the direction of the shortest axis while phases like Cu do not. Since all valence electrons in Ni_2Si belong to one and the same component, the valence-electron correlation is more easily deformed than in Cu, where each valence electron belongs to another atom; the core-electron correlation in Ni_2Si may therefore go over more easily to the favourable core-electron commensurability of In, than the core-electron correlation in Cu. A further argument is that the neighbouring minority atoms support the strain in the direction of the shortest axis. Another question is why in the mixture Ni–Ga is no Ni_2Si-type found. This may be answered by remarking that the small atomic volume of Ni does not allow a strong displacive change in the structure. A third question is connected with the finding that Pt_2Al.*h* is of the Ni_2Si-type (Chattopadhyay & Schubert, 1975) while Pt_2Al.*r* (Fig. 5) (Chattopadhyay & Schubert, 1976) shows a similar but characteristically different structure. It might be assumed that Pt_2Al.*h* has the valence electron concentration of 1·5 and consequently a 2-factorially commensurable valence-electron correlation; at lower temperatures the electron contribution of the Pt atoms is decreased, so that a 2-factorially commensurable valence correlation is no longer possible; to preserve it in certain planes the Al atoms move towards these planes and thus form a new type of superstructure.

A $T-T$ branch of the Cu family occurs in mixtures of the kind T^5-T^{10} or similar. To understand these structures it is useful to begin with the $TiAl_3$ representative VNi_3. One finds $\mathbf{a}_{VNi3}=(3{\cdot}542,0,0;\ 0,3{\cdot}542,0;\ 0,0,7{\cdot}213)$ Å$=\mathbf{a}_{A2}(1,-1,0;\ 1,1,0;\ 0,0,2{\cdot}9\approx3)=\mathbf{a}'_{A2}(2,-2,0;\ 2,2,0;\ 0,0,6)$ which is a factorial commensurability between valence and outer-core electrons; as $N_P/C=12$, the correlation is not fully occupied, but the electrostatic energy is minimized, and the weakly strained substructure axial ratio $|a_3|/2|a_1|$ is explained.

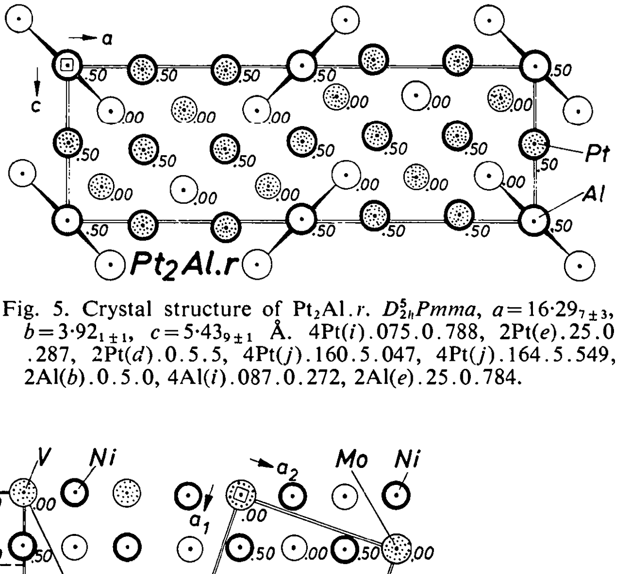

Fig. 5. Crystal structure of Pt_2Al.*r*. D_{2h}^5,*Pmma*, $a=16{\cdot}29_{7\pm3}$, $b=3{\cdot}92_{1\pm1}$, $c=5{\cdot}43_{9\pm1}$ Å. 4Pt(*i*).075.0.788, 2Pt(*e*).25.0 .287, 2Pt(*d*).0.5.5, 4Pt(*j*).160.5.047, 4Pt(*j*).164.5.549, 2Al(*b*).0.5.0, 4Al(*i*).087.0.272, 2Al(*e*).25.0.784.

