

Crystal Structures of Beta Brass Like Alloy Phases

By Konrad Schubert*

A survey is given on the structural family of beta brass related structural types. The members of this family are given by a vacancy forming process, by different possibilities of strains and by shifts. The multitude of structural types may be rationalized by a model which considers two spatial correlations of electrons, one for the valence electrons and the other for the outer core electrons.

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I. The Beta Brass Phase

In a brass like alloy generally all components have a filled d -electron core, so that the core electron correlation may be considered as constant when the atomic concentration changes. For valence electron concentrations $V = 1.0, \dots, 1.4$, close packed structures which display shift variants, stacking variants and mixed structures are observed in such a multitude that a fairly well-established model for the valence electron correlation may be inferred. It is therefore probable that in the family of beta brass phases which are akin to the W structure or CsCl structure similar interpretations are possible. The beta phases are stable at the valence electron concentration 1.5, a fact which led Hume-Rothery⁽¹⁾ to the assumption of a valence electron correlation $a = a_{A1}$ (a = lattice constant of the crystal, a_{A1} = lattice constant of the A1 correlation of the valence electrons) in which one electron place per cell is occupied by one atom (Fig. 1). This is in fact the oldest specified proposal for a valence electron correlation, but it became soon forgotten, so that it was independently rediscovered by later authors.

II. Vacancy Formation in Beta Brass Phases

A formation of statistically distributed vacancies was at first observed in the phase NiAl, which shows at underideal Al-contents a substitution of Ni-atoms

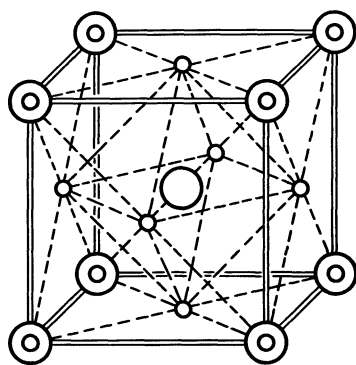


Fig. 1 Hume-Rothery's proposal for the valence electron spatial correlation in CuZn.

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(1) W. Hume-Rothery: J. Inst. Met., **35** (1926), 295.

for Al-atoms, while at overideal Al-contents Ni-places are left vacant⁽²⁾. An interpretation of this effect can be given by means of the band model of electron theory⁽³⁾ or by means of the electron spatial correlation model⁽⁴⁾ assuming that for each missing atom a new electron place is available (Norbury rule). The interpretation by means of the spatial correlation fits in the case of $\text{Cu}_4\text{Sn}(h)$ and other cases better than by the band model (Fig. 2). In NiAl the number of the vacancies fits surprisingly to the expectation of the band model. However this cannot be considered as confirmation of the validity of the band model influence. To fulfill the Norbury rule, one Al on a Ni place should attract 3 vacancies at the same time, a quite seldom event. Nevertheless these vacancies may be called "Norbury vacancies", as they are intimately connected with spatial correlation effects, and Norbury was the first who gave an acceptable interpretation.

There are phases which are more stable with Norbury vacancies than without: $\text{Cu}_4\text{Sn}(h)$ should be stable without vacancies at Cu_5Sn but it is stable (at sufficiently high temperatures) even at Cu_3Sn ; $\text{Cu}_3\text{Sb}(h)$ should be stable at Cu_7Sb , but its maximum stability temperature is at $\text{Cu}_{72}\text{Sb}_{28}$. The phenomenon is easy to be understood considering the fact that the equidistribution of the valence electrons required by a lattice like valence electron correlation implies a high ionization of the second component; the energy necessary for this may be reduced choosing a state of higher electron concentration. The fact that many beta phases

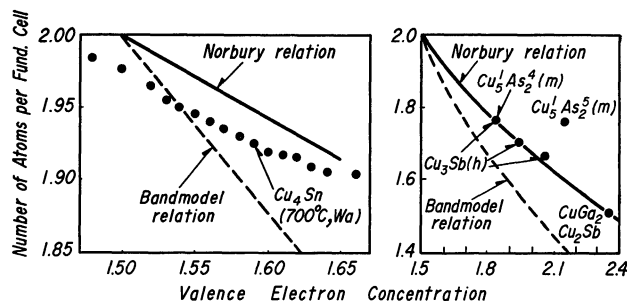


Fig. 2 Vacancies in dependence of valence electron correlation follow Norbury's rule; in the phase Cu_5As_3 the valence electrons should be counted $\text{Cu}_5^1\text{As}_2^4$.

(2) A. J. Bradley and A. Taylor: Proc. Roy. Soc. Lond., **A159** (1937), 56.

