

A new stacking motif: complex alloy structures interpreted as modulated structures

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The structures of λ -Al₄Mn, manganese aluminide, κ -Al₁₇₇Cr₄₉Ni, chromium nickel aluminide, and ε -Al₄Cr, chromium aluminide, which have been described in terms of the aggregation of clusters until now, are interpreted as modulated structures. They are basically composed of close-packed layers with ordered atomic vacancies. The observed stacking motif of the atoms can be found in many phases related to icosahedral and decagonal quasicrystals. This analysis will be helpful in the study of not only many complex alloys, but also quasicrystals.

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1. Introduction

A number of complex alloys have been discussed in terms of clusters (Kreiner & Franzen, 1995; Nelson & Spaepen, 1989). This is also true of quasicrystals and approximants which are currently believed to have similar clusters, arranged quasi-periodically in the former and periodically in the latter (Yamamoto, 1996). The μ -Al₄Mn phase is one of the approximants and its structure has been described in terms of the aggregation of clusters (Shoemaker *et al.*, 1989; Kreiner & Franzen, 1995). Shoemaker and co-workers (Shoemaker *et al.*, 1989; Le Lann & Shoemaker, 1993) used it to deduce structure models of the icosahedral quasicrystal.

Recently we presented a new interpretation of the μ -Al₄Mn phase as a modulated crystal (Uchida & Horiuchi, 1999). It was shown that the structure is basically composed of close-packed layers with ordered atomic vacancies owing to the occurrence of charge-density waves. This interpretation is essentially different from the idea of packing clusters in the following respect: the existence of a basic structure with long-range translational periodicity such as a close-packed layer. In the present paper we report a similar study to see whether our interpretation without clusters can be extended to other phases, which have been described in terms of the aggregation of clusters. It is also important to find clues for building quasicrystals directly in the three-dimensional space. Examples are the λ -Al₄Mn (Kreiner & Franzen, 1997), κ -Al₁₇₇Cr₄₉Ni (Sato *et al.*, 1997; Marsh, 1998) and ε -Al₄Cr (Li, Sugiyama *et al.*, 1997) phases related to icosahedral quasicrystals.

2. A new stacking motif

Many complex alloys, including approximants such as the μ -Al₄Mn phase, are composed of stacked atom layers (Kreiner & Franzen, 1995). Examination of the μ -Al₄Mn structure allowed us to find a characteristic stacking motif of atoms (Uchida & Horiuchi, 1999). The stacking motif is illustrated in Fig. 1. It basically comprises three different types of layers A, B and C, which are stacked in the order C B A B C. The A

layer is a close-packed layer with atomic vacancies. Solid circles and squares in Fig. 1(a) represent atoms and atomic vacancy sites in the *A* layer, respectively. Atoms in the *B* layer are located above and below the atomic vacancy sites in the *A* layer, while atoms in the *C* layer are above and below the interstices in the *A* layer (Fig. 1b). Such a stacking motif can be found in many alloys, such as $\text{Al}_{10}\text{Mn}_3$ (Taylor, 1959), Al_5Co_2 (Newkirk *et al.*, 1961), Al_{23}V_4 (Ray & Smith, 1960), $\text{Mg}_{51}\text{Zn}_{20}$ (Higashi *et al.*, 1981), $\text{Al}_{12}\text{Fe}_2\text{Cr}$ (Sui *et al.*, 1997), $\lambda\text{-Al}_4\text{Mn}$ (Kreiner & Franzen, 1997), $\kappa\text{-Al}_{177}\text{Cr}_{49}\text{Ni}$ (Sato *et al.*, 1997; Marsh, 1998) and $\varepsilon\text{-Al}_4\text{Cr}$ (Li, Sugiyama *et al.*, 1997), phases which are related to icosahedral or decagonal quasicrystals (Uchida, 1998). We provide some examples in the following section.

3. Some examples of complex metallic alloys

3.1. $\lambda\text{-Al}_4\text{Mn}$ phase

There are two hexagonal structures with large unit cells near the composition of the icosahedral and decagonal

quasicrystals in the Al–Mn system, the $\lambda\text{-Al}_4\text{Mn}$ phase ($P6_3/m$, $a = 28.382$, $c = 12.38$ Å) and the $\mu\text{-Al}_4\text{Mn}$ phase ($P6_3/mmc$, $a = 19.98$, $c = 24.673$ Å). Their electron diffraction patterns (EDPs) are very similar to those of icosahedral quasicrystals (Bendersky, 1987). Kreiner & Franzen (1995, 1997) have determined the structure of the $\lambda\text{-Al}_4\text{Mn}$ phase by the single-crystal X-ray diffraction method and described it in terms of the aggregation of clusters.

