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Electron microscopy study of approximant phases in Al-Cr-Fe system

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We have characterized by transmission electron microscopy several new phases we have discovered in bulk alloys of the Al-Cr-Fe system. These structures are an icosahedral compound and several approximants of the decagonal phase. According to the indexation of the electron diffraction patterns (EDPs), some of the approximants are not of Fibonacci type. These EDPs correspond to nanodomains, which are due to disorder introduced by quenching the alloys after melting the pure constituent metals. For these new types of approximants, we propose a crystallographic description related to the usual Fibonacci description. In addition, we suggest a construction of the corresponding tilings. The orientation relationships between these structures are described.

Keywords: Quasicrystal; Approximant; Al-Cr-Fe system; Electron transmission microscopy

1. Introduction

The Al-Cr-Fe system is known to contain a metastable icosahedral phase (i-AlCrFe) [1] and several orthorhombic approximants of the decagonal phase. These structures are: the so-called O₁-AlCrFe orthorhombic compound [2], originally discovered in the Al-Cu-Cr-Fe system by Dong and Dubois [3], the O₂-AlCrFe compound [4], also first observed in the same Al-Cu-Fe-Cr system [3], whereas the C_{3,I}-AlCrFe compound [1] was first discovered in the Al-Mn-Ni system [5]. All these phases are Fibonacci approximants. The lattice parameters of Fibonacci orthorhombic approximants were expressed by Zhang and Kuo as [6]:

$$\begin{aligned} a &= \frac{\sqrt{5}a_R \tau^{n+1}}{\sqrt{2+\tau}} = 4.73\tau^{n+1} \\ c &= \sqrt{5}a_R \tau^n = 9.01\tau^n \end{aligned} \quad (1)$$

where τ is the golden number ($\tau = \frac{1+\sqrt{5}}{2} = 1.618 \dots$), a_R is the edge length of the Penrose rhombus ($a_R = 4.03 \text{ \AA}$ for the decagonal phase [7]) and n is an integer.

These relationships could be rewritten as:

$$\begin{aligned} a &= a_{\frac{p}{q}} = \frac{\sqrt{5}a_R (p\tau + q)}{\sqrt{2+\tau}} \\ c &= c_{\frac{p}{q}} = \sqrt{5}a_R \left(p + \frac{q}{\tau}\right) \end{aligned} \quad (2)$$

where p , q and p' , q' are consecutive numbers of the Fibonacci sequence (i.e. 0, 1, 1, 2, 3, 5, 8, ...). It is well known that the link between a quasicrystal and one of its approximant corresponds to replacing the golden number τ by the ratio between two terms of the Fibonacci

sequence (actually by any rational close to τ). The obtained values of lattice parameters for orthorhombic approximant phases are listed in table I.

Sui *et al.* have observed and described another orthorhombic phase in the Al-Cr-Fe system, namely the O-phase, and demonstrated that this compound is not of Fibonacci type along the [001] direction [8]. This phase was previously discovered in several other alloy systems [9].

2. Observation and description of non-Fibonacci compounds

We have prepared bulk Al-Cr-Fe alloys with the help of an induction furnace, with a fast air cooling, and then obtained samples suitable for transmission electron microscopy (TEM) by crushing small alloy pieces or by mechanical polishing followed by an ion milling treatment.

We have observed the icosahedral phase previously reported in the system. Figure 1 shows EDPs taken along two main zone axes of the structure. Indexation of these patterns allows us to ascertain this sample as a F-type icosahedral phase.

We have observed two new orthorhombic approximant phases by TEM, designated in the following by O_A and O_B , respectively. The O_A -phase was already observed in the Ga-Mn system [10]. Figure 2 presents the EDPs of both phases along their respective [010] zone axis. Indexation of these patterns gives the following lattice parameters: $a = 45.4 \text{ \AA}$, $b = 12.4 \text{ \AA}$, $c = 14.7 \text{ \AA}$ for O_A and $a = 70.5 \text{ \AA}$, $b = 12.4 \text{ \AA}$, $c = 14.7 \text{ \AA}$ for O_B .