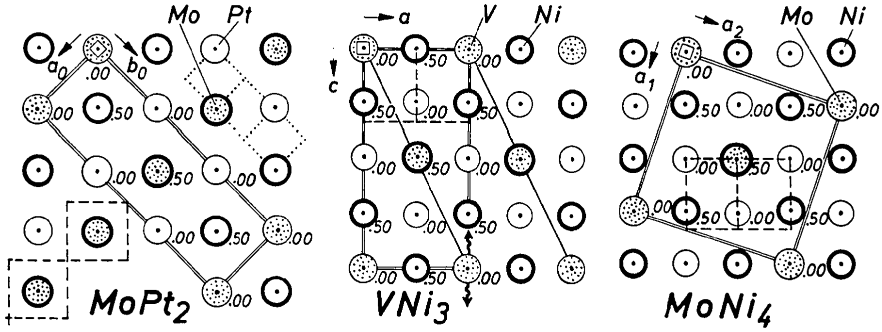

Fig. 6. VNi_3 family: $MoPt_2$ (*P*1·2, structural type following Schubert, 1964; SR20, p. 29), $\mathbf{a}=(2{\cdot}76,0,0;\ 0,8{\cdot}30,0;\ 0,0,3{\cdot}94)$ Å$=\mathbf{a}_{Cu}(0{\cdot}5,-1{\cdot}5,0;\ 0{\cdot}5,1{\cdot}5,0;\ 0,0,1)=\mathbf{a}_{A0}(1,-3,0;\ 1,3,0;\ 0,0,2)=\mathbf{a}'_{A2}(2,0,0;\ 0,6,0;\ 0,0,2{\cdot}83)$. VNi_3 ($TiAl_3$-type), $\mathbf{a}=(3{\cdot}54,0,0;\ 0,3{\cdot}54,0;\ 0,0,7{\cdot}21)$ Å$=\mathbf{a}_{Cu}(1,0,0;\ 0,1,0;\ 0,0,2)=\mathbf{a}_{A2}(1,-1,0;\ 1,1,0;\ 0,0,2{\cdot}9\approx3)=\mathbf{a}'_{A2}(2,-2,0;\ 2,2,0;\ 0,0,6)$. $MoNi_4$ (*U*1·4; SR9, p. 110), $\mathbf{a}=(5{\cdot}72,0,0;\ 0,5{\cdot}72,0;\ 0,0,3{\cdot}56)$ Å$=\mathbf{a}_{Cu}(1{\cdot}5,-0{\cdot}5,0;\ 0{\cdot}5,1{\cdot}5,0;\ 0,0,1)$, binding of VNi_3. — shearplane, ⇝ shear-vector, --- valence-electron correlation, ... core-electron correlation.

To preserve factorial commensurability when instead of a T^5 element a T^6 element is alloyed, Nature uses the mechanism of abnormal shears (Schubert, 1964) in $\mathrm{MoNi_4}$ (SR 9, p. 110) which has the commensurability $\mathbf{a}_{\mathrm{MoNi4}}=\mathbf{a}_{\mathrm{Cu}}(1{\cdot}5, -0{\cdot}5, 0;\ 0{\cdot}5, 1{\cdot}5, 0;\ 0, 0, 1)$. The shears represented in Fig. 6 lead to a tetragonal structure, so that the factorial correlation, which remains the same as in $\mathrm{VNi_3}$, must be assumed to be twinned. Taking the same shear on $\mathrm{VNi_3}$ with the opposite abnormal shear vector leads to the structure of $\mathrm{MoPt_2}$ (SR 20, p. 29). To reconcile this contractive shear with the increase in valence-electron concentration to the value 2, another type of valence-electron correlation must be assumed. It is found that $\mathbf{a}_{\mathrm{MoPt2}}=(2{\cdot}765, 0, 0;\ 0, 8{\cdot}296, 0;\ 0, 0, 3{\cdot}938)\ \text{Å}=\mathbf{a}_{\mathrm{Cu}}(0{\cdot}5, -1{\cdot}5, 0;\ 0{\cdot}5, 1{\cdot}5, 0;\ 0, 0, 1)=\mathbf{a}_{A0}(1, -3, 0;\ 1, 3, 0;\ 0, 0, 2)=\mathbf{a}'_{A2}(2, 0, 0;\ 0, 6, 0;\ 0, 0, 2{\cdot}83)$; the valence-electron correlation is fully occupied and the quasi-tetragonal strain is explained by the core-electron correlation. Since the $\mathrm{MoPt_2}$ structure also occurs in the mixture V–Ni, and is there in equilibrium with a sigma phase it may be anticipated that the $A0$ correlation plays an important role in the $\mathrm{Cr_3Si}$ family, which no longer belongs to the brass-like phases.

