JOURNAL OF SOLID STATE CHEMISTRY 53, 246–252 (1984)

On the Shear Homeotypism in the $MgCu_2$ Family

K. SCHUBERT

Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaften, Seestr. 75, D-7000 Stuttgart 1, Federal Republic of Germany

Received October 21, 1983; in revised form January 3, 1984

It is well known that there are several homeotypes of $MgCu_2$ which are distinguished by different shears between double layers of atoms parallel to (111) $MgCu_2$ (Friauf–Laves phases) and that they are stable at specific valence electron concentrations (rule of Komura). This phenomenon may be interpreted by the two-correlations model, a valence model for metallic phases. The correlation of the peripheral core electrons (c correlation) and its commensurability to the crystal cell a is the same for all quasi-homologous shear homeotypes of $MgCu_2$, but the correlation of the valence electrons (b correlation) depends on the valence-electron concentration. The b correlation exhibits different discrete commensurabilities with respect to the c correlation in the hexagonal basal plane of a. Also, the distances of the b correlation planes parallel to the hexagonal basal plane exhibit energetically favorable commensurabilities to a. These different commensurabilities correspond to observed phases. The b electron correlation induces transitory electrical dipole vectors at the atoms with component in a_3 direction (the hexagonal axis) and the interactions of the dipoles determine the stacking sequence of the double layers.

Introduction

The homeotypic phases $MgCu_2$(F2.4, SR1.490, 531, (*1*)), $MgZn_2$(H4.8, SR1.180, 228, (*2*)), and $MgNi_2$(H8.16, SR3.31, 316, (*3*)) (Friauf-Laves phases) involve close packings of components with different atomic radius (SR1.490 = Structure Reports, Vol. 1, p. 490; F2.4 = cubic face-centered structure with 2 *A* atoms and 4 *B* atoms in the primitive cell, see Ref. (*4*); *A* and *B* atoms are defined in Ref. (*5*)). In these structures close-packed hexagonal planes with 4 atom places per mesh alternate with close-packed hexagonal planes with 3 places per mesh. In the 3-site mesh there exist two larger atoms and one smaller one, in the 4-site mesh there exist three smaller atoms and one vacancy. The vacancy determines by its position whether the layer couple is named A, B, or C (not to be confused with atom kinds *A*, *B*). A layer couple B is therefore nothing other than a shifted layer couple A. The vacancy provides space for a greater atom (of a neighboring 3-site layer) which is stacked on the vacancy by the support number (see (*4*)) one i.e., the larger atom at the shortest distance touches only the vacancy in the lower layer. The three-site layer is therefore not quite planar but studded; it splits into three partial layers, so that the coalescence of a 4-site layer with a 3-site layer may also be considered as a quadruple layer (*6*). If the quadruple layer is so defined that the Mg atoms of a studded 3-site layer belong to different quadruple layers, then, for example, A may be followed only by B or B′ (*6*).

0022-4596/84 $3.00

However, if a quadruple layer contains a full 4-site layer and a full 3-site layer, then A may be followed either by B or by C, as is usual for shear homeotypes of Cu. The exact structure of the 3-site layer of a layer couple depends on its successive 4-site layer. If a 4,3-layer A is followed by a 4,3-layer B, then the first 4,3-layer is of type A; but if A is followed by C then it is of type A′. For the other types this relationship applies with cyclic changes. This rule permits one to recover the primed symbol (*6*) from the unprimed symbol; here the unprimed symbols are used. The different stacking of the coalescent layers has been described frequently (see, e.g., Ref. (*7*)) and several additional stacking homeotypes have been found (*6, 8, 9, 17, 18, 19*) including 2, 3, 4, 6, 8, 9, 10, 14, 16, 21 layer types. Furthermore it has been discovered that the structure family of 4,3-coalescence structures is not only restricted to shear homeotypes of $MgCu_2$ but includes various replacement homeotypes (*4, 10, 11*) as, for instance, $CaCu_5$(H1.5).

