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# A Model for the Stacking Variation of Two-Atom-Replacement Structures Containing Mg

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A model which was formerly used for the interpretation of shift variants of the $Cu_3Au$ type and for the brass-like stacking variants of closest packings of equal spheres is extended to the interpretation of stacking variation in brass-like two-atom-replacement structures (*i.e.* in brass-like homotypes of $Cu_2Mg$ in which each Mg atom replaces two Cu atoms of a Cu-type structure). One assumption is that the spatial correlation of the valence electrons is of the $A1$ (or the $C11$) type. It builds up in the crystal an array of electric dipole vectors, the energy of which is minimized by the choice of the stacking sequence. The stacked unit is the so-called quadruple layer. The dipole vector of such a layer may be derived by comparing a mean layer of the quadruple layer with the mean layer of two corresponding electron layers.

## Introduction

One of the first valence rules for alloy phases affirms that in brass-like alloys the valence-electron-rich homogeneity limit of the Cu-type structure lies near the valence-electron concentration (*i.e.* number of valence electrons divided by the number of atoms), $N_V = 1{\cdot}4$. At the valence-electron concentration $N_V = 1{\cdot}5$ phases with the Mg structure (or also with the *W* structure) may occur (Hume-Rothery, 1926). These rules have been interpreted by the band model [*i.e.* by the energy gain which is available when the Fermi sphere touches a Brillouin plane system of high Fourier coefficient of the electrostatic potential (Mott & Jones, 1936)]. Later on, further close-packed structures were found in brass-like alloys which had (besides an ordering of the component atoms, which is not essential here) a stacking sequence of the close-packed-hexagonal atom layers which was neither of the Cu type, characterized by the (Jagodzinski) stacking symbol *ccc* nor of the Mg type characterized by *hh*, but of an intermediate type (Wegst & Schubert, 1958). A remarkable result was that these structures obeyed a valence-electron rule, in that the *h* density $D_h$ (*i.e.* the number of *h* symbols divided by the number of *h and c* symbols in the stacking symbol) depends on $N_V$ by the approximate empirical relation $D_h/2 = N_V - 1$ (Burkhardt & Schubert, 1965). Somewhat earlier a similar relation had been found to be valid for the so-called shift variants of the $Cu_3Au$ structure, where the shift density $D_S$ [*i.e.* the number of shift planes parallel to (001)$Cu_3Au$ per atom layer parallel to (001)$Cu_3Au$] depends on $N_V$ by the approximate empirical relation $D_S = N_V - 1$ (Schubert, Kiefer, Wilkens & Haufler, 1955). As the latter $D_S$ phenomenon could be explained by the spatial correlation model of the valence electrons (Schubert, 1964, 1973) it was satisfactory that an explanation of the $D_h$ relation was successful by the same model (Schubert, 1968). While an explanation of the $D_S$ phenomenon was proposed on the basis of the band model by Sato & Toth (1965) this is not yet the case for the $D_h$ phenomenon.

## Valence-electron rule for two-atom-replacement structures

A similar rule to the above-mentioned Hume-Rothery rule was observed for the structural family of $Cu_2Mg$, $MgZn_2$, $Ni_2Mg$ (two-atom-replacement structures, or so-called Friauf–Laves–Komura phase structures) by Laves & Witte (1936): they found the following $N_V$ ranges for the structure types: $Ni_2Mg$ $0{\cdot}7\cdots1{\cdot}0$, $Cu_2Mg$ $1{\cdot}0\cdots1{\cdot}8$, $Ni_2Mg$ $1{\cdot}8\cdots1{\cdot}9$, $MgZn_2$ $1{\cdot}9\cdots2{\cdot}2$. These ranges were essentially confirmed by Komura, Mitarai, Nakaue & Tsujimoto, 1972, who also found further stacking variants of the two-atom-replacement structures, and fixed their $N_V$ ranges; further publications of Komura and coworkers are cited by Komura *et al.* (1972). Because $Cu_2Mg$ may be deduced from a Cu structure by successively replacing two Cu atoms by one Mg atom (Schubert, 1964), the $N_V$ values of the two-atom-replacement structures may be reduced to $N_V$ values of close-packed structures by multiplying by the factor $\frac{3}{4}$ (Schubert, 1952), so that the reduced transition values of the above ranges become $0{\cdot}75$, $1{\cdot}35$ and $1{\cdot}42$. The last value of the reduced transition valence-electron concentrations compares favourably with Hume-Rothery's value $1{\cdot}45$ for the transition of the Cu type into the Mg type of structure; therefore it is of interest to try the explanation of the stacking variants of the two-atom-replacement structures by the model of the spatial correlation of the valence electrons (Schubert, 1964).