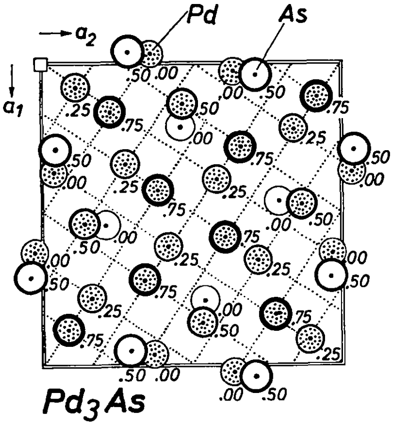

Fig. 7. Binding in $\mathrm{Pd_3As}$. $\mathrm{Pd_3As}$ ($\mathrm{Fe_3P}$-type), $I\bar{4}$, $a=9{\cdot}986$, $c=4{\cdot}836$ Å. $3\times 8\mathrm{Pd}(g)$ .080 .109 .250 .363 .030 .000 .164 .220 .750, $8\mathrm{As}(g)$ .290 .042 .500. $\mathbf{a}(\mathrm{Pd_3As})=\mathbf{a}'_{A2}(6, -4, 0;\ 4, 6, 0;\ 0, 0, 3{\cdot}5)$.

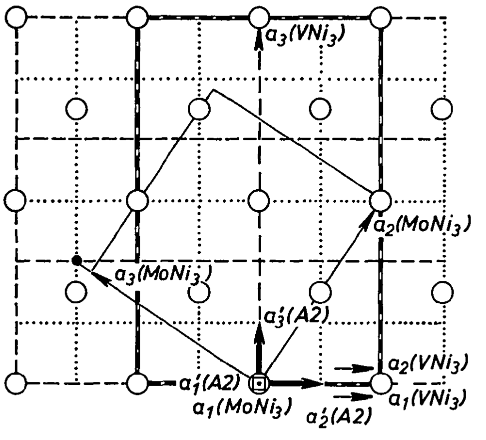

Fig. 8. Binding in $\mathrm{VNi_3}$ and $\mathrm{MoNi_3}$.

If the minor component in a Cu related structure of the type T^5-T^{10} is a B^5 element instead of a T^5 element, we find for instance the phase $\mathrm{Pd_3As}$ (of $\mathrm{Fe_3P}$-type, SR 19, p. 237); the $\mathrm{Fe_3P}$ structure no longer belongs to the Cu family, but is in close relation to the Cu structure. Comparison of the elementary cell $\mathbf{a}_{\mathrm{Pd3As}}=(9{\cdot}97, 0, 0;\ 0, 9{\cdot}97, 0;\ 0, 0, 4{\cdot}82)$ Å with $\mathbf{a}_{\mathrm{Pd}}=3{\cdot}89$ Å gives the core-electron commensurability $\mathbf{a}_{\mathrm{Pd3As}}=\mathbf{a}'_{A2}(6, -4, 0;\ 4, 6, 0;\ 0, 0, 3{\cdot}5)$ (Fig. 7). The commensurability element 3·5 indicates that the support number 'Stützzahl' (Schubert, 1964) of the $(001)_{\mathrm{Cu}}$ layers has changed from 4 in a Cu structure to essentially 1. The decrease of the support number with increasing valence-electron concentration has also been observed in morphotropies between a closest-packed structure and the $\mathrm{MoSi_2}$-type structure. Besides the decrease of the support number in $\mathrm{Pd_3As}$ a shearing is to be observed, not of layers, but of rods parallel to the $\mathbf{a}_3$ axis; reducing this shear results in a two-layer structure. One $\mathbf{a}_1\times\mathbf{a}_2$ mesh should contain $\frac{52}{4}=13$ atoms; however, 16 atoms are observed. It must therefore be concluded that the minority atoms are essentially interstitially inserted into the planes of the majority atoms; this insertion is favoured by the small core of the As atoms which is effective as the valence electrons have diffused far away from the cores. On the other hand in order to have sufficient core-electron places the last commensurability element increases to 3·5. If we assume a 2-factorial commensurability of the valence electrons, we get $N_P/C=52\times\frac{7}{8}=45{\cdot}5$ valence-electron places per cell while only 40 are needed. It must therefore be concluded that the valence-electron correlation is not completely occupied or that the Pd contributes some valence electrons. The difference between $\mathrm{VNi_3}$ and $\mathrm{Pd_3As}$ lies, therefore, in the number and distance of the outer core electrons of the minor component.