While the geometry of the 4,3-coalescence is well understood (*3, 7*), a challenging problem lies in the explanation in terms of energies of the different stacking sequences of the Friauf–Laves phases, especially after it was discovered (*12, 13, 15*) that the number of valence electrons per atom $N_b^{/A}$ (valence electron concentration) affects the stacking. The valence electron gas has a spatial correlation leading to an averaged correlation (*14*) which may be assumed to be lattice-like, with an elementary cell b (3 by 3 matrix); therefore, the valence electrons will be simply named "b electrons." The $N_b^{/A}$-ranges for the structure types are (*12*).

$MgNi_2$0.7 . . . 1.0, $MgCu_2$1.0 . . . 1.8, $MgNi_2$1.8 . . . 1.9, $MgZn_2$1.9 . . . 2.2. These ranges essentially have been confirmed and further ranges for more complicated homeotypes (*15*) (designated as L^4, L^6, L^3, etc.) were found: L^4, 0.7 . . . 1.0; L^6, 1.0 . . . 1.1; L^3, 1.1 . . . 1.7; L^4, 1.8 . . . 1.9; L^{10}, 1.93; L^9, 1.95; L^8, 1.98; L^2, 2.0. For the stacking sequence of the double layers in the different homeotypes the c,h symbol may be designated "cubic" or "hexagonal" stacking of the A, B, C symbols; then the observed sequences obey the condition of most uniform distribution of c and h (*16*). When for the stacking symbol the h-share $N_h^{/a}$ is defined as $N_h^{/a} = N_h/N_a$ (N_h = number of h stackings, N_a = number of layers in the cell) (see (*4*), p. 120) then it appears that $N_h^{/a}(N_b^{/A})$ decreases for increasing $N_b^{/A}$ from $N_b^{/A} = 0.7$ to 1 and increases from $N_b^{/A} = 1.0$ to 2.0 (*15*). This is reminiscent of the shear density in shear homeotypes of Cu_3Au ((*4*), p. 94) where the dependence of shear density D_s on b electron concentration was simplified when the D_s values for $N_b^{/A} < 1$ were taken to be negative. The same result is encountered here. When the $N_h^{/a}$ for $N_b^{/A} < 1.3$ are taken to be negative then there is a general increase of $N_h^{/a}$ for increasing $N_b^{/A}$. This has led to a rule for the influence of a valence electron correlation on the stacking (*16*). The present analysis intends to show that reasonable assumptions for the bonding type (*14*) yield the observed stacking.

Analysis

Because of the vacancy in the 4-site layer into which one of the larger atoms of a neighboring 3-site layer partially enters, a 4,3-layer couple must be considered as the stacking unit. As has been mentioned, the stacking units are not generally all translationally equivalent. This is only the case for $MgCu_2$ (stacking ABC); in $MgZn_2$(AB), the neighboring 3-site layers are only equivalent by an additional 2-rotation around a_3. Therefore, A etc., have to be distinguished from A′ (*6*). However, if the studding of the 3-place layers and the difference of atoms in them is disregarded, then the layer couples may be considered as translationally equivalent and the stacking sequence may be specified by the unprimed A, B, C symbols. As has been noted the priming is found by specific rules from the unprimed symbol. Occasionally the above mentioned *c*, *h* symbol indicating whether a layer symbol is not equal or equal to the second previous symbol are useful, since they express a quasi-local property of a sequence, just as the second derivative of a curve is a local property of it.

