# CONDITIONS FOR THE EXISTENCE OF ORDERED STRUCTURE IN BINARY ALLOY SYSTEMS

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# CONDITIONS FOR THE EXISTENCE OF ORDERED STRUCTURE IN BINARY ALLOY SYSTEMS

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**Résumé.** — Nous discutons les conditions d'existence de surstructures dans le cas d'alliages binaires cfc par la détermination de l'état fondamental pour une concentration arbitraire dans un modèle d'interaction de paires. Nous supposons que l'interaction s'étend jusqu'aux quatrièmes voisins. Plusieurs états ordonnés typiques sont obtenus comme états fondamentaux. L'analyse est combinée avec un calcul de l'interaction entre deux atomes d'élément de transition pour expliquer une tendance générale observée dans le cas des alliages des métaux de transition.

**Abstract.** — The conditions for the existence of superlattice structures of fcc binary alloys are discussed by determining the ground state of the pairwise interaction model for arbitrary concentration. The interaction is assumed to extend to the fourth neighboring sites. Many typical ordered structures are obtained as the ground state. The analysis is combined with a calculation of the interaction between two transition element atoms to explain a general tendency observed in transition metal alloys.

1. **Introduction.** — Many ordered states of binary alloys or vacancies correspond to superlattice structures on the bcc, fcc and hcp lattices. Certain types of such orderings belonging to the same lattice appear quite often successively in a concentration range of a binary alloy system. In order to elucidate the conditions for the appearance of such a sequence of orderings, we determine the ground state of the lattice gas model with the pairwise interaction of finite but extended range. The lattice distortion accompanying the ordering is neglected in the analysis. We present in sections 2 through 4 the result of a detailed analysis of the fcc lattice case with up to fourth neighbor interactions in which the first neighbor one is sufficiently repulsive to keep the number of the nearest neighboring pairs of particles minimum for a given concentration. The bcc and hcp lattice cases will be briefly discussed in section 5.

The present problem has been discussed by many authors so far. The discussions, however, have been confined mostly to the cases of the first and second neighbor interactions only; some arguments which include the third neighbor interaction seem to lack mathematical rigor. As will be discussed below, the inclusion of the fourth neighbor interaction is essential for obtaining many interesting ordered structures of the fcc case as the unique ground state of the model. In the analysis we use the method of geometrical inequalities which is capable of determining the ground state in the whole concentration range; the method has been developed by Kaburagi and Kanamori [1-3].

In section 6 we discuss a general tendency in fcc transition metal alloys. We mention briefly a calculation of the electronic contribution to the pairwise interaction between two transition element atoms; when combined with the analysis of the lattice gas model, it will explain certain aspects of the observed tendency.

2. **Definitions and the method of analysis.** — The energy of the present model is defined by

$$E = \Sigma_k V_k p_k , \tag{1}$$

where $V_k$ is the interaction constant of the $k$-th neighbor interaction and $p_k$ is the total number of the $k$-th neighboring pairs of particles in a given configuration. The particles correspond to atoms of minority component of binary alloys, since the concentration $x$ will be confined to the range $x \leq 1/2$. The total energy of an alloy $A_xB_{1-x}$ can be reduced to $E$ given by Eq. (1) if we drop a term depending on $x$ only; $V_k$ is given by

$$V_k = V_k^{AA} + V_k^{BB} - 2\, V_k^{AB}$$

in terms of the interaction constants between A-A, B-B and A-B pairs. In order to denote a structure at a concentration $x$, we use the symbol

$$S(p_1/Nx, p_2/Nx, \dots ; x) ,$$

where $N$ is the total number of the lattice sites and thus $p_k/Nx$ gives the number of the $k$-th pair per particle. The symbol may not define the structure uniquely in some cases; such a degeneracy will be mentioned in each case.

When the interaction is of finite range, the ground state energy, $E_g$, follows a broken line as function of $x$, changing the slope $dE_g/dx$ at several characteristic values of $x$. At the inflection point the ground state is an ordered structure, while it is generally a two-phase mixture of the ordered structures corresponding to near-by inflection points at an intermediate $x$, though an ordered structure may happen to be degenerate with the two-phase mixture in some cases. This $E_g$ *vs.* $x$ relation of the lattice gas model was rigorously derived first by the method of geometrical inequalities [1]. We summarize the method by explaining the analysis for the case of the fcc lattice with $V_1$ and $V_2$ only. We can derive the following inequalities for $p_1$ and $p_2$ [3] :

