

## Origin of cluster ordering in complex alloys

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Recently, we presented a new concept to describe crystal structures of complex alloys without clusters (M. Uchida and Y. Matsui, *Acta Crystallogr.*, B56, 654 (2000)). Here we discuss the origin of cluster ordering in complex alloys from the view point of our concept. Examples are the  $\mu$ -Al<sub>4</sub>Mn and  $\lambda$ -Al<sub>4</sub>Mn phases related to icosahedral quasicrystals, which have been described in terms of the aggregation of clusters. The difference between these phases is basically understood by the difference in the ordered arrangements of atomic vacancies in the close-packed layers (or the modulation wave vectors). The modulation is considered to be due to the rearrangement of atomic vacancies as a response to the occurrence of charge density waves.

Key words: complex alloys, modulated structure, stacking motif, cluster, charge density wave (CDW)

### 1. INTRODUCTION

A number of complex alloys have been discussed in terms of clusters [1]. This is also true of quasicrystals and approximants which are currently believed to have similar clusters, arranged quasiperiodically in the former and periodically in the latter. Recently, we presented a new concept to describe crystal structures of complex alloys without clusters [2][3]. Here we discuss the origin of cluster ordering from the view point of our concept. Examples are the  $\mu$ -Al<sub>4</sub>Mn [4] and  $\lambda$ -Al<sub>4</sub>Mn [5] phases related to icosahedral quasicrystals, which have been described in terms of the aggregation of clusters until now.

### 2. RESULTS AND DISCUSSIONS

#### 2.1 DESCRIPTION OF THE STRUCTURES

There are two hexagonal phases with large unit cells near the composition of the icosahedral and decagonal quasicrystals in the Al-Mn system, the  $\mu$ -Al<sub>4</sub>Mn phase (P6<sub>3</sub>/mmc, a=19.98 Å, c=24.673 Å) and the  $\lambda$ -Al<sub>4</sub>Mn phase (P6<sub>3</sub>/m, a=28.382 Å, c=12.389 Å). Their electron diffraction patterns (EDPs) are very similar to those of icosahedral quasicrystals [6]. Structures of the  $\mu$ -Al<sub>4</sub>Mn phase and the  $\lambda$ -Al<sub>4</sub>Mn phase have been determined by the single-crystal X-ray diffraction method by Shoemaker et al. [4] and by Kreiner and Franzen [5], respectively.

The  $\mu$ -Al<sub>4</sub>Mn phase and the  $\lambda$ -Al<sub>4</sub>Mn phase are composed of flat and puckered layers, six and twelve

layers along the c axis, respectively. We now focus on the flat layer with z=0.50 in the  $\mu$ -Al<sub>4</sub>Mn phase. Solid circles in Fig.2 show the c-projection of the arrangement of atoms in the flat layer. This layer forms a triangular arrangement of atoms, and contains apparent holes marked by squares. Here, we call them the atomic vacancy sites in the close-packed layer.

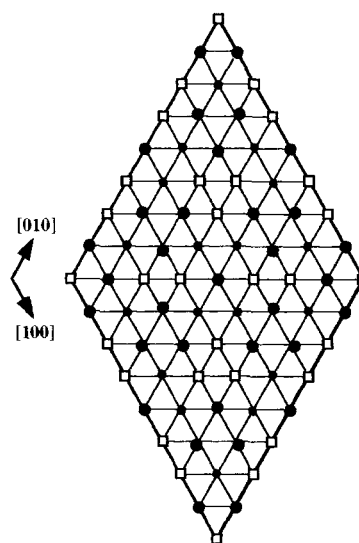


Fig.1. Structure in the flat layer with z=0.50 of  $\mu$ -Al<sub>4</sub>Mn. The small and large solid circles represent Mn and Al atoms, respectively. The squares represent the atomic vacancy sites. A triangular net represents a close-packed layer.