In order to find an energetic explanation for the shear homeotypes of $MgCu_2$ it is appropriate to start from the bonding type (*binding*) of the phase $MgCu_2$ having the broadest stability range in the coordinate of valence electron concentration. The bonding type specifies the type of *b* electron correlation and its commensurability to the crystal cell *a*, and the type of correlation of the peripheral core electrons with cell *c* (do not confuse with stacking symbol *c*) and its commensurability to *a*, and it always indicates a low energy because of lattice-like property and integer-numbered commensurability (*14*). Using abbreviated symbols for matrices (*14*) the binding is found for $MgCu_2$ by the method (*14*): $a = 7.03$ Å $= b_F(2) = c_F(4)$. These equations show that *b* is of the F type, and *b* is to be multiplied by the matrix (2) to be equal to *a*, and analogously for *c*. It may be summarized as *FF2 binding* which states that *b* is of the F type (cubic face-centered) and *c* is of the F type and the first eigenvalue of the commensurability $c^{-1}b$ is 2. The very simple binding is compatible with the two-atom-replacement homeotypism of $MgCu_2$ to Cu ((*4*), p. 158). Each Mg replaces two Cu atoms in a F1 structure of Cu because of its great volume, but the number of *b* electrons per cell, $N_b^{/a}$, is conserved because of the two-valency of Mg, and together with $N_b^{/a}$ the b_F correlation is conserved. On the other hand, the number of *c* electrons per cell in Cu(F1) is strongly decreased by the two-atom-replacement process; therefore, the c_B correlation of Cu (*14*) may transform into a c_F type correlation. The distance d_c in the *c* correlation is strongly increased, but Fig. 1 of (*14a*) shows that the electron density scarcely reflects this increase. The strong increase might point to a participation of Cu 3*sp* electrons in the binding; however, this is not the problem of the present study. The FF2 binding of $MgCu_2$ belongs to the *b* electron concentration $N_b^{/A} = 1.33$, as 32 *b* places come on 24 atoms, but as stated above the experimental range of homogeneity allows even $N_b^{/A} = 1.7$. It must therefore be assumed that the *b* correlation suffers a tetragonal compression, just as in Cu_3Au Zn_m ((*4*), p. 99) (m = small mole number) and is twinned, so that no information on the compression is given by the crystal structure.

The hexagonal aspect of $MgCu_2$ yields the ABC stacking sequence of the double layers. The b_F correlation may be assumed as congruent to the Cu sites of $MgCu_2$. Therefore, each layer couple in $MgCu_2$ has the same transitory resultant dipole vector and also the same dipole component in a_3 direction.

From this observation it may be inferred that a change in sign of the dipole component in a_3 direction causes a *h* stacking instead of a *c* stacking (*16*). This method for assessing the stacking sequence is similar to the method which explained the shear density in shear homeotypes of Cu_3Au ((*4*), p. 99).

In equilibrium with $MgCu_2$ is Mg $Cu_{0.5}Zn_{1.5}$($MgNi_2$-type, H8.16, SR16.83 (*13*)) a = H5.124;16.82 Å and it contains $N_b^{/a} = 44$ *b* electrons per cell. (Note that in an abbreviated hexagonal matrix the symbol *H* has to be added (*14*).) A possible binding by the criteria (*14*) is $a = b_{UH}(\sqrt{(16/3)};\ 8.7/2) = c_{FH}(4;\ 16/3)$, where UH is the hexagonal aspect of U, a tetragonally deformed cubic body-centered type, and FH the H aspect of F (*14*). The *c* correlation is analogous to that in $MgCu_2$ and cannot therefore be the cause for the stacking homeotypism $MgCu_2$–$MgCu_{0.5}Zn_{1.5}$; the cause must rather lie in the *b* electron correlation. The *b* correlation utilizes the favorable $\sqrt{3}$ commensurability (*14*) in the basal plane to the *c* correlation and succeeds in reproducing the observed *b* electron number per cell. The commensurability element 8.7/2 of the binding of $MgCu_{0.5}Zn_{1.5}$ may be idealized to 9/2, so that there are 9 *b* layers parallel to the basal plane in the cell. Such an idealization amounts to neglecting long distant shears, which tend to be statistically distributed and are therefore not detected by structural analysis. Comparing a 9-layer *b* correlation with a 4-layer crystal structure gives rise to the following assessment method (*16*): at the layers 1, 2, 3, 4, the dipole components in the a_3 direction are of sign $++--$, abbreviated as 1+, 2+, 3−, 4−.[1] Using the above rule for the dipole sign leads to the stacking sequence *hchc* = ABAC, i.e., to just to the observed sequence.

