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## Short Communication

# Theory of the formation of quasicrystals

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**Résumé.** — Un modèle théorique est proposé pour expliquer la formation des alliages quasicristallins. La phase icosahédrique résulte dans ce modèle, d'une transition reconstructive de type displacif à partir d'une phase mère cristalline. Le mécanisme de la transition met en jeu deux paramètres d'ordre distincts : un champ de déplacements qui transforme certains sous-réseaux cristallins en assemblages icosahédriques, et une onde de densité qui brise de façon incommensurable l'ordre translationnel de la phase mère. Les principaux aspects de la théorie sont introduits à travers l'exemple de AlMnSi.

**Abstract.** — A theoretical model is proposed for the formation of quasicrystalline alloys. The icosahedral phase is shown to result from a reconstructive transition of the displacive type from a parent crystalline structure. Two order parameters are involved in the transition mechanism: a displacement field which transforms a number of sublattices into icosahedral clusters, and an icosahedral density wave which breaks incommensurately the initial translational order. The main features of the model are introduced through the illustrative example of AlMnSi.

The phenomenological models which have been proposed to explain the stability of the icosahedral (Ic) phases [1-4] refer to the ideas introduced by Landau [5], and to their extension by Alexander and McTague [6], for the description of the liquid-to-solid transition. The choice of the isotropic liquid as a parent phase for the Ic structure stems from the fact that initially this structure could only be obtained in certain cooling conditions, below the range of stability of the liquid phase. However, more recent experiments [7-9] revealed that one could get an Ic structure under as-equilibrium conditions, and that a quasicrystalline phase could coexist with, or could be obtained from, other crystalline structures. Following these considerations, the theory presented in this paper starts from a solid crystalline phase as the parent structure for the Ic phase. More precisely, the Ic phase is shown to result from a reconstructive transition of the displacive type [10] from a crystal phase. The transition mechanism occurs in two steps: a displacement field which leads to the formation of icosahedral atomic clusters, preserving the initial unit-cell, and an icosahedral density wave, which destroys the initial periodicity and leads to icosahedral quasiperiodicity.

Let us introduce the essential features of our model through the illustrative example of AlMnSi,

and start from the cubic  $\alpha$ -AlMnSi structure as described by Cooper [11]. The 138 atoms contained in one unit-cell of the  $\alpha$  phase (space-group Pm3) decompose into 11 orbits which, according to the labelling of reference [11], can be shared into three groups: Al(1), Al(2), and Al(7) are characterized by a 6-fold position; Al(3), Al(4), Al(8), Al(9), Mn(1), and Mn(2) possess a 12-fold degeneracy; Al(5) and Al(6) display a 24-fold degeneracy.

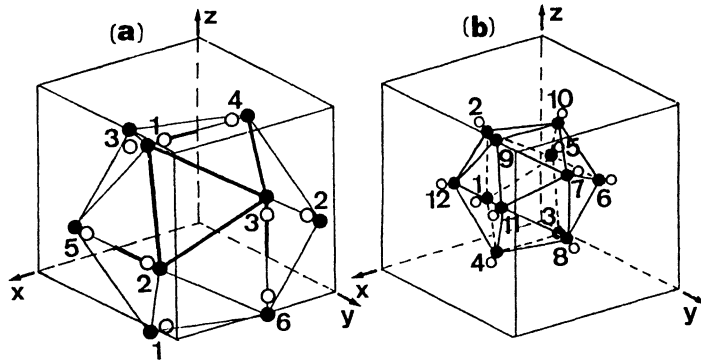


Fig. 1. — Icosahedra formed by the atoms belonging to the Al(7) (Fig. 1a), and Mn(2) (Fig. 1b) sublattices. White and black atoms represent the cubic and icosahedral positions, respectively.