It is then understood that the flat layer is a close-packed layer with an ordered arrangement of atomic vacancies forming a hexagonal supercell. Fig.2 shows the c-projection of atoms in both the flat and puckered layers with  $z=0.40-0.50$ , where solid circles represent atoms in the flat layer, open circles those in the puckered A layer with  $z=0.43-0.44$  and gray circles those in the puckered B layer with  $z=0.40-0.41$ . Atoms in the puckered A layer are located below the atomic vacancy sites in the flat layer, while atoms in the puckered B layer are below the interstices in the flat layer. The  $\lambda$ - $\text{Al}_4\text{Mn}$  phase has the same stacking motif as that of the  $\mu$ - $\text{Al}_4\text{Mn}$  phase, but the ordered arrangements of atomic vacancies are different (Fig.3 and Fig.4).

## 2.2 EDP ANALYSIS

To elucidate a relationship in reciprocal space between the  $\mu$ - $\text{Al}_4\text{Mn}$  phase and the  $\lambda$ - $\text{Al}_4\text{Mn}$  phase, we calculated the intensity distribution in EDPs from the flat layer with  $z=0.50$  of the  $\mu$ - $\text{Al}_4\text{Mn}$  phase and the flat layer with  $z=0.25$  of the  $\lambda$ - $\text{Al}_4\text{Mn}$  phase.

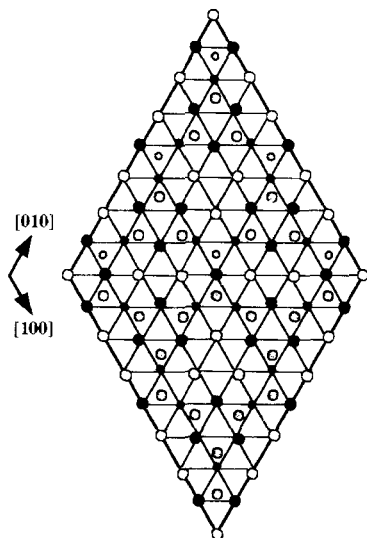


Fig.2. Structure in the flat and puckered layers with  $z=0.40-0.50$  of  $\mu$ - $\text{Al}_4\text{Mn}$ . The small and large solid circles represent Mn and Al atoms, respectively, in the flat layer. The open circles represent Al atoms in the puckered A layer. Al atoms in the puckered A layer lie below the atomic vacancy sites of the flat layer. The small and large gray circles represent Mn and Al atoms in the puckered B layer, respectively. The atomic positions of the puckered B layer are below the interstices in the flat layer.

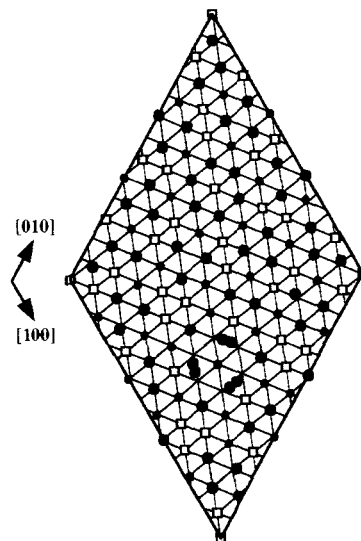


Fig.3. Structure in the flat layer with  $z=0.25$  of  $\lambda$ - $\text{Al}_4\text{Mn}$ . The small and large solid circles represent Mn and Al atoms, respectively. The squares represent the atomic vacancy sites. A triangular net represents a close-packed layer.

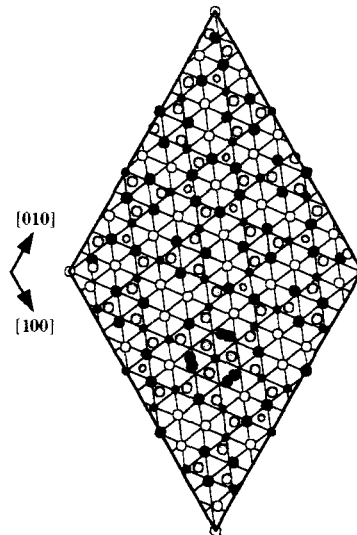


Fig.4. Structure in the flat and puckered layers with  $z=0.05-0.25$  of  $\lambda$ - $\text{Al}_4\text{Mn}$ . The small and large solid circles represent Mn and Al atoms, respectively, in the flat layer. The open circles represent Al atoms in the puckered A layer. Al atoms in the puckered A layer lie below the atomic vacancy sites of the flat layer. The small and large gray circles represent Mn and Al atoms in the puckered B layer, respectively. The atomic positions of the puckered B layer are below the interstices in the flat layer.