(3) S. Konobejewski: J. Inst. Met., **63** (1938), 161.

(4) A. L. Norbury: J. Inst. Met., **65** (1939), 355.

exist only as high temperature phases, has been explained⁽⁵⁾ by a low shear rigidity leading to low phonon frequency and energy or high phonon number and high entropy increasing the relative stability at high temperatures.

III. Structures Obeying the Norbury Rule

There are several phases whose structures obey the Norbury rule: e.g. AuAl_2 has a fluorite structure, each Al is on the corner of a CsCl-cube and each second cube only is filled with an Au atom; we count therefore $2 \times 3 = 6$ Hume-Rothery electrons and 1 Norbury electron per formula unit in agreement with the valence electron number offered by the compound. An extreme case is the diamond with 8 atoms per cell and 8 Norbury vacancies; as each C atom corresponds to one CsCl-cell and each cell has one vacancy we have $3 + 1 = 4$ electron places per atom in agreement with the well-known Grimm-Sommerfeld rule; the valence electron correlation of the diamond structure may therefore be described by $a/2 = a_{A1}$. Another famous structure obeying the Norbury rule is the gamma brass structure, e.g. Cu_5Zn_8 . In the cubic cell there are 4 Cu_5Zn_8 —or $84 \approx 83$ valence electrons and $3 \times 27 = 81$ Hume-Rothery places and 2 Norbury places. The gamma phases were in fact the empirical basis for Norbury which lead him to his rule. Another well-known phase obeying the rule is CuAl_2 ; the strong tetragonal compression of this structure as compared with CsCl will be explained later on. CuGa_2 is another type obeying the rule; it is strained in the opposite sense as CuAl_2 which also will be understood later. There is no lack of further⁽⁶⁾ structural types obeying the rule, but there are also phases which do not obey it, e.g. PtSn_2 crystallizing in the fluorite type or PdSn_3 crystallizing in a type related to the CuAl_2 type. This observation corresponds to the knowledge in shift variants of Cu_3Au , where only at lower valence electron concentrations electron places were occupied by atom cores. Similar to the come back event VNi_3 , . . . TiAl_3 there exists a beta related structure in NiHg_4 , a cubic structure with 8 Hg in a primitive cubic partial lattice and 2 Ni in two of the interstices. The spatial correlation is here⁽⁶⁾ $a/2 = a_{A2}$.

IV. Extension of the Valence Electron Correlation Found in Norbury Phases

There are phases closely related to Norbury phases which permit an extension of the correlations found until now. Extending the spatial correlation proposal for the diamond structure of grey tin to indium we get $a/\sqrt{2} = a_{A1} l_c = 3$, where the quasi cubic cell with the content of 4 In is considered. A quite surprising phenomenon is that the valence electron correlation remains almost unstrained while the crystal lattice is

heavily strained. This makes a marked contrast to the shift variants of the Cu_3Au type, where the crystal lattice is approximately unstrained while the valence electron correlation is strongly strained. From this it must be concluded that there is a core electron correlation present, which favours the crystal strain in the case of indium. This assumption permits to infer the kind of electrons taking part in that core electron correlation and at the same time the type of the correlation: 10 electrons of the outer d shell of each In atom take part in a correlation of $a/\sqrt{8} = a'_{A2} l'_c = 6$; this correlation gives 48 places while only 40 electrons are to be correlated, and consequently the electron lattice is only partly occupied contrary to the valence electron correlation which is generally completely occupied. It is quite satisfactory that the core electron correlation is an A2 correlation, as this type gives a good expression to the correlation holes connected with the spins of the electrons. However this A2 correlation is fairly easily deformed: If about 15 at % Sn is alloyed into the In phase, a tetragonally compressed Cu type structure becomes stable with the lattice constants $a = 4.88 \text{ \AA}$ $c = 4.40 \text{ \AA}$. The simplest assumption is that the core electron correlation has been homogeneously deformed together with the crystal lattice. Such a deformed A2 correlation may be called a C11 correlation, after the structure of MoSi_2 . The characteristic of this MoSi_2 structure is that the plane $(011)_{A2}$ has been hexagonalized. As this is energetically favourable with respect to the electrostatic repulsion, we have to assume that the C11 correlation is another possibility for the core electron correlation⁽⁷⁾.