$$\begin{aligned} A &= p_1 \geqq 0 \quad \text{for} \quad x \leqq 1/4\,, \\ &N(4x-1) \quad \text{for} \quad 1/4 \leqq x \leqq 1/2\,, \\ B &= 2p_1 + p_2 \geqq 0 \quad \text{for} \quad x \leqq 1/6\,, \\ &N(6x-1) \quad \text{for} \quad 1/6 \leqq x \leqq 1/3\,, \\ &N(12x-3) \quad \text{for} \quad 1/3 \leqq x \leqq 1/2\,, \\ C &= p_2 \geqq 0 \quad \text{for} \quad x \leqq 1/2\,, \\ D &= -p_1 + p_2 \geqq -3x \end{aligned}$$

and

$$F = -p_2 \geqq -3x\,. \tag{2}$$

Note that the r.h.s. for $A$, $B$ and $C$ have the inflection points. We rewrite the energy given by Eq. (1) in terms of the l.h.s., for example, as

$$E = (V_1 - 2V_2)A + V_2 B$$

which determines $E_g$ in the regime $V_1 > 2V_2 > 0$ provided that we can find the ordered structures satisfying the equality at the inflection points of the inequalities used in rewriting of $E$. In the present case we can determine the ground state in the whole regimes of the $V_1 - V_2$ plane, concluding that it is divided into five regimes,

(I) $V_1 > 0$ and $V_2 < 0$,
(II) $V_1 > 2V_2 > 0$,
(III) $2V_2 > V_1 > 0$,
(IV) $0 > V_1 > -V_2$ and (V) $-V_2 > V_1$.

See table I for the result.

In the regimes (I) and (II), where $p_1$ is minimum, we find the wellknown $Cu_3Au$, $Al_3Ti$, $Pt_2Mo$ and CuAuI types among the ordered structures appearing at the inflection. As was pointed out by Allen and Cahn [4] who derived most of the result independently by use of a different method, the $Ni_4Mo$ type is degenerate with the two phase mixture at $x = 1/5$ between $S(0, 0, 4, 1; 1/6)$ and $S(0, 2, 4, 2; 1/4)$ ($Al_3Ti$) as far as $V_1$ and $V_2$ are concerned. Also complicate structures such as $Au_5Mn_2$, $Pd_2Mn$ and $Pd_5Mn_3$ are not obtained as the distinct structures at the inflection of the $E_g$ *vs.* $x$ curve, though $p_1$ is kept minimum in these structures. The inclusion of $V_3$ in the analysis does not improve the situation very much. Thus we extend the range of interaction to the fourth neighbors. In order to simplify the analysis, we assume that $p_1$ is kept minimum for given concentrations, satisfying the equality in the inequality $A$ in Eqs. (2). The structures which lie outside the scope of the analysis in the following section are the CuPt family in the regimes (III) and (IV) where $p_2$ is minimum [5] ([1]). We defer the analysis for this case to future publication.

TABLE I

*The ordered structures in the fcc case with $V_1$ and $V_2$ only. The regimes, I, II, etc. are defined in the text. The number given in bold-face refers to the unit cell shown in figure 1. Only those which appear at the inflection points of the $E_g$ vs. $x$ curve are listed.*

| Structure | | Reg. | Structure | | Reg. |
|---|---|---|---|---|---|
| $S(0,3,0,6;1/4)$ | **17** | I | $S(0,2,4,2;1/4)$ | **18** | II |
| $S(2,3,4,6;1/2)$ | **39** | I | $S(1,1,6,1;1/3)$ | **23, 24** | II |
| $S(0,0,4,1;1/6)$ | **11** | II, III | $S(1,1,6,3/2;1/3)$ | **25** | |
| $S(3/2,0,5,7/2;1/3)$ | **42** | III | $S(2,2,8,2;1/2)$ | **40** | II |
| $S(3,0,6,6;1/2)$ | **44** | III, IV | No structure in V. | | |

