Transactions of the Materials Research Society of Japan 25 [4] 1033-1036 (2000)

Are there clusters in alloys ?

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The structures of λ-Al_4Mn and ε-Al_4Cr, 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 atoms can be found in many phases related to icosahedral and decagonal quasicrystals.

Key words: complex alloys, modulated crystal, stacking motif, cluster, quasicrystal

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. The μ-Al_4Mn phase is one of the approximants and its structure has been described in terms of the aggregation of clusters [1][2]. Recently, we presented a new interpretation of the μ-Al_4Mn phase as a modulated crystal [3]. It was shown that the structure is basically composed of close-packed layers with ordered atomic vacancies due to the occurrence of charge-density waves. This interpretation is essentially different from the idea of packing clusters. 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. Examples are the λ-Al_4Mn [4] and ε-Al_4Cr [5] phases.

2. EXAMPLES OF COMPLEX ALLOYS

2.1 λ-Al_4Mn 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 λ-Al_4Mn phase ($P6_3/m$, a=28.382 Å, c=12.389 Å) and the μ-Al_4Mn phase ($P6_3/mmc$, a=19.98 Å, c=24.673 Å). Their electron diffraction patterns (EDPs) are very similar to those of icosahedral quasicrystals [6]. Kreiner and Franzen have determined the structure of the λ-Al_4Mn phase by the single-crystal X-ray diffraction method and described in terms of the aggregation of clusters [1][4].

Fig.1 shows the projection of the structure along the [100] axis. Like the μ-Al_4Mn phase, the λ-Al_4Mn phase has a 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 of 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.

We now focus on the F layer with z=0.25. Solid circles in Fig.2 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. Here, we call them 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.

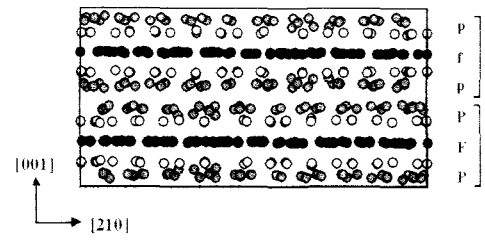

Fig.1. Projection of the structure of λ-Al_4Mn along the [100] axis. There are six layers of the flat and puckered type along the [001]. The solid circles represent atoms in the flat layers. The open and gray circles represent atoms in the puckered A and puckered B layers, respectively.

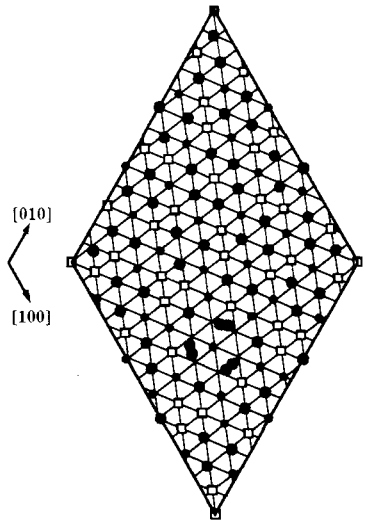

Fig.2. Structure in the F layer with z=0.25 of λ-Al_4Mn. The small and large solid circles represent Mn and Al atoms, respectively. The squares represent the atomic vacancy sites. A triangular net represents a close-packed layer.

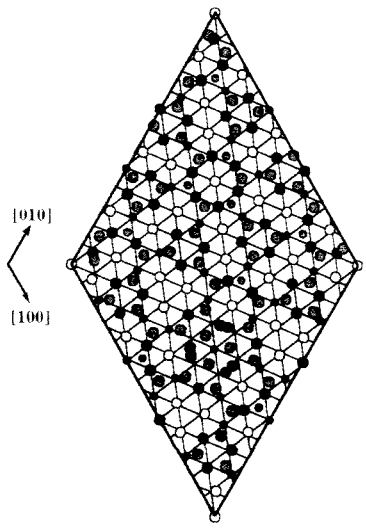

Fig.3. Structure in the F and P layers between z=0.05 and 0.25 of λ-Al_4Mn. The small and large solid circles represent Mn and Al atoms, respectively, in the F layer. The open circles represent Al atoms in the puckered A layer. Al atoms in the puckered A layer lie below the atomic vacancy sites of the 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.