Structures of the Mg family

Many brass-like phases have a structure which differs from the Cu structure by shears of the closest-packed layers. Several of these so-called stacking variants of the Cu structure occur at the valence-electron concentration $N_V/A=1{\cdot}5$, so that in these representatives a factorial commensurability between valence electrons and core electrons may be assumed. Knowing that in heavy phases displacive structures occur more frequently than in less heavy phases as the outer core electrons are pressed more strongly away from the inner part in heavy atoms, we consider $\mathrm{Au_3In}$ (SR 21, p. 13) or $\mathrm{MoNi_3}$ (SR 23, p. 181), which have $N_V/A=1{\cdot}5$ and crystallize in an orthorhombically distorted $\mathrm{Cu_3Sb}$-type of structure [SR 22, p. 31, formerly named by the representative $\mathrm{TiCu_3}$ which does not exist (SR 33, p.

152)]. $\mathbf{a}_{\mathrm{Au3In}}=(5\cdot86,0,0;\ 0,4\cdot74,0;\ 0,0,5\cdot17)$ Å. The ratio $2\times5\cdot17/5\cdot86=1\cdot76>\sqrt{3}$, similar to the strained $|a_3|/|a_1|$ ratio of the tetragonal shear variants of the $\mathrm{Cu_3Au}$ type with $N_V/A>1\cdot0$, and the superstructure in the $(\mathbf{a}_1\times\mathbf{a}_3)_{\mathrm{Au3In}}$ plane is the same as that of $\mathrm{TiAl_3}$ in the $(112)_{\mathrm{TiAl3}}$ plane, which is also realized in $(112)_{\mathrm{VNi3}}$. It is therefore probable that the binding in $\mathrm{Au_3In}$ (or $\mathrm{MoNi_3}$) is similar to that in $\mathrm{VNi_3}$. If we assume (considering Fig. 8) that the factorially commensurable electron correlation is compressed somewhat in the direction $\mathbf{a}_3(\mathrm{MoNi_3})$ or, what amounts to the same, in the direction $(\mathbf{a}_3-\mathbf{a}_2)_{A2}$, then the Mg type of stacking is favoured against the Cu type by commensurability of the core electrons.