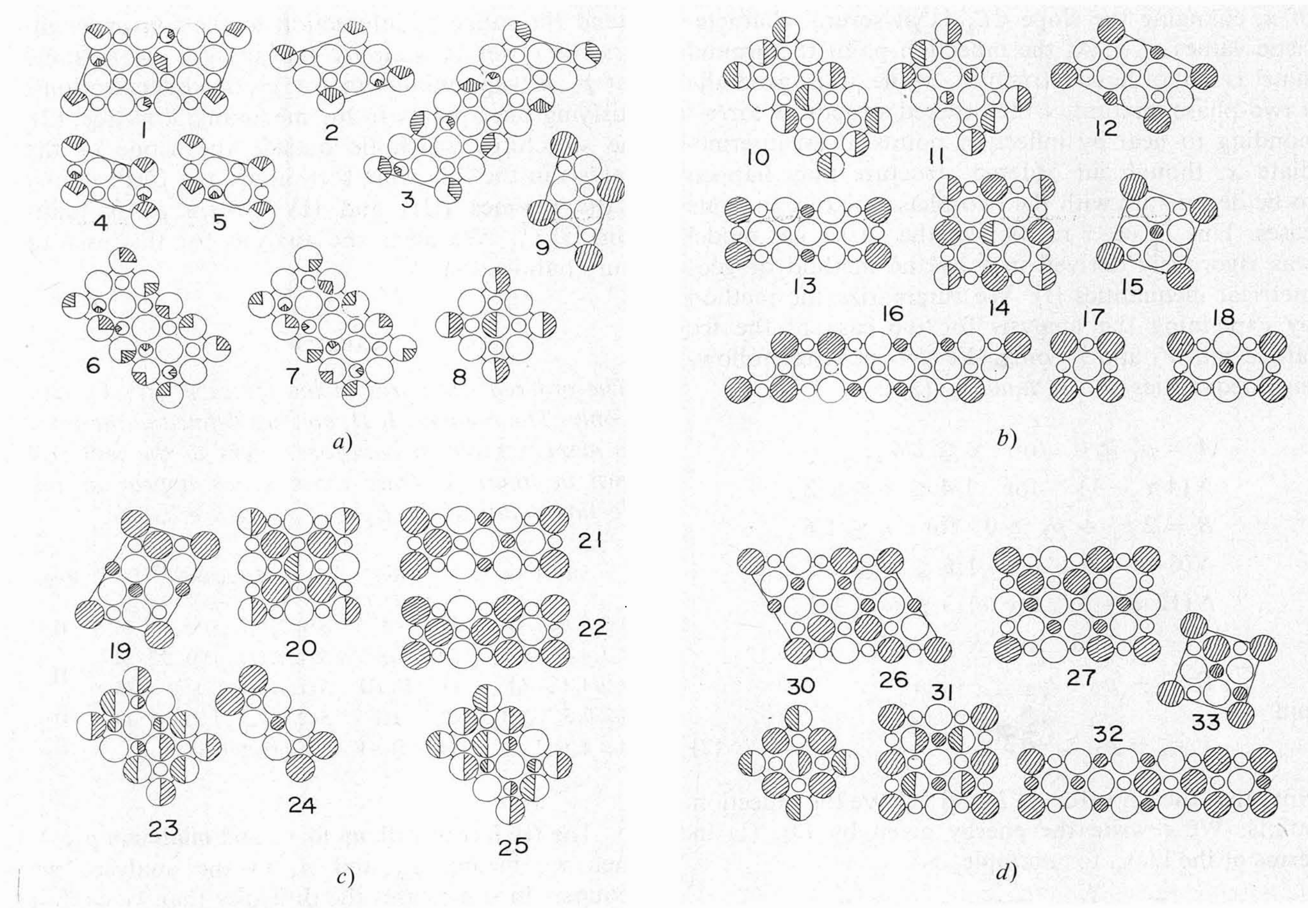
3. **The fcc lattice with up to $V_4$ and minimum $p_1$.** — When we include $p_3$ and $p_4$ in the analysis, we encounter in some cases the difficulty that we cannot find the ordered structure satisfying the equality in the relevant inequalities. We can overcome the difficulty in most cases of the present analysis by improving the inequalities by use of an argument utilizing the minimum $p_1$ condition. All the structures listed in table II can be proved to be of lowest energy in certain regimes in the space spanned by the interaction constants. There are, however, certain regimes in which we cannot determine the $E_g$ *vs.* $x$ curve rigorously. In such regimes we make conjecture by assuming that the ordered structures proved rigorously in adjacent regimes may appear in the regime in point and determine the state of lowest energy by energy comparison. Though we shall not specify the regimes in which such a conjecture is made in this paper, we mention that we encounter the problem mostly in the hatched region in figures 2 and 3.

Table II and figures 1-4 summarize the result of the analysis. Under the minimum $p_1$ condition $x = 1/4$ and $1/2$ are always the inflection points according to the inequality $A$ in Eq. (1). Defining $\xi$ by

$$\xi = V_2 - 4V_3 + 4V_4\,, \tag{3}$$

we can prove rigorously that $S(0, 2, 4, 2; 1/4)$ ($Al_3Ti$) and $S(2, 2, 8, 2; 1/2)$ are the corresponding ordered

([1]) The $CuPt_7$ structure is obtained in the present analysis, since $p_1 = 0$ is satisfied. If $p_1$ is minimum under the minimum $p_2$ condition, we obtain $CuPt_7$ (No. 8) and Nos. 11, 41, 42, 43, 44 in figure 1.