Fig. 2 shows the projection of the structure along the [100] axis. As in the $\mu\text{-Al}_4\text{Mn}$ phase, the $\lambda\text{-Al}_4\text{Mn}$ phase has a

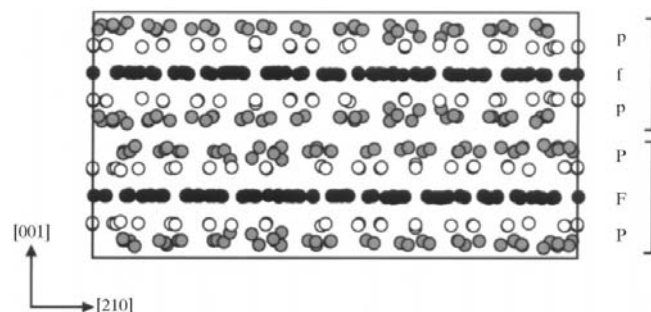


Figure 2

Projection of the structure of $\lambda\text{-Al}_4\text{Mn}$ along the [100] axis. There are six layers of the flat and puckered type along [001]. The solid circles represent atoms in the flat layers. The open and gray circles represent atoms in the puckered *A* and puckered *B* layers, respectively.

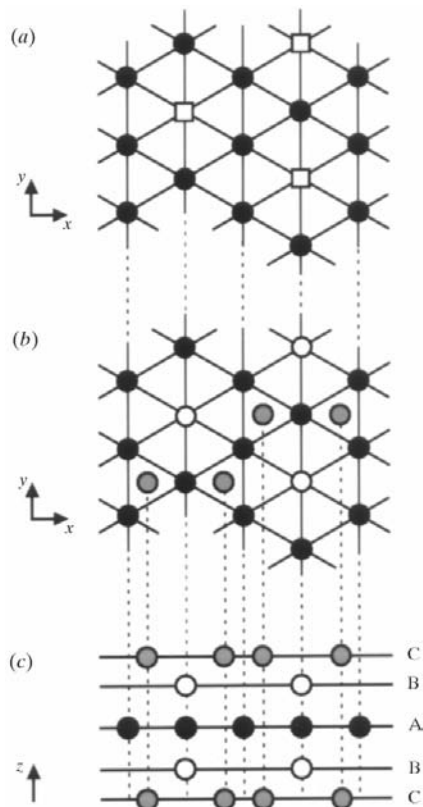


Figure 1

The stacking motif of atoms, as observed in the $\mu\text{-Al}_4\text{Mn}$ phase. (a) Structure in the *A* layer. The solid circles and squares represent atoms and atomic vacancy sites in the *A* layer, respectively. A triangular net represents a close-packed layer. (b) Structure of the *A*, *B* and *C* layers. The solid circles represent atoms in the *A* layer, the open circles those in the *B* layer and the gray circles those in the *C* layer. Atoms in the *B* layer are located above and below the atomic vacancy sites in the *A* layer, while atoms in the *C* layer are above and below the interstices in the *A* layer. (c) Side projection of the structure. The *A*, *B* and *C* layers are stacked in the order *C B A B C*.

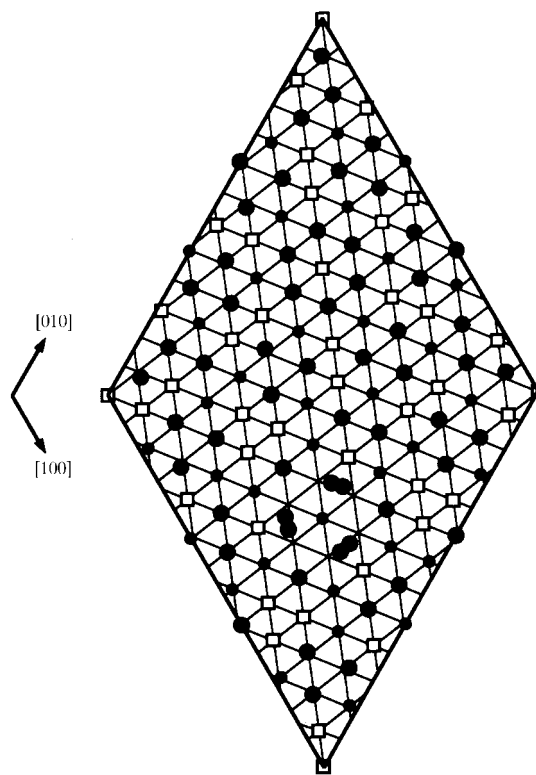


Figure 3

Structure in the *F* 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.