The previously mentioned rule that a change of sign of dipole vector component in a_3 direction causes a h type stacking may appear somewhat formal, so that an additional less formal argument might be desirable. When a *b* electron correlation with 9 layers parallel to the hexagonal basal plane is represented by a "momentary" electron lattice, in fact a 3-dimensional section through the spatial correlation (a density in a 6-dimensional space (*14*)) is involved. There are positions of the lattice relative to the structure in which the average dipole distribution is better represented by 1(0), 2+, 3(0), 4−, i.e., some of the dipoles are very small as compared to others. The energy of the array is low when 2+ is occupied by a B layer and 4- by a C layer, as dipoles of opposite sign repel each other and dipoles of equal sign attract each other when they lie on a straight line parallel to a_3. As two B or two C cannot exist as neighbors, the position 1(0) and 3(0) can only be occupied by A; therefore, the ABAC stacking is in fact energetically preferred. It is clear that the consideration of momentary alignment is not satisfactory for an energy assessment, an averaging procedure over all situations is necessary. However, since the comfirmation of the usefulness of the two-correlation model rather than the improvement of the energy assessment is the aim of the present analysis this train of thought will not be followed here.

Before considering the L^{10}, L^9, L^8, structures it is appropriate to examine the L^2 phase $MgZn_2$(H4.8, SR1.180) which has $N_b^{/a}$ = 24 *b* electrons per *a* cell. The following binding is probable: a = H5.16; 8.49 Å = $b_{FH}(\sqrt{16/3}; 4.6/3) = c_{FH}(4; 8/3)$. The *c* correlation is once more retained from $MgCu_2$, and the *b* correlation has the same basal commensurability as in $MgCu_{0.5}Zn_{1.5}$; however, the type is now FH instead of UH in order to account for the greater valence electron concentration $N_b^{/A}$. Idealizing the commensurability element 4.6/3 to 5/3 produces the following assessment (*16*) in the dipole sequence, namely 1+, 2−, and therefore *hh* = AB stacking, which is, in fact, observed.

Between $MgCu_{0.5}Zn_{1.5}$ and $MgZn_2$ three additional phases have been detected: $MgCu_{0.23}Zn_{1.77}$($MgAg_{0.20}Zn_{1.80}$, H20.40, ABCBCACBCB(*15, 19*)SR32.97, 46.95), $MgCu_{0.19}Zn_{1.81}$($MgAg_{0.14}Zn_{1.86}$, H18.36, ABABCBCAC, (*15, 19*), SR27.12, 46.95), and $MgCu_{0.10}Zn_{1.90}$($MgAg_{0.06}Zn_{1.94}$, H16.32, ABABACAC, (*15, 19*)SR46.95). The structures probably are best determined for the mixture $MgAg_MZn_{M'}$ (SR46.95, Ref. (*17*)), but the occurrence of this sequence of phases is well confirmed, not only for the mixture $MgAg_MZn_{M'}$ but also for other mixtures (*15*). The *c*, *h* symbols of the phases are *chchhchchh, hchhchhch, hchhhchh,* so

---

[1] If x_3 is the coordinate along a_3 and the next layer of the *b* correlation to an atomic layer is at a smaller x_3, then the dipole component points to greater x_3.

that the rules of most uniform distribution of *ch* symbols (no unnecessary clustering (*16*)), and pertaining to the increase of *h*-share with increasing valence electron concentration ((*4*, p. 120, *15*, *16*) are fulfilled. According to the above binding scheme for $MgCu_{0.5}Zn_{1.5}$ and $MgZn_2$ the propositions of (*16*) requiring a uniform strain of the *b* correlation are fulfilled so that the conclusion (*16*) with respect to stacking sequence holds. Therefore the assumptions on the bonding type (binding) (*14*) also explain the shear-homeotypism of phases in the mixture $MgCu_MZn_{M'}$ and in homologous or quasi-homologous mixtures.