The causes for this compression should be sought in the following circumstances. The commensurability of the $\mathrm{TiAl_3}$ type of structures in the subtype with $N_V/A\approx1$ is to be assumed as $\mathbf{a}_{\mathrm{subtype}}=\mathbf{a}'_{A2}(2,-2,0;\ 2,2,0;\ 0,0,6)$ giving $N_{P'}/C=96$ and because of 2-factorial commensurability $N_V/A=1\cdot5$; in reality $\mathrm{Au_3In}$ or $\mathrm{MoNi_3}$ probably have a somewhat higher valence-electron concentration because of the abnormal valence-electron contribution of 1·15 of Au in alloys with a not too high valence-electron concentration. A possibility for increasing the valence-electron concentration is the vacancy formation, which has been found in the W family of structures of the brass-like phases; but in closest-packed structures this process is not energetically preferred, as the atoms cannot move towards the vacancy as in W-related structures. Therefore the only possibility for increasing the valence-electron concentration somewhat is to compress the electron correlation by a small amount against the crystal lattice. The exact nature of this interesting process must be investigated by means of the structures of all the known phases which display stacking variance and shearing of the superstructure at the same time. To mention only one example, it has been found that $\mathrm{Au_3Cd}$ (SR 22, p. 67) has a $\mathrm{ZrAl_3}$-type of structure, while $\mathrm{Au_{75}Cd_{13}In_{12}}$ (SR 22, p. 68) shows the same shear density of the superstructure but a stacking variation of the type *chhchhchh*. As may be seen in Fig. 8 the shear density of $\frac{1}{4}$ may be achieved when the correlations are rotated about the $\mathbf{a}_1$ ($\mathrm{MoNi_3}$) axis by 11°; in this case the core-electron commensurability favouring the Mg-type stacking is very nearly attained; in the mixture Au–Mg (SR 30, p. 112) similar results are found: $\mathrm{Au_{80}Mg_{20}}$ ($\mathrm{ZrAl_3}$-type) and $\mathrm{Au_{76}Mg_{24}}$ (SR 30, p. 58) and $\mathrm{Au_{74}Mg_{26}}$ (SR 30, p. 57) show stacking variants with the superstructure shear density $\frac{1}{4}$. Evidently the Mg-type stacking is the valence-electron-rich end of the closest-packed brass-like phases. The weak orthorhombicity found in $\mathrm{Au_3In}$ and $\mathrm{MoNi_3}$ may be destroyed by a disorder of the component atoms, so that hexagonal structures appear, the typical epsilon brass phases, in which no superstructure and no sheared superstructure exists. Comparing these phases with the correlation proposed for the superstructures with shear density $\frac{1}{4}$ we find 5 layers of the core-electron correlation per substructure a_3 axis. It is probable, that this is a preferential commensurability, so that further increase in valence-electron concentration is reached by straining the structure in the basal plane, so that the $|a_3|/|a_1|$ axial ratio is decreased with increasing valence-electron concentration in agreement with observation (Löhberg, 1949; Schubert, 1964). It might be possible that the loss of orthorhombicity is connected with a transition of the core-electron correlation from the $A2$ type to the $C11$ type, which is a tetragonally compressed $A2$ type leading to hexagonal $(110)_{A2}$ planes.