The stacking motif of atoms in the P layers is the same as in the μ-Al_4Mn phase. Fig.3 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 ε-Al_4Cr phase

The ε-Al_4Cr phase (Cmcm, a=12.521 Å, b=34.705 Å, c=20.223 Å) is a orthorhombic phase related to icosahedral quasicrystals. It gives EDPs similar to those of icosahedral quasicrystals [7]. Li et al. have determined its structure and described it in terms of the aggregation of clusters [5].

Fig.4 shows the projection of the structure along the [010] axis. The structure of the ε-Al_4Cr 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 of F P p f p P F. The F layer is located on the mirror plane at x=0, 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 n-glide mirror plane, (a+b)/2 shift.

We now focus on the F layer with x=0. Solid circles in Fig.5 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

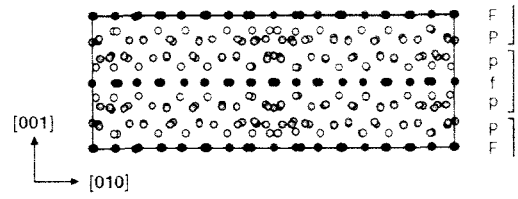

Fig.4. Projection of the structure of ε-Al_4Cr along the pseudo-fivefold [010] axis. There are six layers of flat and puckered type along the [100]. The solid circles represent atoms in the flat layers. The open and gray circles represent atoms in the puckered A and puckered B layers, respectively.

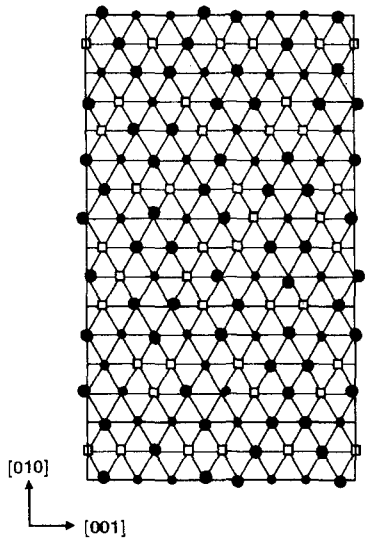

Fig.5. Structure in the F layer with x=0 of ε-Al_4Cr. The small and large solid circles represent Cr and Al atoms, respectively. The squares represent the atomic vacancy sites. A triangular net represents a distorted close-packed layer.

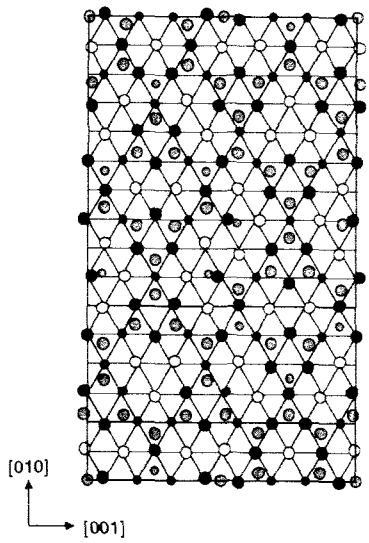

Fig.6. Structure of the F and P layers between x=0 and 0.20 of ε-Al_4Cr. The small and large solid circles represent Cr and Al atoms, respectively, in the F layer. The open circles represent Al atoms in the puckered A layer. Al atoms in the puckered A layer lie above the atomic vacancy sites of the F 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.

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 in the μ-Al_4Mn phase. Fig.6 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. 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.

3. CONCLUSION

We have given two 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. We can also find the stacking motif in many alloys, such as $Al_{10}Mn_3$ [8], Al_5Co_2 [9], $Al_{23}V_4$ [10], $Mg_{51}Zn_{20}$ [11], $Al_{12}Fe_2Cr$ [12] and κ-$Al_{177}Cr_{49}Ni$ [13][14], phases related to icosahedral and decagonal quasicrystals [15]. Our results lead 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.

ACKNOWLEDGMENTS

The authors would like to thank Dr. S. Horiuchi of NIRIM for discussions.

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(Received December 17, 1999; Accepted August 16, 2000)