The next problem of shear homeotypism in the $MgCu_2$ family occurs for the phase $MgNi_2$(H8.16, SR3.31, 46.96) which contains $N_b^{/a} = 16$ *b* electrons per cell but tolerates (*15*) admixture of $MgCu_2$ up to $MgNi_{1.05}Cu_{0.95}$ with $N_b^{/a} = 24$. The analysis of the binding following the rules of (*14*, *20*) permits a = H4.834; 15.798 Å = $b_{UH}(\sqrt{3}; 6.5/2) = c_{FH}(4; 16/3)$. The *b* electron correlation commensurability element 6.5/2 may be idealized to 7/2 so that 7 *b* layers contribute to dipole formation. The sequence of signs then becomes 1+, 2+, 3−, 4−, just as in $MgCu_{0.5}Zn_{1.5}$, and therefore the $MgNi_2$(H8.16) types is stable. The fact that the *b* electron number per cell is ideally 19.5 is compatible with the great solubility of $MgCu_2$ in $MgNi_2$. It appears remarkable that the *b* correlation has good commensurability to *a* but to a much lesser degree to *c*.

Between $MgNi_2$ and $MgCu_2$ a L^6 phase $MgNi_{0.9}Cu_{1.1}$(H12.24, ABCACB = *cchcch*, (*18*)) has been found with $N_b^{/a} = 37$. The binding may be a = H4.917; 24.040 Å = $b_{FH}(\sqrt{13}/2; 11/3) = c_{FH}(4; 24/3)$; this conserves the *c* correlation and takes for b_{FH} an intermediary commensurability. Once more every *b* layer must be taken into account to reproduce the observed stacking sequence: for 6 double layers with 11 electron layers the dipole sequence results are 1+, 2−, 3−, 4−, 5+, 6+; following the rule (*16*), the stacking sequence cchcch becomes stable.

Discussion

Although there is some scope for the choice of the binding it does not stand to reason that the method of transient dipoles should always apply; it should be taken as an indication for the applicability of the model that the stacking sequences could be reproduced. Furthermore, quite independent additional features may be interpreted with the assumptions as to the binding.

For a long time it remained a puzzle why the shear homeotypes of $MgCu_2$ may change their stacking sequence without essentially changing their axial ratio $|a_3|/|a_1|$ (of, say, a coalescent layer), in contrast to the brass-like shear homeotypes of Cu which exhibit a marked dependence of axial ratio on valence-electron concentration. The present analysis of binding associates the same *c* correlation for every phase and as the *c* correlation is stiffer than the *b* correlation, especially when Cu 3*sp* electrons take part, it appears quite natural that the axial ratio should be independent of valence electron concentration.

Another puzzle was the observation that $MgZn_2$ has a quite high and congruent melting point, while its binding is not factorial (i.e., the commensurability between *b* and *c* is not a factor). The commensurability rule (*14*) gives to phases with two-factorial binding (like FF2 of $MgCu_2$) an elevated and therefore congruent melting point. The strongly increased $d_c(MgZn_2)$ = 1.30 Å, as compared with $d_c(Zn)$ = 1.15 Å, points to a participation of Zn 3*sp* electrons in the *c* correlation by filling in the F correlation the octahedral interstices so that the C type is formed (*14*) near the atomic core; this is a stabilizing factor. The strong elongation of d_c in homeotypes of $MgCu_2$ derives from the fact that one Mg with 8 *c* electrons replaces in copper two Cu with altogether 20 *c* electrons. It is seen from these arguments that the two-correlations model even anticipates the melting temperature.