## Interpretation of stacking variations in the closest packings of equal spheres

Let us consider first the hexagonal basal plane of a closest-packed structure of essentially equal spheres (hexagonal lattice constants: $a, c$). Assume in that plane a hexagonal primitive net of a valence-electron correlation of the $A1$ type [*i.e.* of a correlation $D(x_1^i, x_2^i)$ (where $x_n^i$ is the spatial coordinate of the $n$th valence electron and $y^i$ a fixed vector) which gives $\int^S D(y^i + x_2^i, x_2^i) dx_2^1 dx_2^2 dx_2^3$ ($S$ = all space) a high similarity to an all-face-centred cubic lattice]; and assume that the closest distance in the $A1$ correlation $d_{A1}$ is equal to the lattice constant $a$ of the crystal structure. This is a congruence between structure and correlation and it may be anticipated that it is energetically so favourable, that it is essentially common to all structures of the family of brass-like closest packings of equal spheres. In the case of the valence-electron concentration $N_V = 1$ the $A1$ correlation has the best fit to the Cu-type structure as here all valence electrons may be together in a position of low potential energy. Deviations from the electron concentration 1 result in contractions or dilatations of the correlation in some direction, as could be concluded from the successful explanation of the shift variants of the $Cu_3Au$ structure (Schubert, 1964). If the difference $N_V - 1$ is sufficiently great the concentration may occur in the **c** direction. Such a misfit of the valence-electron correlation in a crystal structure leads to an array of average electric dipole vectors in the direction of the contraction of the correlation, which has been assumed to be the stacking normal of the atom layers. The dipole vector of an atom is found by inserting the electron lattice related to the correlation into the structure: the electron layer which is next to the considered atom determines the direction of a vector parallel to **c** (Schubert, 1968). The dipole vector must be understood as an average vector as it was derived by a lattice rather than by the correlation. The energy of such an array should be minimized by the choice of the stacking sequence. It should be noted that a dipole vector may exist in a metal, as the shielding radius is about 50 Å (Schubert, 1964, p. 100). If now in the course of stacking the sign of the dipole vector for an atom layer remains the same as in the preceding layer a $c$ stacking results; if the sign of the vector is changed an $h$ stacking results (Schubert, 1968). This empirical rule may be understood as an extension of the relation of the electron correlation to the crystal in the Cu structure, where all vectors must be the same because of the congruence of structure and correlation. The rule essentially compares the number per $c$ length of atom layers $l_c^A$ and of electron layers $l_c^E$. In Table 1 the sequence of structures is given (following Schubert, 1968) for different values of $l_c^E/l_c^A$ which (under the assumption of congruence in the basal plane) is equal to $N_V$. All possible structures have not been observed as yet, but the sequence of 4, 6, 3, 6, 4, 10, 9, 8, 21, 2 as really observed in close-packed structures is well reproduced; also the observed maximal correlation between $c$ and $h$ symbols in the stacking sequence (most uniform distribution) is correctly borne out by the model.

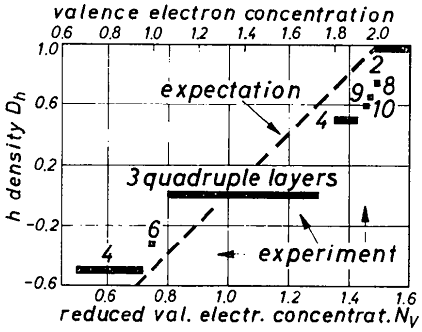

Fig. 1. Stacking of quadruple layers in two-atom-replacement structures.

Table 1. *Expected stacking sequence in close-packed and in two-atom-replacement structures*

| $l_c^E/l_c^A = N_V$ | Stacking sequence | |
|---|---|---|
| $\frac{3}{4} = 0{\cdot}75$ | *chch* | (4 layers) |
| $\frac{5}{6} = 0{\cdot}83$ | *chcchc* | (6 layers) |
| $\frac{1}{1} = 1{\cdot}00$ | *c* | (3 layers) |
| $\frac{11}{10} = 1{\cdot}10$ | *cccchcccch* | |
| $\frac{10}{9} = 1{\cdot}11$ | *cccchccch* | |
| $\frac{9}{8} = 1{\cdot}13$ | *ccchccch* | |
| $\frac{8}{7} = 1{\cdot}14$ | *ccchcch* | |
| $\frac{7}{6} = 1{\cdot}16$ | *cchcch* | (6 layers) |
| $\frac{6}{5} = 1{\cdot}20$ | *cchch* | |
| $\frac{11}{9} = 1{\cdot}22$ | *cchchchch* | |
| $\frac{5}{4} = 1{\cdot}25$ | *chch* | (4 layers) |
| $\frac{14}{11} = 1{\cdot}27$ | *chchchchchh* | |
| $\frac{9}{7} = 1{\cdot}28$ | *chchchh* | |
| $\frac{13}{10} = 1{\cdot}30$ | *chchhchchh* | (10 layers) |
| $\frac{4}{3} = 1{\cdot}33$ | *chh* | (9 layers) |
| $\frac{11}{8} = 1{\cdot}38$ | *chhhchhh* | (8 layers) |
| $\frac{7}{5} = 1{\cdot}40$ | *chhhh* | |
| $\frac{10}{7} = 1{\cdot}43$ | *chhhhhh* | (21 layers) |
| $\frac{3}{2} = 1{\cdot}50$ | *hh* | (2 layers) |
| $\frac{8}{5} = 1{\cdot}60$ | *chhhh* | |
| $\frac{5}{3} = 1{\cdot}67$ | *chh* | |
| $\frac{7}{4} = 1{\cdot}75$ | *chch* | |
| $\frac{9}{5} = 1{\cdot}80$ | *chchc* | |
| $\frac{11}{6} = 1{\cdot}83$ | *chcchc* | |
| $\frac{2}{1} = 2{\cdot}00$ | *c* | |