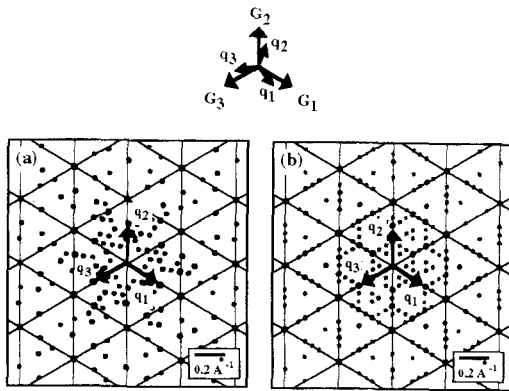


Fig.5. (a) Calculated EDP from the flat layer with  $z=0.50$  of  $\mu\text{-Al}_4\text{Mn}$  (b) that from the flat layer with  $z=0.25$  of  $\lambda\text{-Al}_4\text{Mn}$ . The diffraction spots located at the intersections of the solid lines are the basic spots. The radius of the diffraction spots is proportional to the diffraction intensity. The difference in the commensurate modulation wave vectors between the  $\mu\text{-Al}_4\text{Mn}$  phase and the  $\lambda\text{-Al}_4\text{Mn}$  phase is basically understood by the difference in the commensurate modulation wave vectors.

The results are shown in Fig.5. The spot positions can be interpreted by modulated structures as follows. In the case of the  $\mu\text{-Al}_4\text{Mn}$  phase, intense spots located at the intersections of solid lines are the basic spots of the hexagonal close-packed lattice. The magnitude of the reciprocal-lattice vectors corresponding to the basic spots is  $|G_i|=0.46 \text{ \AA}^{-1}$ , where the  $G_i$  are in-plane three reciprocal-lattice vectors and make angles of  $120^\circ$  with each other ( $i=1,2,3$ ). The other weak spots can be explained by assuming triple modulation waves. Two sets of the triple modulation waves have commensurate modulation vectors  $q_i$  with a magnitude  $(5/8)|G_i|$  and  $q'_i$  with a magnitude  $(3/8)|G_i|$  along the three  $G_i$  directions, respectively ( $i=1,2,3$ ). These are equivalent because their wavevectors can be mapped to each other by the translation of the reciprocal-lattice vector of the basic hexagonal lattice. The other spots are higher-order satellite spots.

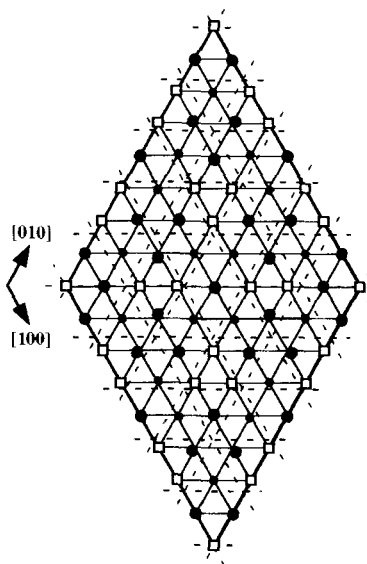


Fig.6. Schematic diagram showing the relationship between the atomic vacancy sites and CDWs in the flat layer with  $z=0.50$ . The small and large solid circles represent Mn and Al atoms, respectively. The squares represent the atomic vacancy sites. The dashed lines represent the minima of negative charge due to CDWs. The atomic vacancies locate at the sites near the minima in the negative charge derived by the superposition of triple CDWs.