Structures of the W family

The extended structural material of the Cu and Mg family has allowed the analysis of the spatial correlations of the electrons in the members of that family. It is therefore desirable to analyse similarly the W family which is, in brass-like alloys, neighboured to the Cu and Mg family. We cannot hope to find the true correlation considering the simple structures like the CsCl structure of beta brass, since the electron correlations in such phases are presumably twinned. Following Hume-Rothery, the CuZn-type phases are stable at the valence-electron concentration $N_V/A=1\cdot5$. However this valence-electron concentration is also favourable for 2-factorial commensurability of the electron correlations, for at an occupation ratio (Schubert, 1964) of 0·83 in the core-electron correlation we have $N_{P'}/A=12$ and consequently $N_V/A=\frac{12}{8}=1\cdot5$. Since the type of the core-electron correlation is not strongly influenced by the crystal structure, we have to expect an $A2$ correlation of the core-electrons and because of the factorial commensurability also an $A2$ correlation of the valence electrons. It is easily seen that such a correlation with the appropriate electron distances is not well commensurable to the crystal cell of CuZn. We must therefore look for displacive variants, *e.g.* for $\mathrm{Ag_2Zn}.r$ (SR 15, p. 120). In the cell $\mathbf{a}_{\mathrm{Ag2Zn}.r}=([1,0,0;\ -\frac{1}{2},\sqrt{3}/2,0]\ 7\cdot64;\ 0,0,2\cdot82)^T$ Å $=\mathbf{a}_{\mathrm{NiAs}}(1,1,0;\ -1,2,0;\ 0,0,0\cdot5)$ are 9 atoms and to fit into it an $A2$ correlation we take advantage of the cell $\mathbf{a}_{A2h}=\mathbf{a}_{A2}(-1,0,1;\ 0,1,1;\ 1,-1,1)R$ where R is an appropriate rotation. We find $\mathbf{a}_{\mathrm{Ag2Zn}\cdot r}=\mathbf{a}_{A2h}(4,0,0;\ 0,4,0;\ 0,0,1\cdot21\approx1\cdot17)$ so that $N_{P'}/A=12\cdot4$ and $N_P/A=1\cdot55$ if 2-factorial commensurability is realized. The value $N_P/A=1\cdot55$ does not fit very well the reported, but not very definite, homogeneity range $\mathrm{Ag_{63\ldots48}Zn_{37\ldots52}}$, but fits fairly well to the phase $\mathrm{Ag_{70}Ga_{30}}$, which is isotypic. It seems remarkable that the last commensurability element is not a whole number; but a structure $\mathrm{Au_7Ga_2}.h$ has been analysed (Frank, 1971), which shows a tripled $\mathbf{a}_3$ axis: $\mathbf{a}_{\mathrm{Au7Ga2}.h}=([1,0,0;-\frac{1}{2},\sqrt{3}/2,0]\,7\cdot724;0,0,8\cdot751)^T$ Å $=\mathbf{a}'_{A2h}(4,0,0;\ 0,4,0;\ 0,0,3\cdot7\approx3\cdot5)$ and for which factorial commensurability also applies. An earlier assumed $C11$ correlation (Frank, 1971) is less satisfactory.

The structure of $\mathrm{Ag_2Zn}.r$ is similar to the structure of $\mathrm{Fe_2P}$ (SR 23, p. 88) and therefore to NiAs (SR 1, p. 84); $\mathrm{Fe_2P}$ may be considered as displacive and a distorted variant of the W structure. The minority component of Fe_2P has a great valence-electron contribution; therefore its core is relatively small and enters into a triangle of the major component layers parallel to the basal plane, so that the structure goes over from a W-like three-layered structure into a two-layered structure. The analysis of the structural distances leads to the binding (*e.g.* for Pd_2Ge) $\mathbf{a}_{\mathrm{Pd2Ge}}=([1,0,0;\ -\frac{1}{2},\sqrt{3}/2,0]\ 6{\cdot}71;\ 0,0,3{\cdot}41)^T$ Å $=\mathbf{a}_{\mathrm{NiAs}}(1,1,0;\ -1,2,0;\ 0,0,0{\cdot}5)=\mathbf{a}'_{A2h}(2,2,0;\ -2,4,0;\ 0,0,1{\cdot}5)=\mathbf{a}_{A2h}(1,1,0;\ -1,2,0;\ 0,0,0{\cdot}75)$. The electron correlations are factorially commensurable, but the commensurability in the basal plane is different from that in Ag_2Zn: one finds $N_{P'}/A(\mathrm{Ag_2Zn})=12{\cdot}4$ and $N_{P'}/A(\mathrm{Pd_2Ge})=12{\cdot}0$. Perhaps these numbers are an argument for the structural difference $Ag_2Zn\ldots Fe_2P$; another argument is contained in the fact that all valence electrons are contributed by the minor component in Fe_2P; since the minor atoms tend toward a most uniform distribution in the structure because of the valence-electron correlation, there is a considerable strain in the a_3 direction.

There are other superstructures of the W structure, for instance (Heinrich & Schubert, 1975) $\mathbf{a}_{\mathrm{Pd12Ga2Ge5}}=\mathbf{a}_{\mathrm{NiAs}}(1,2,0;\ -2,3,0;\ 0,0,0{\cdot}5)=([1,0,0;\ -0{\cdot}5,\sqrt{3}/2,0]\ 9{\cdot}448;\ 0,0,3{\cdot}684)^T$ Å $=\mathbf{a}'_{A2h}(5,0,0;\ 0,5,0;\ 0,0,1{\cdot}58)$ (Th_7S_{12}-type) or (Engström, 1965) $\mathbf{a}_{\mathrm{Rh20Si13}}=\mathbf{a}_{\mathrm{NiAs}}(1,3,0;\ -3,4,0;\ 0,0,0{\cdot}5)$; these structures are caused by different metric relations between the spatial correlation of the electrons and the crystal structure.