## Interpretation of stacking variations in two-atom-replacement structures containing Mg

In the two-atom-replacement structures two layers of a close-packed structure combine to form a tightly bound double layer (which is often named a quadruple layer, as one of the layers splits to three near-neighbour layers – compare, *e.g.*, Schubert (1964), p. 161, Fig. 2). Within one quadruple layer a change of stacking sequence is not possible because of the tight binding or geometric hindrance; but between two quadruple layers the choice of sequence is free. As the quadruple layer is now the stacked unit, and as the sequence of layer numbers per elementary cell as a function of $N_V$ remains the same as in simple close packings (according to experimental findings), there must exist a mechanism which causes only each second electron layer to be effective for the stacking sequence – such a mechanism could be the transition of the $A1$ correlation to a $C11$ correlation which has its hexagonal plane congruent to the hexagonal plane of the majority component in the two-atom-replacement structure. The $C11$ correlation is a tetragonally compressed $A2$ correlation (having some similarity to the structure of $MoSi_2$); it gives therefore a good possibility that parallel spins avoid each other (Schubert, 1964, pp. 59, 123), which will be necessitated by the Mg atoms contributing two valence electrons occupying the same orbital. The $C11$ correlation has, as is well known, a plane of perfect hexagonal measure and the distance of neighbouring lattice points of different planes relatively to the distance in the planes is equal to that in the $A1$ correlation if the distortion is neglected; however, the stacking sequence normal to the hexagonal plane of the $C11$ correlation is not *ABC* as in the $A1$ correlation but *AB*. This stacking sequence of the correlation may cause only each second electron layer to be effective for the stacking sequence of the structure. This essential proposal may be explained by the circumstance that only one of the two partial correlations of $C11$ is able to give strong dipole vectors in the direction of the stacking normal. Another argument for the mechanism mentioned may be found in the fact that a double layer which cannot change its inner stacking bears a resultant dipole moment which must be derived by comparing the layer of gravity of the quadruple layers with the layer of gravity of two electron layers. [The fact that the point symmetry of $C11$ does not contain a hexad axis is without influence on the crystal structure, because of a presumable twinning of the correlation (Schubert, 1964, p. 69); an $A1$ correlation does not need this assumption.] Similarly to the shift variants of $Cu_3Au$ where the shift density $D_S$ can have negative values, one has to count the density $D_h$ negative when the reduced valence electron concentration becomes smaller than 1. In Fig. 1 the experimental findings are compared with the expectation from the above model. A remarkable feature is that simple stacking variants, such as *ccc*, *chch* or *hh*, have a broader stability range than the complicated variants. This *plateau formation* was also observed in shift variants of the $Cu_3Au$ structure (Schubert, 1964), which is an indication of the fact that simple structures have simple dipole fields and therefore lower energy. It could be asked why the $C11$ correlation is not of influence in simple close packing. In principle the $C11$ correlation could also be real in a simple close packing, but in the two-atom-replacement structures the quadruple layers may be considered as double layers, the partial layers of which are essentially different and thus fix the correlation (which may be considered as a fluctuating electron lattice) in some sense so that one partial correlation gets a greater weight. On the other hand, the $A1$ correlation might be used for explaining the effects in two-atom-replacement structures. The above interpretation of the stacking sequence in some two-atom-replacement structures is closely connected with the fundamental phenomenon of spatial correlation of electrons in a crystal. As the band model of the electron gas neglects the spatial correlation to a considerable extent, it seems questionable whether a reasonable explanation by means of hat model may be given, although a superficial parallelism of both models has been observed (Schubert, 1964). This superficial parallelism seems to be the cause for the possibility that some findings in the $D_S$ phenomenon could loosely be accounted for by a band-model explanation.

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