similar type of layer structure, *i.e.* six layers along the *c* axis, two flat layers (*F* and *f*) and four puckered layers (*P* and *p*), which are stacked in the order *P F P p f p*. The *F* layer is located on the mirror plane at $z = 0.25$, while the *P* layers are above and below the *F* layer. The *p f p* layers are related to the *P F P* layers by a 2_1 screw axis.

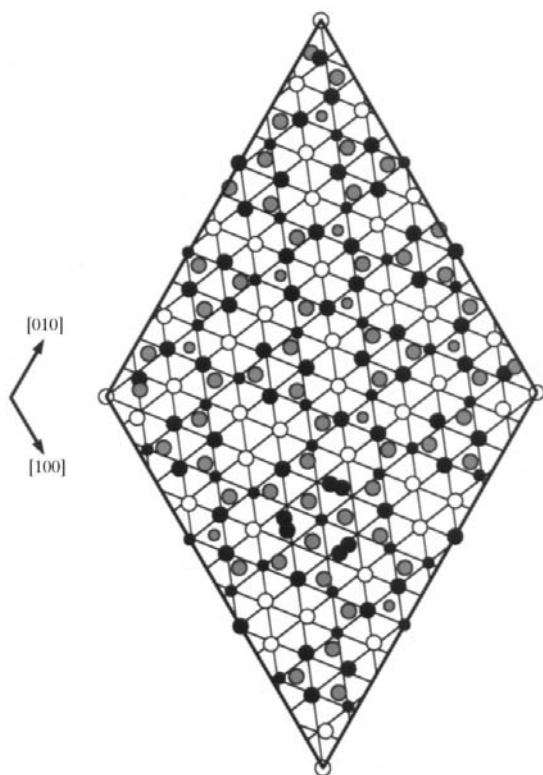


Figure 4
Structure in the *F* and *P* layers between $z = 0.05$ and 0.25 of λ - Al_4Mn . The small and large solid circles represent Mn and Al atoms, respectively, in the *F* layer. The open circles represent Al atoms in the puckered *A* layer. Al atoms in the puckered *A* layer lie below the atomic vacancy sites of the *F* 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 *F* layer.

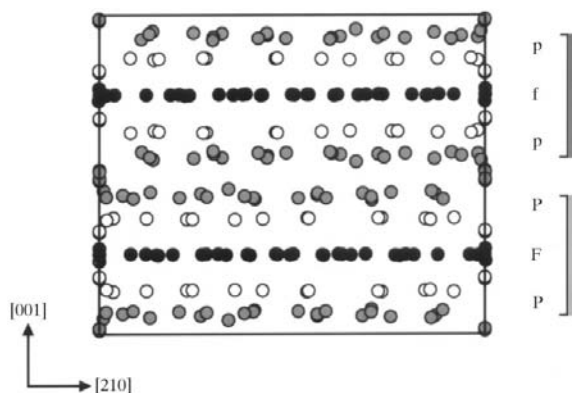


Figure 5
Projection of the structure of κ - $\text{Al}_{177}\text{Cr}_{49}\text{Ni}$ along the $[100]$ axis. There are six layers of flat and puckered type along $[001]$. The solid circles represent atoms in the flat layers. The open and gray circles represent atoms in the puckered *A* and *B* layers, respectively.

We now focus on the *F* layer with $z = 0.25$. Solid circles in Fig. 3 show the *c* projection of the arrangement of atoms in the *F* layer. This layer forms a triangular arrangement of atoms and contains apparent holes marked by squares, hereafter known as the atomic vacancy sites in the close-packed layer. It is then understood that the *F* layer is a close-packed layer with an ordered arrangement of atomic vacancies forming a hexagonal supercell.