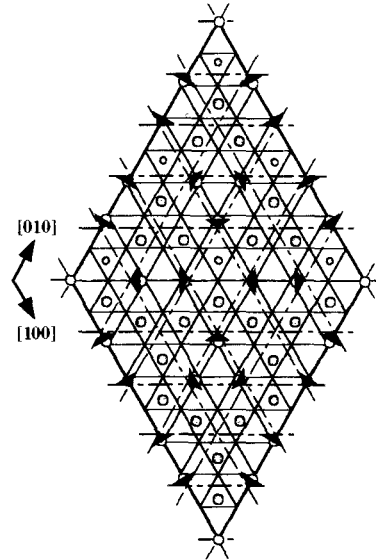


Fig.7. Atomic positions and displacements in the P layer with  $z=0.40-0.44$ . The open circles represent Al atoms in the puckered A layer. The small and large gray circles represent Mn and Al atoms, respectively, in the puckered B layer. The dash-dotted lines represent the maxima of negative charge due to CDWs. Al atoms in the puckered A layer locate at the sites near the maxima in the negative charge derived by the superposition of triple CDWs.

In the case of the  $\lambda$ -Al<sub>4</sub>Mn phase, the intense spots are built by the same reciprocal-lattice vectors of the basic hexagonal lattice as those of the  $\mu$ -Al<sub>4</sub>Mn phase, but triple modulation wave vectors are slightly different. The modulation wave vectors  $\mathbf{q}_i$  rotate away from the corresponding  $\mathbf{G}_i$  directions by an angle  $0.62^\circ$  ( $i=1,2,3$ ). The magnitude of the modulation wave vectors is  $0.616 |\mathbf{G}_i|$  ( $i=1,2,3$ ). It should be noted that the triple modulation waves are commensurate with the basic hexagonal lattice. That is, the difference between the  $\mu$ -Al<sub>4</sub>Mn phase and the  $\lambda$ -Al<sub>4</sub>Mn phase is basically understood by the difference in the commensurate modulation wave vectors.

### 2.3 ORIGIN OF THE MODULATION

We suggested that the modulation of the  $\mu$ -Al<sub>4</sub>Mn phase is due to the rearrangement of atomic vacancies as a response to the occurrence of charge density waves (CDWs) [2]. We consider a response of lattice system to the occurrence of CDWs. Since atoms in an alloy are positively ionized, the atoms occupy the atomic sites close to the maximum in the negative charge distribution due to CDWs, while the atomic vacancies rearrange to occupy the sites close to the minimum in the charge distribution. By the aforementioned procedure, it is possible to determine the atomic sites (atomic vacancy sites). Their wave vectors are known from the satellite positions given by  $\mathbf{q}_i$  in Fig.5(a). In the case of the flat layer with  $z=0.50$ , we assume the triple CDWs with wave vectors  $\mathbf{q}_i$  in the close-packed layer shown in Fig.6. The dashed lines represent the minimum of the CDW. The atomic vacancies locate at sites near the positions of the minimum in the the negative charge derived by the superposition of triple CDWs. The predicted atomic vacancy sites in the flat layer agree with the experimentally determined positions. In the case of the puckered layer with  $z=0.40$ - $0.44$ , the dash-dotted lines represent the maximum of the CDW with wave vectors  $\mathbf{q}_i$  as shown in Fig.7. The atoms in the puckered A layer occupy the atomic sites close to these maximum positions, and their sites agree with the experimentally determined positions. Furthermore, it can be seen that some of the Al atoms in the puckered A layer displace slightly but clearly toward the maximum in the negative charge due to the CDWs, as indicated by arrowheads in Fig.7. The

observed atomic arrangement in each layer strongly supports that the modulation is due to the occurrence of CDWs. Also in the  $\lambda$ -Al<sub>4</sub>M phase, we can explain the atomic arrangements as a response to the occurrence of the triple CDWs.

### 3. CONCLUSION

This result suggests that cluster ordering in complex alloys should be understood as a result of the rearrangement of atomic vacancies due to the CDWs.

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(Received December 8, 2000; Accepted February 8, 2001)