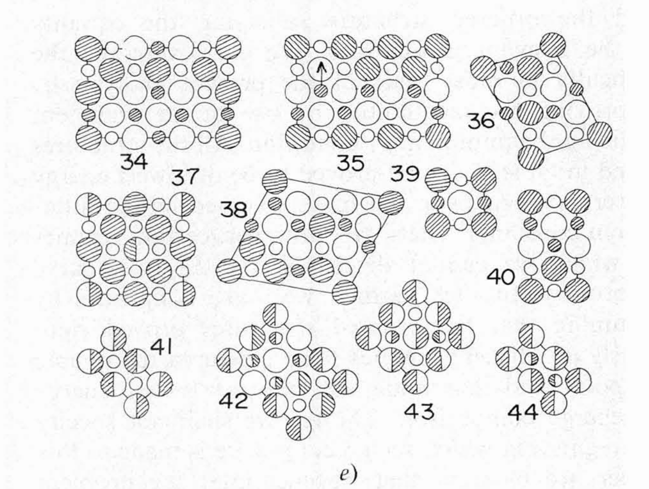




FIG. 1. — Unit cells of the fcc ordered structures projected on the (001) plane. Large circles are the sites on the (00$n$) planes with integral $n$ and small ones are those on the (00$n$ + 1/2) planes. Circles with a shaded quadrant correspond to particles occupying every fourth sites in the [001] direction. Particles on the planes with $z = 4n$, $4n + 1/2$, $4n + 1, \dots$ are distinguished by rotating clockwise the shaded quadrant by 45°, 90°, .... The circles with a shaded 120° sector represent particles on every third sites similarly. For half-shaded circles we do not rotate the shaded part by 90° between large and small circles for simplicity. Figures Nos. 1-40 belong to the case of minimum $p_1$. Nos. 41-44 are examples of the CuPt family. No. 15 is $Ni_4Mo$, 17 $Cu_3Au$, 18 $Al_3Ti$, 19 $Au_5Mn_2$, 24 $Pt_2Mo$, 28 $Pd_2Mn$ (shown in figure 5), 39 CuAuI. No. 23 has the same $p_k$'s up to $k = 4$ as $Pt_2Mo$. The arrow in No. 35 means that the particle can be shifted with no cost of energy.

structures for the case $\xi > 0$ and $S(0, 3, 0, 6; 1/4)$ ($Cu_3Au$) and $S(2, 3, 4, 6; 1/2)$ (CuAuI) for the case $\xi < 0$. For other values of $x$ we obtain many ordered structures which we divide into four groups : 1) the $Al_3Ti$ family appearing mostly in the region $\xi > 0$ of the $V_2$-$V_3$ plane and satisfying the condition that $p_2$ is minimum under the minimum $p_1$ condition, 2) the $Cu_3Au$ family appearing mostly in the region $\xi < 0$ and satisfying the condition that $p_3$ is minimum under the minimum $p_1$ condition, 3) intermediate structures appearing in the hatched region of figures 2 and 3, and 4) structures satisfying $p_2 = p_3 = 0$ such as $CuPt_7$ and appearing in both $\xi > 0$ and $\xi < 0$ with $x \leqq 1/8$.

In order to illustrate the analysis we mention the inequality,

$$4p_2 + 2p_3 + p_4 \geqq N(42x - 6) \quad \text{or} \quad N(10x + 2) \quad \text{or} \quad N.17x \quad \text{or} \quad N(32x - 5) \quad \text{or} \quad N(47x - 11) \quad \text{or} \quad N(58x - 16) \tag{4}$$

which is valid under the minimum $p_1$ condition. In the l.h.s. the first expression is applicable to