The stacking motif of atoms in the *P* layers is the same as that mentioned in §2. Fig. 4 shows the *c* projection of atoms in both the *F* and *P* layers with $z = 0.05$ – 0.25 , where solid circles represent atoms in the *F* layer, open circles those in the puckered *A* layer with $z = 0.12$ – 0.14 and gray circles those in the puckered *B* layer with $z = 0.05$ – 0.10 . Atoms in the puckered *A* layer are located below the atomic vacancy sites in the *F* layer, while atoms in the puckered *B* layer are below the interstices in the *F* layer.

3.2. κ - $\text{Al}_{177}\text{Cr}_{49}\text{Ni}$ phase

The κ - $\text{Al}_{177}\text{Cr}_{49}\text{Ni}$ phase with large unit cell ($P6_3/m$, $a = 17.674$, $c = 12.516$ Å) is a hexagonal phase related to icosahedral quasicrystals (Sato *et al.*, 1997; Marsh, 1998). It gives EDPs similar to those of icosahedral quasicrystals (Li, Hiraga & Yamamoto *et al.*, 1997). Li, Hiraga *et al.* (1997) described the structure of the κ - $\text{Al}_{177}\text{Cr}_{49}\text{Ni}$ phase in terms of the aggregation of clusters.

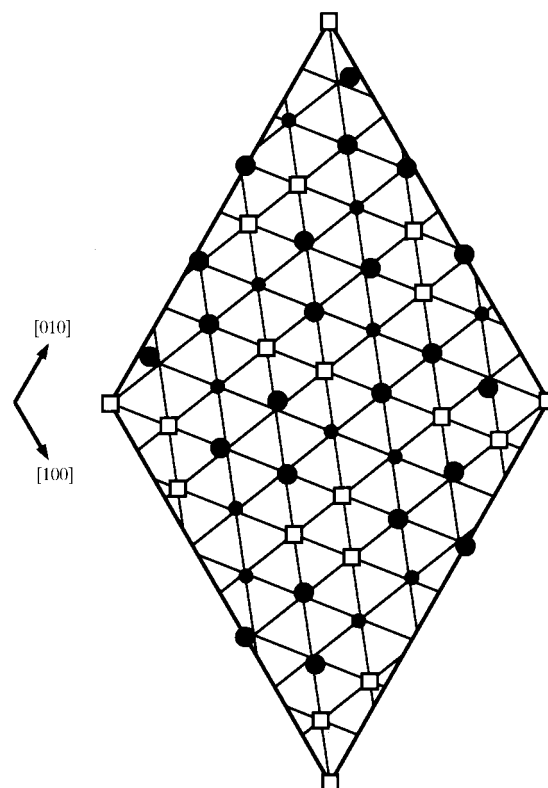


Figure 6
Structure in the *F* layer with $z = 0.25$ of κ - $\text{Al}_{177}\text{Cr}_{49}\text{Ni}$. The small and large solid circles represent Cr (Ni) and Al atoms, respectively. The squares represent the atomic vacancy sites. A triangular net represents a close-packed layer.

Fig. 5 shows the projection of the structure along the [100] axis. The structure of the κ -Al₁₇₇Cr₄₉Ni phase is composed of six layers stacked perpendicularly to the *c* axis, *i.e.* two flat layers (*F* and *f*) and four puckered layers (*P* and *p*), which are stacked in the order *PFPpfP*. The *F* layer is located on the mirror plane at *z* = 0.25, while the *P* layers are above and below the *F* layer. The *pfP* layers are related to the *PFP* layers by a 2₁ screw axis.

We now focus on the *F* layer with *z* = 0.25. Solid circles in Fig. 6 show the *c* projection of the arrangement of atoms in the *F* layer. As in the λ -Al₄Mn phase, it is understood that the *F* layer is a close-packed layer with an ordered arrangement of atomic vacancies forming a hexagonal supercell.

The stacking motif of atoms in the *P* layer is the same as that mentioned in §2. Fig. 7 shows the *c* projection of atoms in both the *F* and *P* layers with *z* = 0.01–0.25, where solid circles represent atoms in the *F* layer, open circles those in the puckered *A* layer with *z* = 0.13–0.18 and gray circles those in the puckered *B* layer with *z* = 0.01–0.08. Although with some exceptions, atoms in the puckered *A* layer are located below the atomic vacancy sites in the *F* layer, atoms in the puckered *B* layer are below the interstices in the *F* layer.