V. Tetragonal Variants of Beta Brass Phases

A prominent representative of this class is CuAl_2 which obeys the Norbury rule but is strongly compressed along the c axis—Fig. 3. This must be traced back to the core electron correlation. We describe the spatial correlation by $a/2 = a_{A1} l_c = 4$ for the valence electrons and $a/4 = a'_{C11} l'_c = 8$ for the core electron correlation. The number of core electron places is 128 while $40 + 64 = 4 \times 26 = 104$ core electrons are offered. The C11 correlation gives the atom-electron coordination number 10 if an atom core lies on a correlation place; this number is well adapted to the 10 d electrons per Cu atom. Several stacking variants of this structure are known⁽⁶⁾ such as CoGe_2 , PdSn_2 , PdSn_3 , and PdSn_4 . Proceeding to the chemically homologous phase CuGa_2 , we find another structure which also obeys the Norbury rule: two CsCl cells are stacked in the c direction so that Cu is at the corners of the cell and 2 Ga fill the cell while one place is left vacant⁽⁸⁾ (Fig. 3). As a layer of the kind (001) consists of vacancies one would expect that $c < 2a$; surprisingly enough it is found $a = 2.83 \text{ \AA}$ $c = 5.83 \text{ \AA}$ so

(5) C. Zener: Phys. Rev., **15** (1947), 846.

(6) K. Schubert: *Kristallstrukturen Zweikomponentiger Phasen*, Springer, Berlin, (1964).

(7) K. Schubert: Helv. Phys. Acta, **41** (1968), 1155.

(8) M. El-Boragy and K. Schubert: Z. Metallk., **63** (1972), 52.

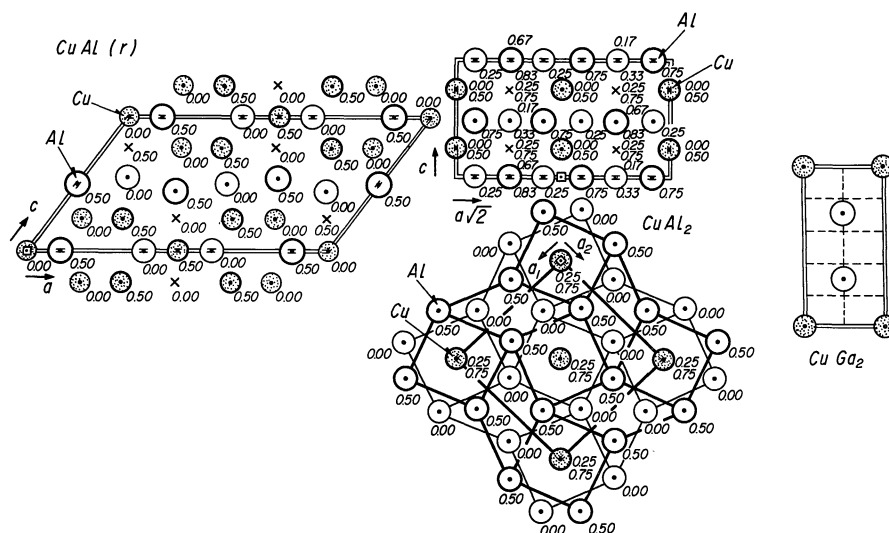


Fig. 3 Crystal structure of CuAl, CuAl₂ and CuGa₂.

CuAl: $C_{2h}^3 C2/m$ $a = 12.066\text{\AA}$ $b = 4.105\text{\AA}$ $c = 6.913\text{\AA}$ $\beta = 55.04^\circ$

$2\text{Cu}(a), 0,0,0$ $4\text{Cu}(i), 257,0,760$ $4\text{Cu}(i), 109,0,227$ $2\text{Al}(d), 0,5,5$ $4\text{Al}(i), 153,0,548$ $4\text{Al}(i), 385,0,001$

that $c > 2a$. This must be caused by the core electron correlation. On the analogy with the CuAl₂ structure, we can assume $a = a_{A1}$ $l_c = 4 a/2 = a'_{C11}$ $l'_c = 10$; this may be easily interpreted by remarking that the number of core electrons is 30 (instead of 26 in CuAl₂). This higher electron number can no more be accommodated in the correlation for the CuAl₂ type, therefore the mechanism found in the shift variants is applied: further electron planes parallel to the tetragonal basis are inserted so that instead of $l'_c = 8$ the value $l'_c = 10$ is reached. This makes the Cu places energetically different, so that the vacancies gather in a plane parallel to the tetragonal basal plane, which is more favourable to them.