### TABLE II*a*

*The ordered structure in the case of $V_4 > 0$ and $x \geqq 1/4$. See figure 2 for the regimes. Each structure can exist in a regime in the hatched region besides in those marked with circle.*

| Group 1 $Al_3Ti$ family | | I | II | III | IV | V |
|---|---|---|---|---|---|---|
| $S(0, 2, 4, 2; 1/4)$ | **18** | ○ | ○ | ○ | ○ | ○ |
| $S(1/2, 3/2, 5, 1; 2/7)$ | **19** | | ○ | ○ | ○ | ○ |
| $S(1, 1, 6, 1; 1/3)$ | **23, 24** | | | ○ | ○ | ○ |
| $S(4/3, 4/3, 16/3, 10/3; 3/8)$ | **31** | | | | | ○ |
| $S(3/2, 3/2, 6, 3/2; 2/5)$ | **33** | | | | ○ | ○ |
| $S(2, 2, 8, 2; 1/2)$ | **40** | ○ | ○ | ○ | ○ | ○ |

| Group 2 $Cu_3Au$ family | | VI | VII | VIII | IX | X |
|---|---|---|---|---|---|---|
| $S(0, 3, 0, 6; 1/4)$ | **17** | ○ | ○ | ○ | ○ | ○ |
| $S(4/5, 12/5, 8/5, 24/5; 5/16)$ | **20** | ○ | ○ | ○ | | |
| $S(1, 5/2, 2, 4; 1/3)$ | **22** | | | ○ | ○ | |
| $S(4/3, 2, 8/3, 6; 3/8)$ | **30** | ○ | ○ | | | |
| $S(4/3, 7/3, 8/3, 13/3; 3/8)$ | **29** (*) | | | ○ | | |
| $S(3/2, 5/2, 3, 4; 2/5)$ | **32** | | ○ | ○ | ○ | |
| $S(12/7, 18/7, 24/7, 36/7; 7/16)$ | **37** | ○ | ○ | ○ | | |
| $S(2, 3, 4, 6; 1/2)$ | **39** | ○ | ○ | ○ | ○ | ○ |

Group 3 The regimes are in the hatched region

| | | | |
|---|---|---|---|
| $S(1, 3/2, 11/2, 1; 1/3)$ | **26, 27** | $S(8/5, 9/5, 32/5, 8/5; 5/12)$ | **35** |
| $S(1, 2, 4, 2; 1/3)$ | **21** | $S(8/5, 2, 28/5, 2; 5/12)$ | **34** |
| $S(1, 2, 3, 3; 1/3)$ | **28** (*) | $S(5/3, 2, 16/3, 8/3; 3/7)$ | **36** |
| (*) See figure 5. | | $S(9/5, 2, 6, 14/5; 5/11)$ | **38** |

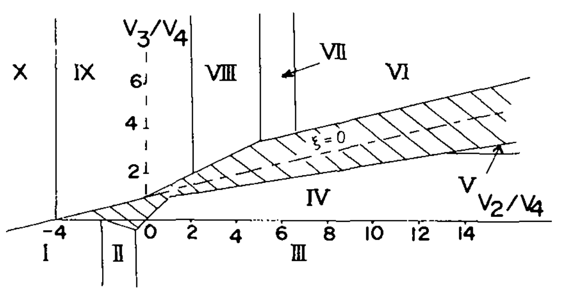



FIG. 2. — The regimes in the case of $V_4 > 0$ and $x \geqq 1/4$ (see table II*a*).

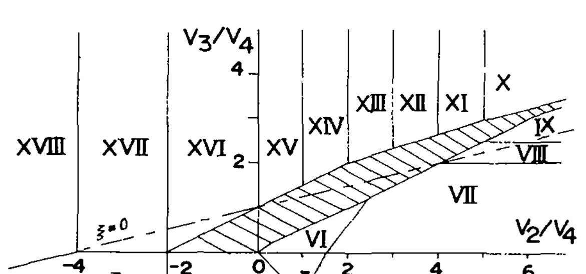



FIG. 3. — The case of $V_4 > 0$ and $x < 1/4$.

### TABLE II*b*

*The case of $V_4 > 0$ and $x < 1/4$. See figure 3. No ordered structure appears in the regimes I and VIII which coincide with I and X in figure 2 for $x \geqq 1/4$. All the structures except* $S(0, 0, 3, 0; 1/8)$ **7** *appear in certain regimes in the hatched region. We have found two structures belonging to the group* 3, $S(0, 1, 2, 1; 1/6)$ **12** *and* $S(0, 2, 1, 3; 1/5)$ **16** *which appear in a part of the hatched region only. We have three structures of the group* 4 : $S(0, 0, 0, 0; 2/27)$ **1** *in the regimes VI through XV*, $S(0, 0, 0, 1; 1/12)$ **2** *in VIII through XII and* $S(0, 0, 0, 6; 1/8)$ **8** ($Pt_7Cu$) *in IX and X*.