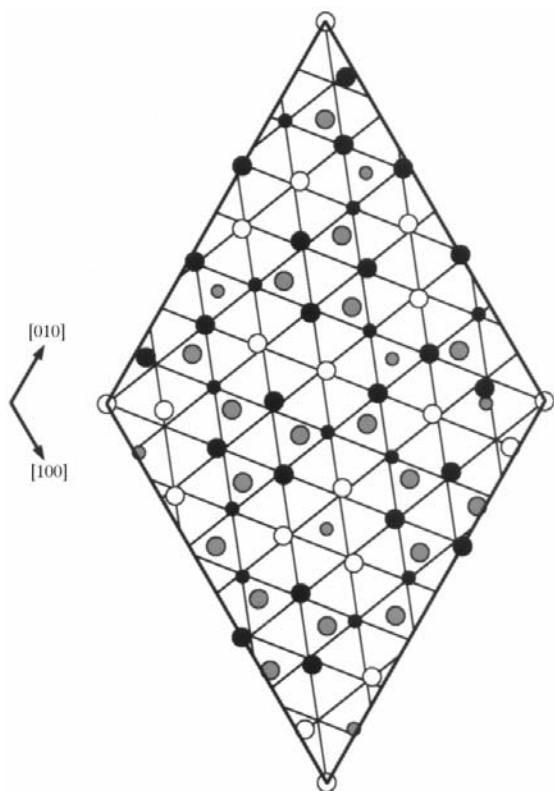


Figure 7
Structure in the *F* and *P* layers between *z* = 0.01 and 0.18 of κ -Al₁₇₇Cr₄₉Ni. The small and large solid circles represent Cr (Ni) and Al atoms, respectively, in the *F* layer. The open circles represent Al atoms in the puckered *A* layer. Al atoms in the puckered *A* layer lie below the atomic vacancy sites of the *F* layer. The small and large gray circles represent Cr (Ni) and Al atoms in the puckered *B* layer, respectively. The atomic positions of the puckered *B* layer are below the interstices in the *F* layer.

3.3. ϵ -Al₄Cr phase

The ϵ -Al₄Cr phase (*Cmcm*, *a* = 12.521, *b* = 34.705, *c* = 20.223 Å) is an orthorhombic phase related to icosahedral quasicrystals. It gives EDPs similar to those of icosahedral quasicrystals (Wen *et al.*, 1992). Li, Sugiyama *et al.* (1997) have determined its structure and described it in terms of the aggregation of clusters.

Fig. 8 shows the projection of the structure along the [001] axis. The structure of the ϵ -Al₄Cr phase is made of six layers stacked perpendicularly to the *a* axis, *i.e.* two flat (*F* and *f*) layers and four puckered (*P* and *p*) layers, which are stacked in the order *F P p f p P F*. The *F* layer is located on the mirror

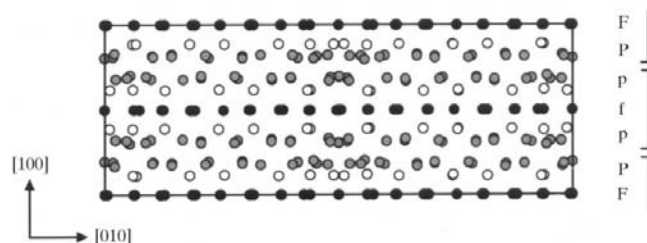


Figure 8
Projection of the structure of ϵ -Al₄Cr along the pseudo-fivefold [001] axis. There are six layers of flat and puckered type along [100]. The solid circles represent atoms in the flat layers. The open and gray circles represent atoms in the puckered *A* and puckered *B* layers, respectively.