VI. An Orthorhombic Norbury-Phase

In the mixture Cu–Ge there exists a high temperature phase Cu₅Ge₂(*h*) which has a Fe₃Si type structure⁽⁹⁾ with vacancies and cell content Cu₁₀Ge₄. The 26 valence electrons per cell satisfy exactly the Norbury rule. Curiously enough there exists⁽⁹⁾ the isotype Cu₅As₂(*h*). Obviously for As there are to be assumed only 4 electrons per atom, the fifth filling the A1 correlation of the valence electrons in B1 manner. With a medium fast quench a metastable phase Cu₅As₂(*m*) appears (Fig. 4) which displays an orthorhombic ordering of the vacancies⁽¹⁰⁾. The valence electron correlation becomes $a/2 \approx b/4 = a_{A1}$ $l_c = 4$ and the core electron correlation $a/4 \approx b/8 = a'_{C11}$ $l'_c = 9$. The causes of the stabilisation of the structure may be thus rationalized. An A2 crystal structure should be expected at the composition “Cu₅Ge” or “Cu₇As”; actually there are stable disordered Mg type structures, as an A2 array would necessitate much ionization energy of the second component; the composition of

the phase is therefore shifted to 29 at %Ge, as at this composition there are 4 Ge(or As) atoms in the elementary cell of the Fe₃Si type, giving an A1 sublattice which is energetically favorable. As there are too many valence electrons the Norbury mechanism applies. For the outer core electrons an intermediary case between CuAl₂ and CuGa₂ is stabilized. Therefore the vacancies follow the chain array of CuAl₂, however the $l'_c = 9$ commensurability should cause a shifting of the chains which was not observed; the reason for this is at present not yet clear. As the surplus As-electrons will prefer the vacancy chains they are loaded and the minimization of this field doubles the *b* axis. In the prototype of this phase, Mg₅Ga₂, the valence electron correlation is the same, only the Norbury rule is not fulfilled, as the Mg atom is big and has a quite small core. In the same sense point the CsCl structure of MgHg and the CaF₂ structure of Mg₂Si which do not obey the Norbury rule.

VII. A Monoclinic Norbury Phase

With the Norbury phase CuAl₂ a phase CuAl is in equilibrium which is a monoclinic vacancy variant⁽¹¹⁾ of the CsCl structure (Fig. 3). A CsCl type of structure is impossible because of the valence electron concentration 2. As the composition is 1:1 we have to expect vacancies in the Cu partial lattice and in the Al partial lattice. As the Al vacancies are filled with Cu atoms all vacancies are in the Cu partial lattice. In the monoclinic cell are 10Cu, 10Al and 4 vacancies, so that $12 \times 3 + 4 = 40$ electron correlation places in it correspond exactly with a supply of 40 valence electrons. The plane (001)_{CuAl} corresponds to (001)_{CuAl₂} and the lattice constants compare as follows $\sqrt{2}b_{\text{CuAl}} = 5.8 \text{\AA}$ $c \times \sin \beta_{\text{CuAl}} = 5.6 \text{\AA}$ $a_{\text{CuAl}_2} = 6.1 \text{\AA}$ $c_{\text{CuAl}_2} = 4.9 \text{\AA}$. Consequently the valence electron

(9) J. Lenz and K. Schubert: Z. Metallk., 62 (1971), 810.

(10) W. Liebisch and K. Schubert: J. Less-Common Metals, 23 (1971), 231.

(11) M. El-Boragy, R. Szepan and K. Schubert: J. Less-Common Metals, 29 (1972), 133.

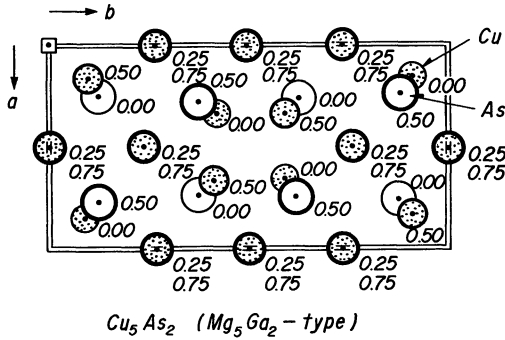


Fig. 4 Crystal structure of $Cu_5As_2(m)$.
 D_{2h}^{2f} Ibam $a = 5.97_{7\pm 1}\text{\AA}$ $b = 11.57_{7\pm 2}\text{\AA}$ $c = 5.49_{1\pm 1}\text{\AA}$
 $8Cu(j), 335, 409, 0$ $8Cu(g), 0, 264, 25$ $4Cu(b), 5, 0, 25$
 $8As(j), 238, 118, 0$

correlation is $a/6 \approx b/2 = a_{A1}/\sqrt{2}$ $l_c = 3.9 \approx 4$ giving 48 places from which 8 are occupied by atoms; the core electron correlation is $a/6 \approx b/2 = d'_{C11}/\sqrt{2}$ $l'_c = 2 \times 4.8 = 9.6 \approx 10$. The higher Cu content and the smaller fraction of vacancies raises the number of core electrons, so that l'_c must increase. If each second electron layer is counted the method⁽⁶⁾ of deriving the dipole moment array gives two shifts per c axis in the vacancy chain, as it is in fact observed; the crystal structure becomes monoclinic by the shifts.