The fact that the present investigation has omitted the averaging over several "momentary" dipole distributions shows that the present analysis is based on an approximative model and needs refinement later on. However, the two-correlations model provides a first insight into how the shear homeotypism in the $MgCu_2$ structure family is caused energetically. Although the considerations on atomic radii (*21, 22, 4*) provide some understanding for the stability, and are not supplanted but supplied by the present model, it appears that they cannot solve the problem of shear homeotypism in Friauf–Laves phases. For this problem a model is needed which is based on electron counting. However, neither does the *band model* or pseudo-potential model appear to have explained Komura's rule; the slow convergence of this model does not account for spatial correlation between the valence electrons and even less for spatial correlation between electrons of the peripheral atom core shells. Although the correlations have not yet been determined deductively it may be possible to find them inductively, just as atomic charges and atomic radii have been found first by the inductive technique. It is clear that such inductive models are not appropriate for energy calculation; nevertheless, they yield a valence classification of the large set of metallic compounds. The result of the classification, a bonding type (binding) provides valuable hints for future experiments aiming at investigations on structure and stability. However, the influence of the two-electron probability density on the crystal structures has not yet been exhaustively investigated. The present analysis shows that electrical dipole vectors at atoms play an important role. They are effective in van der Waals' binding and in metallic phases. It is probable that similar to the van der Waals' bond there is here a vanishing averaged dipole vector, as opposed to a transient dipole vector at the atoms that hides the effect. The present considerations are subject to further improvements. To be sure, the task of the present investigation cannot be the further improvement of the model; rather, its acceptability must be confirmed at present by showing that old grown crystallographic problems like the present one or like the problem of the sigma phases (*23*) or Nowotny's defect disilicides (*24*) may be successfully treated by it. The necessity of confirming the acceptability of the model results from the inductive method: the correlations have not yet been proved directly by diffraction experiments (although this should be possible by carefully measuring the feet of single crystal reflexes at low temperature). However, the more specific a phenomenon is, the more it becomes probable that a successful interpretation by a model is caused by the approach of the model to chemical reality.

References

1. J. B. Friauf, *J. Amer. Chem. Soc.* **49,** 3107 (1927).

2. J. B. Friauf, *Phys. Rev.* **29,** 35 (1927).

3. F. Laves and H. Witte, *Metallwirtsch. Metallwiss. Metalltech.* **14,** 645 (1935).

4. K. Schubert, "Kristallstrukturen zweikomponentiger Phasen," Springer, Berlin (1964).

5. "International Union Pure and Applied Chemistry: Nomenclature of Inorganic Chemistry," Butterworths, London (1971).

6. Y. Komura, *Acta Crystallogr.* **15,** 770 (1962).

7. A. K. Sinha, *Progr. Mater. Sci.* **15,** 79 (1972).

8. Y. Komura, *Acta Crystallogr. Sect. B* **33,** 2496 (1977).

9. P. I. Kripiakevich and E. B. Malnik, *Metallofizica* **52,** 71 (1974).

10. W. B. Pearson, "Crystal Chemistry and Physics of Metals and Alloys," Wiley, New York (1972).

11. P. I. Kripiakevich, "Strukturnye Tipy Intermet. Soedinenii," Isd. Nauka, Moscow (1977).

12. F. Laves and H. Witte, *Metallwirtsch. Metallwiss. Metalltech.* **15,** 840 (1936).

13. K. H. Lieser and H. Witte, *Z. Metallkd.* **43,** 396 (1952).

14. K. Schubert, (a) *Chem. Scr.* **19,** 224 (1982); (b) *J. Less-Common Met.* **70,** 167 (1980).

15. Y. Komura, M. Mitarai, A. Nakaue, and S. Tsujimoto, *Acta Crystallogr. Sect. B* **28,** 976 (1972).

16. K. Schubert, *Acta Crystallogr. Sect. B* **30,** 1538 (1974).

17. Y. Komura, *Acta Crystallogr. Sect. B* **36,** 1548 (1980).

18. Y. Komura, A. Nakaue, and M. Mitarai, *Acta Crystallogr. Sect. B* **28,** 727 (1972).

19. Y. Komura, M. Mitarai, I. Nakatani, H. Iba, and T. Shimizu, *Acta Crystallogr. Sect. B* **26,** 666 (1970).

20. K. Schubert, *Commun. Math. Chem.* **73,** 75 (1982).

21. R. L. Berry and G. V. Raynor, *Acta Crystallogr.* **6,** 178 (1953).

22. W. B. Pearson, *Acta Crystallogr. Sect. B* **37,** 1174, 1183 (1981); *Z. Kristallogr.* **151,** 301 (1980).

23. K. Schubert, *Z. Metallkd.* **75,** 175 (1984).

24. K. Schubert, *J. Solid State Chem.* **43,** 97 (1982).