What will be the commensurability for a cubic structure G to the W cell, when the twinned correlation of Ag_2Zn or $Au_7Ga_2.h$ is made evident by displacements. Since the vector $(-\mathbf{a}_1+\mathbf{a}_2)_{\mathrm{Ag2Zn}}$ has the direction of a face diagonal of the W structure, this diagonal must be tripled, *i.e.* $\mathbf{a}_G=\mathbf{a}_W.3$, which is the famous commensurability of the gamma brass phases. The gamma phases have therefore the (quadruply) twinned spatial correlation of Ag_2Zn. Why then is the cell edge of the beta phases (*e.g.* CuZn) not tripled? It must be assumed that in CuZn the correlation is translationally twinned; this kind of twinning is possible for spatial correlations, for crystals it is not possible; for correlations it is no longer possible when vacancies pin the correlations to the crystal; in this case only angular twinning is possible and realized. The present spatial correlation model for the beta brass phases is at variance with Hume-Rothery's (1926) first model; but this does not mean that Hume-Rothery's model nowhere applies; only for CuZn and similar phases does it not apply. However, the question then arises as to how may the Bradley & Taylor (1937) vacancy mechanism, which has formerly been interpreted by Hume-Rothery's model, be explained. In the present model it is explained by the factorial commensurability. If this is energetically favourable, then an increase of valence-electron concentration may be attained, preserving the commensurability of the valence-electron correlation to the crystal by dropping atoms out of the cell. The commensurability of the electron correlations to the crystal favours the gamma cell and therefore also favours numbers of vacancies characteristic for this structure by producing more or less preferential places.

When the valence-electron concentration increases over the value 1·5, then the vacancy mechanism tends to compress the valence-electron correlation relative to the core-electron correlation. This gives a stronger tension of the valence electrons on the core-electron correlation, so that the core-electron distance increases with increasing N_V/A. This becomes apparent when the smallest core-electron distance is plotted against the composition of an alloy; it may lead to a new commensurability which is to be assumed in say $AuGa_2$ (CaF_2-type) as $\mathbf{a}_{\mathrm{AuGa2}}=\mathbf{a}_W\times2=\mathbf{a}'_{A2}\times4=\mathbf{a}_{A1}\times2$. The commensurability is very good, which accounts for the high melting temperature of the phase; the commensurability is that found in In, but because of the lower N_V/A of $AuGa_2$ the substructure is of the W family; this commensurability has $N_{P'}/C=8\times16$ so that a CsCl structure is impossible as $N_d/C=8\times20$. The valence-electron correlation of $AuGa_2$ is that proposed by Hume-Rothery for CuZn. Several of the electron places are occupied by atom cores and the number $N_V/C=8\times3+4$ conforms to Norbury's rule (Schubert, 1964). It has been shown that this correlation also applies to Ge and therefore to the whole diamond family which forms a part of the great family of anion packings (Schubert, 1953; Parthé, 1964). There is a rule that $N_{P'}/A$ increases when (in a homologous series) the average atomic weight decreases (Schubert, 1974). Therefore it cannot be expected that $CuGa_2$ also has the CaF_2 structure of $AuGa_2$. In fact it has the $FeSi_2.h$-type structure (El-Boragy & Schubert, 1972) and the binding $\mathbf{a}_{\mathrm{CuGa2}}=(2{\cdot}83,0,0;\ 0,2{\cdot}83,0;\ 0,0,5{\cdot}84)$ Å $=\mathbf{a}_W(1,0,0;\ 0,1,0;\ 0,0,2)=\mathbf{a}_{A1}(1,0,0;\ 0,1,0;\ 0,0,2)=\mathbf{a}'_{C11}(2,0,0;\ 0,2,0;\ 0,0,5)$. The $\mathbf{a}'_{A2}$ correlation is here compressed to a $C11$ correlation so that $N_{P'}/A=13{\cdot}3$ against $N_{P'}/A=10{\cdot}7$ in $AuGa_2$. The surprising value $|a_3|/|a_1|$ ($CuGa_2$) $=2{\cdot}06$ is explained by this binding.