| Group 1 $Al_3Ti$ family | | II | III | IV | V | VI | VII | VIII | IX |
|---|---|---|---|---|---|---|---|---|---|
| $S(0, 0, 1/2, 0; 1/12)$ | **3** | | | | | ○ | ○ | | |
| $S(0, 0, 5/2, 0; 1/8)$ | **6** | | | | | ○ | ○ | | |
| $S(0, 0, 2, 1; 1/8)$ | **10** | | | | | | | ○ | |
| $S(0, 0, 3, 0; 1/8)$ | **7** | | | ○ | ○ | | | | |
| $S(0, 0, 4, 1; 1/6)$ | **11** | | ○ | | ○ | | ○ | ○ | ○ |
| $S(0, 1, 4, 0; 1/5)$ | **15** | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |

| Group 2 $Cu_3Au$ family | | X | XI | XII | XIII | XIV | XV | XVI | XVII |
|---|---|---|---|---|---|---|---|---|---|
| $S(0, 1, 0, 0; 1/9)$ | **4, 5** | | | ○ | ○ | ○ | ○ | ○ | ○ |
| $S(0, 1, 0, 1; 1/8)$ | **9** | | ○ | ○ | ○ | ○ | | | |
| $S(0, 2, 0, 2; 1/6)$ | **13** | | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| $S(0, 2, 0, 4; 3/16)$ | **14** | ○ | ○ | ○ | ○ | | | | |

### TABLE II*c*

*The case of $V_4 < 0$. See figure* 4. $S(0, 0, 4, 1; 1/6)$ *extends to the regime IV as far as*

$$3\,V_2 - 8\,V_3 + 10\,V_4 \geqq 0$$

*and* $S(1, 1, 6, 3/2; 1/3)$ *to the regime IV as far as*

$$5\,V_2 - 16\,V_3 + 18\,V_4 \geqq 0\,.$$

| Structure | | I | II | III | III′ | IV | V |
|---|---|---|---|---|---|---|---|
| $S(0, 0, 0, 6; 1/8)$ | **8** | | | ○ | ○ | ○ | |
| $S(0, 0, 4, 1; 1/6)$ | **11** | | ○ | ○ | | | |
| $S(0, 2, 4, 2; 1/4)$ | **18** | ○ | ○ | ○ | ○ | | |
| $S(1, 1, 6, 3/2; 1/3)$ | **25** | | ○ | ○ | | | |
| $S(4/3, 4/3, 16/3, 10/3; 3/8)$ | **31** | | | ○ | ○ | | |
| $S(2, 2, 8, 2; 1/2)$ | **40** | ○ | ○ | ○ | ○ | | |
| $S(0, 3, 0, 6; 1/4)$ | **17** | | | | | ○ | ○ |
| $S(4/3, 2, 8/3, 6; 3/8)$ | **30** | | | | | ○ | |
| $S(2, 3, 4, 6; 1/2)$ | **39** | | | | | ○ | ○ |

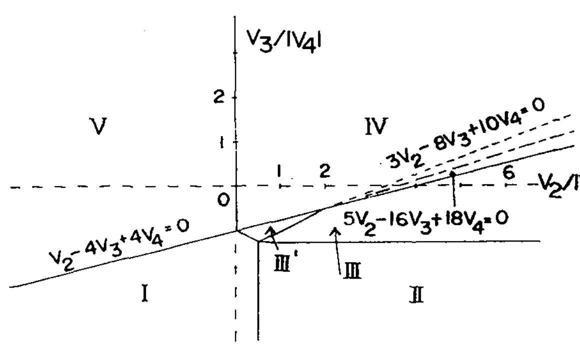



FIG. 4. — The case of $V_4 < 0$.

$1/5 \leqq x \leqq 1/4$, the next one up to $x = 2/7$ and so on with the inflection points at $x = 1/5$, $1/4$, $2/7$, $1/3$, $2/5$, $5/11$ and $1/2$. This inequality is used in the regime (IV) of figure 2 to conclude the sequence, $Ni_4Mo$, $Al_3Ti$, $Au_5Mn_2$, $Pt_2Mo$ and

$$S(3/2, 3/2, 6, 3/2 ; 2/5)$$

there. $x = 5/11$ is not the inflection point, because another inequality takes over in $2/5 \leqq x \leqq 1/2$. Other details of the analysis are omitted.

4. **Comparison with experimental data.** — A typical example of the $Al_3Ti$ family is $Mn_xAu_{1-x}$ [6] which has the $Ni_4Mo$ type ordering at $x = 1/5$, $Al_3Ti$ type at $x = 1/4$ [7] and $Au_5Mn_2$ at $x = 2/7$ [8]. Our analysis concludes that the sequence can appear for $V_4 > 0$ (see figure 2 and table II*a*). The presence of the $Al_3Ti$ type and $Pt_2Mo$ one in Pd-V and Ni-V are consistent also with our analysis, though we expect then the $Au_5Mn_2$ type inbetween [6].