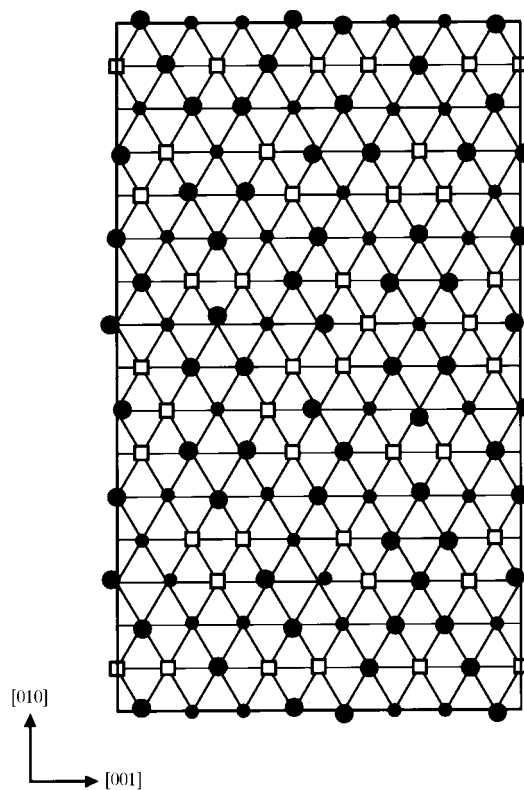


Figure 9
Structure in the *F* layer with *x* = 0 of ϵ -Al₄Cr. The small and large solid circles represent Cr and Al atoms, respectively. The squares represent the atomic vacancy sites. A triangular net represents a distorted close-packed layer.

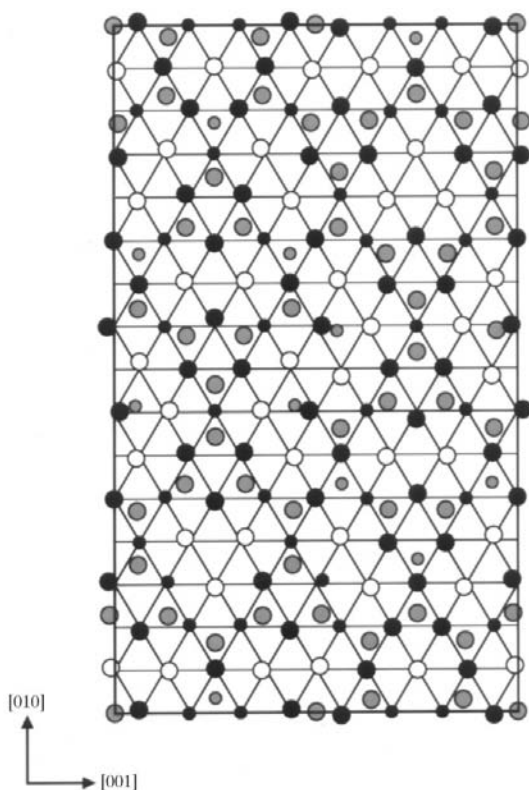


Figure 10

Structure of the F and P layers between $x = 0$ and 0.20 of ε - Al_4Cr . The small and large solid circles represent Cr and Al atoms, respectively, in the F layer. The open circles represent Al atoms in the puckered A layer. Al atoms in the puckered A layer lie above the atomic vacancy sites of the F layer. The small and large gray circles represent Cr and Al atoms in the puckered B layer, respectively. The atomic positions of the puckered B layer are above the interstices in the F layer.

plane at $x = 0$, while the P layers are above and below the F layer. The pfp layers are related to the $PF P$ layers by an n -glide mirror plane, $(a + b)/2$ shift.

We now focus on the F layer with $x = 0$. Solid circles in Fig. 9 show the a projection of the arrangement of atoms in the F layer. As in the λ - Al_4Mn phase, it is understood that the F layer is a layer with an ordered arrangement of atomic vacancies forming a rectangular supercell. It should be noted that this layer is slightly distorted from a close-packed triangular lattice.

The stacking motif of atoms in the P layers is the same as that mentioned in §2. Fig. 10 shows the a projection of atoms in both the F and P layers with $x = 0$ – 0.20 , where solid circles

represent atoms in the F layer, open circles those in the puckered A layer with $x = 0.11$ – 0.12 and gray circles those in the puckered B layer with $x = 0.17$ – 0.20 . Although with some exceptions, atoms in the puckered A layer are located above the atomic vacancy sites in the flat layer, while atoms in the puckered B layer are above the interstices in the F layer.

4. Conclusions

We have given three additional examples. These results indicate that the stacking motif previously reported for the μ - Al_4Mn phase is not an isolated quirk of nature, but seems to be a more general principle. Our result leads us to substitute for the concept of clusters; this approach will be helpful in the study of not only many complex alloys, but also quasicrystals.

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