VIII. Hexagonal Variants of Beta Brass

Similarly, as in close packed structures, there has been observed a variety of hexagonal structures related to the CsCl structure. One of the best known is the NiAs structure. There are alloy systems in which beta brass and NiAs type phases occur at different concentrations for instance Cu-In and Cu-Sn. Such occasions may be utilized to find the electron correlations, as the electron distances are generally smooth functions of the atomic concentration. For the NiAs representative $Pd_{3.3}Sb_2(h)$ the valence electron concentration 2 is so high, that the valence electron correlation is completely occupied: $a/\sqrt{3} = d_{A1}$ $l_c = 2.8$ and this correlation must be partly filled in a B1 manner by the fifth Sb-electron. The core electron correlation may be assumed as $a/\sqrt{12} = d'_{C11}$ $l'_c = 5.2 \approx 5$. It has been found in close packed structures that the commensurability $l'_c = 5$ favours the *chch* stacking of the $TiNi_3$ type. The filled NiAs type may be considered as *chch* stacking if as characteristic of the stacking sequence the majority component is chosen. Therefore in the case of the NiAs structure the core electron correlation must be considered as a structure determining influence. In fact most of the representatives of the NiAs type are brass like phases

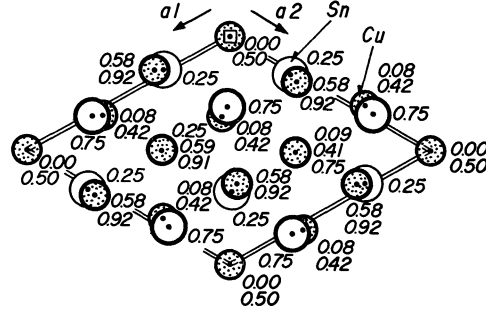


Fig. 5 Crystal structure of $Cu_{10}Sn_3(m)$.
 $Cu_{10}Sn_3(m)$ $C_{2h}^{2h}P6_3/m$ $a = 7.33\text{\AA}$ $c = 7.87\text{\AA}$
 $2Cu(b), 0, 0, 0$ $2Cu(d), 667, 333, 25$ $4Cu(f), 333, 667, 093$
 $12Cu(i), 666, 031, 080$ $6Sn(h), 305, 987, 5$

i.e. both components have an outer *d* core.

If the NiAs type is caused by the core electron correlation on the analogy of the closest packed structures other structure types should exist, which show a more complicated stacking sequence. Such types have in fact been found. The phase $Cu_3Ge(h)$ crystallizes in a filled Na_3As type⁽⁹⁾, which is a 6-layer type characterized by the stacking sequence *hcchcc*. Very similarly crystallize the phases $Cu_7Sn_2(h)$ and $Cu_3As(h)$. The core electron correlation may be assumed as $a/\sqrt{12} = d'_{C11}$ $l'_c \approx 7$, and this in fact causes the above-mentioned stacking sequence. The low temperature modifications of Cu_3As and $Cu_{10}Sn_3(m)$ (Fig. 5) are closely related to the Na_3As type, they are enlarged by a factor of $\sqrt{3}$ as compared with Na_3As . A 10 layer type has also been found in the phases $Ni_{31}Si_{12}$ ⁽¹²⁾ and Pd_5Sb_2 ⁽¹³⁾, and more complicated types have partly been analysed⁽¹²⁾ or expect their investigation.

IX. Conclusion

The family of beta brass like structures is astonishingly multimorph. The model of two electron correlation has helped to make it more transparent. This model is obviously more flexible than the bandmodel. When the task is successfully finished to give probable spatial correlations to all crystal structures the problem may be attacked to understand why certain structures do not become stable in certain alloys. Here a treatment of the correlations as quasi elastic systems will become helpful. Proceeding this way will hopefully lead to an atomic analysis of the thermodynamic functions of alloys.

(12) K. Frank and K. Schubert: Acta Cryst., B27 (1971), 916.
 (13) M. El-Boragy, S. Bhan and K. Schubert: J. Less-Common Metals, 22 (1970), 445.