An interesting example of the intermediate family (the category 3) is $Mn_xPd_{1-x}$ alloys [9]. As is shown in figure 5, the $MnPd_3$ structure is intermediate between $Cu_3Au$ and $Al_3Ti$, being degenerate in energy with them on the boundary $\xi = 0$ in the present model. If more distant neighbors up to the tenth are taken into account, it can be lower in energy than $Cu_3Au$ and $Al_3Ti$ provided that

$$2(V_8 - 4\,V_9) > |\,\xi + 4\,V_6 - 8\,V_7\,| \qquad (5)$$

is satisfied. Here the eighth neighbors are (2, 0, 0) and equivalent sites with respect to the origin; the nineth ones are (2, 1/2, 1/2). $MnPd_2$ appears in the present analysis in a regime near the boundary $\xi = 0$ (see figure 6), which is consistent with the result for $MnPd_3$. $Mn_3Pd_5$ corresponding to

$$S(4/3, 7/3, 8/3, 14/3 ; 3/8)\,,$$

on the other hand, is not obtained as the ground state in our analysis, though $x = 3/8$ can be the inflection point. This is because there is a related structure $S(4/3, 7/3, 8/3, 13/3;\ 3/8)$ (see figure 5) which appears in the regime (VIII) of figure 2 for $V_4 > 0$. When $V_k$'s up to $V_{10}$ are considered, the $Mn_3Pd_5$ one can be lower in energy with the condition $2\,V_5 - 2\,V_6 + 4\,V_7 - 2\,V_8 > V_4$. In our opinion, however, the problem is beyond the capability of the pairwise interaction model with fixed $V_k$'s, since the energy comparison on the $MnPd_2$ structure with a modification $S(2, 3, 3, 7/2;\ 1/3)$ (see figure 5) yields an almost opposite condition

$$V_4 > 2\,V_5 - 2\,V_6 + 4\,V_7 - 2\,V_8 + 2\,V_{10}\,.$$

It is interesting to note also that the $Mn_3Pd_5$ structure has a modification having the same $P_k$'s for all $k$ (see figure 5); the pairwise interaction model cannot distinguish between them energetically. Regardless of these complications we may conclude that the Mn-Pd system belongs to the intermediate class.

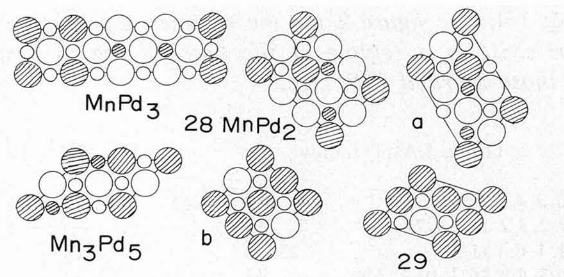



FIG. 5. — The structures of $Pd_3Mn$, $Pd_2Mn$ and $Pd_5Mn_3$. *a* is a modification of $Pd_2Mn$ and *b* and 29 are those of $Pd_5Mn_3$ (see the text).

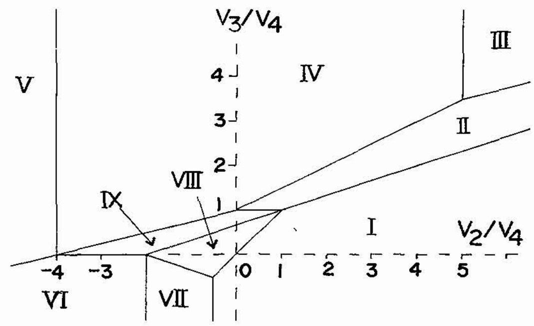



FIG. 6. — The ordered structures at $x = 1/3$. $S(1, 1, 6, 1 ;\ 1/3)$ ($Pt_2Mo$) is of lowest energy in I, $S(1, 2, 3, 3 ;\ 1/3)$ ($Pd_2Mn$) in II, $S(1, 5/2, 2, 4 ;\ 1/3)$ in IV, $S(1, 3/2, 11/2, 1 ;\ 1/3)$ in VIII and $S(1, 2, 4, 2 ;\ 1/3)$ in IX. In other regimes the two phase mixture, for example, that between $Cu_3Au$ and CuAuI in V is of lowest energy.