The O_A and O_B phases are not Fibonacci approximants along the [100] direction according to the definition presented in the first part of this paper. We can however present a new definition for non-Fibonacci compounds that is closely related to the one corresponding to Fibonacci approximants:

$$\begin{aligned}
 a' &= \frac{\sqrt{5}a_R \tau^2}{\sqrt{2+\tau}} (\tau + n - 1) = 12.38(\tau + N) \\
 c' &= \frac{5a_R \tau^2}{2+\tau} (\tau + n - 1) = 14.58(\tau + N)
 \end{aligned}
 \tag{3}$$

The relationships between the lattice parameters of Fibonacci and non-Fibonacci approximants can be deduced from equations (2) and (3):

$$\begin{aligned}
 a' &= a \frac{\tau(n+1) + n}{\tau^{n+1}} = a \frac{n\tau + 1}{\tau^n} \\
 c' &= c \frac{\sqrt{5}}{2+\tau} \frac{\tau(n+1) + n}{\tau^n} = c \frac{n\tau + 1}{\tau^n}
 \end{aligned}
 \tag{4}$$

The so-obtained values of the lattice parameters for non-Fibonacci approximants are listed in table I.

As previously seen in the first part of this article, the Fibonacci-type of approximants is described by an inflation of τ^n . Conversely, in non-Fibonacci-type of approximants, the successive lattice parameters are obtained *via* an increment of $(\tau + N)$ with $N = n-1$. O_A and O_B -phases are then described using an increment of $\tau + 2$ and $\tau + 4$, respectively. Phases with increment of $\tau + 3$, $\tau + 4$ and $\tau + 5$ were observed in the Al-Pd [11, 12], Al-Pd-Mn [13], Al-Pd-Co [14] and Al-Pd-Mn systems [15], respectively (see table II).

This approach is directly linked to the tiling geometry of these approximants. It is well known that an approximant phase of the decagonal quasicrystal can be represented by a model considering the clusters building up the structure. Indeed, looking along the direction that corresponds to the periodic direction of the quasicrystal, allows us to observe the projection of columns of these clusters. A schematic tiling of the structure is then obtained by linking the center of each cluster to the center of the other adjacent clusters. A model of phases

possessing a periodicity $b = 12.5 \text{ \AA}$ is based on elongated hexagons with an edge length equal to 6.60 \AA . As an example, the orthorhombic approximant with a lattice parameter equal to $a = 12.45 \text{ \AA}$, is described by rows of such kinds of hexagons in alternating orientations (then, the increment value is simply τ) (figure 3a). Such a compound was observed in the Al-Mn system [16]. A tiling built up with crown tiles (with the same edge length than the previous hexagon) leads to an orthorhombic cell with $a = 20.3 \text{ \AA}$ (i.e. with an increment of $\tau+0$) (figure 3b). This phase was observed in the Ga-Mn system [17]. A tiling constituted by a succession of rows of elongated hexagons and rows of crowns corresponds to the O_A structure (single row of hexagon, increment of $\tau+2$) (figure 3c) and to the O_B structure (two rows of hexagons, increment of $\tau+4$) (figure 3d). The O_B -phase can therefore be considered as a superstructure of the O_A -phase, with the following orientation relationships: $[100]_{OA} // [100]_{OB}$, $[010]_{OA} // [010]_{OB}$ and $[001]_{OA} // [001]_{OB}$.

It is particularly important to underline here that the same approach using an approximant possessing a periodicity along the pseudo-tenfold axis equal to 16.6 \AA allows us to describe the compounds with increment of $\tau+3$ and $\tau+5$. In this case, the basic tiling unit is a flattened hexagon with an edge length of 7.76 \AA . The tile which is the **equivalent** of the crown for approximants with $b = 12.5 \text{ \AA}$, is a regular pentagon attached to a banana-shaped polygon. The phase with an increment of $\tau+3$ is then described by rows of this large tile separated by one row of flattened hexagons whereas the structure with a $\tau+5$ increment presents two rows of such hexagons (see schemes in [15]). The banana+pentagon tile is considered as a defect in the structure constituted by only flattened hexagons, for example in the ξ' -AlPdMn compound [18]. Indeed, deformation experiments of ξ' -AlPdMn lead to the formation of planar arrays of such defects [19]. Nevertheless, Yurechko *et al.* have demonstrated that the ε_{28} -AlPd phase ($\tau+3$ structure) is a high temperature stable phase and a superstructure of the ε -AlPd phase, or in other words not only a defect structure [12]. In our case, the O_A and O_B phases were

observed in a **air** quenched sample, which is constituted by nanodomains of several other structures. These phases are moreover metastable. It is therefore not possible to decide definitely whether they are defect structures or true phases.