If Al is substituted for Ga we have a decrease in the number of core-electrons in the cell, which leads to the $CuAl_2$ structure (SR 1, p. 491) having the cell and binding $\mathbf{a}_{\mathrm{CuAl2}}=(6{\cdot}06,0,0;\ 0,6{\cdot}06,0;\ 0,0,4{\cdot}89)$ Å $=\mathbf{a}_W\times2=\mathbf{a}_{A1}\times2=\mathbf{a}_{C11}\times4$; although the $A1$ correlation is strongly distorted, the $C11$ correlation of $CuGa_2$ is retained.

Conclusion

The two-correlations model permits an energetic explanation of the many structural phenomena which have been observed in brass-like alloys. Earlier models like that of Hume-Rothery (1926) for CuZn or that of Mott & Jones (1936) for the Hume-Rothery phases or that of Sato (1965) for the shear variants of Cu_3Au explain only a part of the material and have not been generalized until now to cover the neighbouring phenomena also. It seems that the present model is less narrow than the older ones and, therefore, of broader applicability. In fact it is concerned with the analysis of a kind of structure which lies beneath the crystal structure. The electronic structure is at present less exactly known than the set of atomic radii; however it is a natural and necessary extension of that set and it may be analysed by legitimate methods similar to those which have led to the less hidden atomic radii.

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The Monoclinic Crystal Structure of R_5Co_2 (R=Pr, Nd, Sm) with the Mn_5C_2 Structure Type

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Sm_5Co_2 crystallizes in the monoclinic Mn_5C_2 structure type, space group $C2/c$, $a=16{\cdot}282$ (8), $b=6{\cdot}392$ (5), $c=7{\cdot}061$ (5) Å, $\beta=96{\cdot}6$ (1)°, $Z=4$. Patterson method, counter technique, absorption correction, least-squares refinement. $R=0{\cdot}07$ for 664 independent reflexions. Pr_5Co_2 and Nd_5Co_2 are isostructural with Sm_5Co_2. This series is related to Sm_3Co with the Fe_3C structure type. All rare-earth atoms are at the corners of regular trigonal prisms centred by Co atoms. The trigonal prisms are arranged in zigzag chains as in FeB and Fe_3C, but in Sm_5Co_2 the chains are joined by the edges of the prisms to form pairs.

Introduction

The binary phase diagrams of Pr–Co and Nd–Co have been reported by Ray (1974). He showed the existence of phases at about 29% Co and labelled them $Pr_{\sim 7}$ $Co_{\sim 3}$ and $Nd_{\sim 7}$ $Co_{\sim 3}$. These phases are not isotypic with the hexagonal Th_7Fe_3 type which occurs with Ni alloys such as Pr_7Ni_3 and Nd_7Ni_3 (Kissel, Tsuchida & Wallace, 1966). Reported in the binary phase diagram of Sm–Co, Buschow & Van der Goot (1968), is the existence of a phase at 31% Co, which has been labelled Sm_9Co_4. A powder pattern was indexed in terms of an orthorhombic cell, but the structure was not identified. The present investigation was undertaken on a single crystal to determine the stoichiometry of these phases and to verify if some predictions about the atomic model could be postulated from the prism linkage coefficient calculation (Moreau, Paccard & Parthé, 1976).

Experimental

The alloys were made from commercially available elements of high purity: rare earth and Co 99·9%. The constituents were melted under an argon atmosphere. X-ray diffraction patterns of the powders in the as-cast conditions were taken on a Guinier–de Wolff focusing camera with Cu *Kα* radiation. Single crystals of Sm_5Co_2 were isolated by mechanical fragmentation from the crushed melt.

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