Examples of the $Cu_3Au$ family are numerous. Usually only the $Cu_3Au$ and CuAuI are found in the range $1/4 \leqslant x \leqslant 1/2$, which is expected if

$$-\,V_2 > 4\,V_4 > 0 \quad \text{or} \quad V_2 < 0 \quad \text{with} \quad V_4 < 0$$

is satisfied besides $\xi < 0$. In other regimes with $\xi < 0$ we expect the additional appearance of ordered structures such as $S(4/3, 2, 8/3, 6;\ 3/8)$ according to table II.

5. **Remarks about the bcc and hcp cases.** — For the bcc lattice a similar analysis assuming the minimum $p_1$ and $V_k$'s up to $V_4$ has been carried out. Various ordered structures are found at $x = 1/8$, $1/6$, $3/16$, $1/5$, $2/9$, $1/4$, $1/3$, $3/8$ and $1/2$. Since $p_1$ is minimum, the structure at $x = 1/2$ is the CsCl type. If we neglect $V_4$, the $Fe_3Al$ type appears in the regime $V_2 > 5\,V_3$ with $V_2 > 0$ and the $Si_2Mo$ type in the regime, $5\,V_3 > V_2 > 0$ and $4\,V_3 > -\,V_2 > 0$ which do not overlap with the $Fe_3Al$ regime. Even when $V_4$ is considered, the two types share either no regime ($V_4 > 0$) or small overlap for $V_2 > 0$ ($V_4 < 0$). Further details will be published elsewhere.

As for the hcp lattice Kudo and Katsura [10] have carried out the analysis based on the method of geometrical inequalities for the case of the ideal hcp with $V_1$ and $V_2$ only. The $V_1$-$V_2$ plane is divided in the same way as in the corresponding fcc case. Moreover there is one-to-one correspondence between the ordered structures; for example, the MgCd type corresponds to the CuAuI and the $Ni_3Sn$ type to the $Cu_3Au$.

6. **General tendency in the fcc transition metal alloys.** — The $Al_3Ti$ family structures are found in those binary alloys in which the majority component is a metal such as Al, Au, Ni, Pd and Pt and the minority component is a metal with less-than-half or half-filled d shell such as Ti, V, Cr and Mn. In the case of the $Cu_3Au$ family the component metals are closer to each other in the periodic table. In order to understand this general tendency, we calculate the interaction between two transition element atoms embedded in a free electron sea, assuming the Anderson model for the virtual d state of each atom. The interaction arises from the indirect transfer of electrons between the two atoms via free electron states; the formalism is based on the pseudo-Greenian theory previously developed [11]. The calculation is obviously a simplification of the real situation. The general aspect of the result is, however, in agreement with that obtained by Parlebas [12] in his more detailed calculation of the pair energy in Cu. A similar calculation has been carried out by Malmström *et al.* [13] though it aims at the magnetic interaction in alloys. Omitting the details, we mention here briefly the results for nonmagnetic atoms in the free electron sea corresponding to Au. The calculated $V_4$ is positive for the less-half-filled d shell case and changes its sign when we increase the number of electrons per atom, $N_d$ to a value between 7 and 8. $V_2$ and $V_3$ are negative for small $N_d$ and becomes positive in the more-than-half filled region. $\xi$ calculated with these $V$'s is positive in the less-than-half region and negative in the more-than-half region. These results are consistent with the observed tendency according to the analysis given in previous sections. The above-mentioned behaviors of $V_4$ and $\xi$ do not change very much even when atoms have magnetic moment of up to 2 $\mu_B$. We omit the discussion of the high magnetic moment case where the situation is more complicated. When we study the conditions for the appearance of the $Ni_4Mo$ type with the calculated $V$'s, we conclude that it is satisfied for $N_d$ between 3.3 and 5.9 in the nonmagnetic case. Details of the calculation will be reported in near future.

**Concluding remarks.** — The pairwise interaction model is obviously a crude model. More-than-two atom interactions are generally expected from the calculation of the electronic contribution. Also the assumption of a finite interaction range cannot be justified easily. Concentration dependence of $V_k$'s is another factor to be considered. Nevertheless we believe that the analysis presented here will provide us with a useful guide in searching for ordered structures. For example we conclude that when the $Al_3Ti$ and $Pt_2Mo$ types are found as in the case of Pd-V, the complicate $Mn_2Au_5$ should appear as far as $V_k$'s depend smoothly on the concentration. Our calculation of $V_k$'s in transition metal alloys is still preliminary. The results so far obtained, however, seems to be encouraging.

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