3. Conclusion

Our investigation of Al-Cr-Fe alloys by TEM has allowed the observation of two new orthorhombic approximants. These structures are non-Fibonacci approximants along the [100] direction, according to the usual definition of an approximant of the decagonal phase. We proposed here a new crystallographic description for these compounds. A tiling model was also proposed here, based on periodic planar arrays of a suitable defected tile (namely, the crown tile).

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Table I. Values of lattice parameters for Fibonacci and non-Fibonacci approximants of the decagonal phase.

n	Fibonacci approximant		Non-Fibonacci approximant	
	a (Å)	c (Å)	a' (Å)	c' (Å)
0	7.6	9.0	7.6	9.0
1	12.3	14.3	20.6	23.4
2	19.9	23.4	32.5	37.9
3	32.3	37.9	44.9	52.7
4	52.5	61.3	57.3	67.3
5	84.9	99.2	69.7	81.9
6	137.4	160.5	82.1	96.5

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Table II. Examples of non-Fibonacci approximants.

Increment	Lattice parameter a' (Å)	Phase	References
$\tau+2$	44.9	O_A -AlCrFe, Ga_7Mn_5	This study, [10]
$\tau+3$	57.3	ϵ_{28} -AlPd, Ψ -AlPdMn	[11-13, 15]
$\tau+4$	69.7	O_B -AlCrFe, ϵ_{34} -AlPdCo	This study, [14]
$\tau+5$	82.1	ξ_5 -AlPdMn	[15]

Figure captions

Figure 1. EDPs of the icosahedral phase observed in the Al-Cr-Fe system. a) Along the five-fold axis. b) Along the two-fold axis.

Figure 2. EDPs of approximants observed in the Al-Cr-Fe system. a) Along the [010] axis of O_A -AlCrFe. b) Along the [010] axis of O_B -AlCrFe.

Figure 3. Tiling models. a) Al_3Mn phase [16]. b) Ga_7Mn phase [17]. c) O_A -phase. d) O_B -phase.

Figure 1

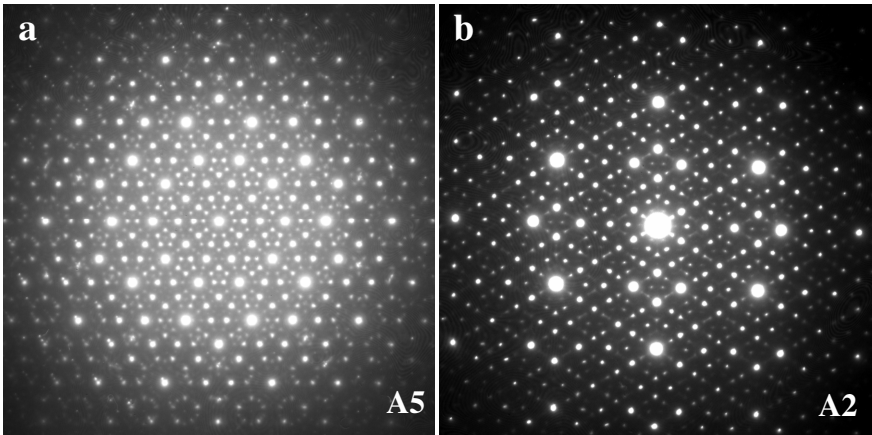


Figure 2

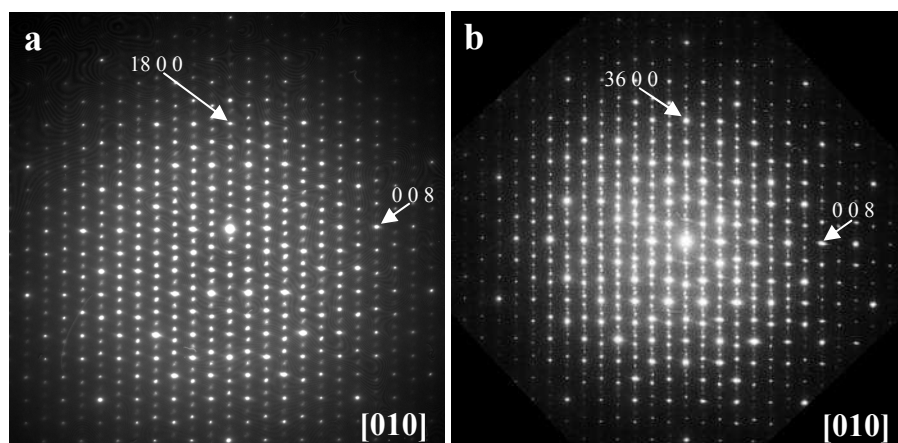


Figure 3