We first focus on the atoms of the Al(7) orbit. From figure 1a one can see that *antiparallel displacements* of each pair of atoms, denoted (1, 4), (2, 5), and (3, 6) in figure 1a, along the respective cubic directions [100], [010], and [001], bring the twelve atoms forming the Al(7) orbit, i.e. the three preceding pairs plus the translationally equivalent atoms, to form an icosahedron for the specific displacements of magnitude  $0.244 \text{ \AA} = 0.0194 a$ , where  $a = 12.56 \text{ \AA}$  is the lattice parameter of the cubic unit-cell [11]. The same displacement field applied to the atoms of the orbits Mn(1), Mn(2), Al(3) and Al(4) also give icosahedral clusters. Thus, Al(3), Mn(1), and Al(7) form three embedded icosahedra of increasing volume, centered at the origin of the unit-cell, whereas Al(4) and Mn(2) form two embedded icosahedra centered at  $1/2, 1/2, 1/2$  (Fig. 1b). Table I summarizes the magnitude of the displacements corresponding to each of the preceding orbits. Besides, one can show that under the same displacement field the atoms pertaining to the Al(1) and Al(2) orbits give *octahedral* clusters (respectively centered at  $1/2, 1/2, 1/2$  and  $0, 0, 0$ ) Al(9) and Al(11) become *cuboctahedra* (centered at  $1/2, 1/2, 1/2$ ), whereas Al(5) and Al(6) remain regular polyhedra with 24 vertices.

Let us now determine the symmetry of the order-parameter associated with the assumed displacive mechanism, and show that the resulting cubic structure with icosahedral clusters is *thermodynamically stable*. The basis function spanning the antiparallel displacements of the Al(7) atoms, can be written, using the notation of figure 1a:  $\psi = x_1 - x_4 + y_2 - y_5 + z_3 - z_6$ . It transforms as the *identity representation*, denoted  $\tau_1$ , of the Pm3 space-group at the center ( $k=0$ ) of the primitive cubic Brillouin-zone. One can easily verify that although the atomic displacements associated with the other orbits are different (i.e. they are spanned by different basis functions), they transform as the same irreducible representation  $\tau_1$ . Accordingly, *the whole displacement field is associated with a one-component order parameter  $\eta$ , which has the symmetry of  $\tau_1$* . The corresponding thermodynamic potential can thus be written [12]:  $F(\eta) = F_0 + \frac{a}{2}\eta^2 + \frac{b}{3}\eta^3 + \frac{c}{4}\eta^4$ .

Because of the magnitude of the atomic displacements which lead to the icosahedral clusters (see Tab. I), it should be unphysical to put forward a linear relation ship between the order-parameter and the displacements, as it is usual in the standard Landau theory of structural transi-

Table I. — *Magnitude of the displacements which lead to the formation of icosahedral clusters. Columns (1) to (5) give respectively: (1) the notation of the sublattices from reference [11]; (2) the crystallographic positions in the cubic unit-cell; (3) experimental positions (from Ref. [11]) for the cubic clusters; (4) calculated positions for the icosahedral clusters; (5) conditions fulfilled by the icosahedral coordinates.  $\phi$  is the golden mean.*

(1)	(2)	(3)			(4)			(5)
		$x/a$	$y/a$	$z/a$	$x/a$	$y/a$	$z/a$	
Mn(1)	12j	0.3271	0.2006	0.0	0.33	0.2039	0.0	$\frac{y_{ic}}{x_{ic}} = \frac{1}{\phi}$
Mn(2)	12k	0.1797	0.3085	0.5	0.18	0.3022	0.5	$\frac{0.5 - y_{ic}}{0.5 - x_{ic}} = \frac{1}{\phi}$
Al(3)	12j	0.1636	0.0997	0.0	0.165	0.102	0.0	$\frac{y_{ic}}{x_{ic}} = \frac{1}{\phi}$
Al(4)	12k	0.3342	0.3990	0.5	0.335	0.398	0.5	$\frac{0.5 - y_{ic}}{0.5 - x_{ic}} = \frac{1}{\phi}$
Al(7)	6f	0.2897	0.0	0.5	0.3091	0.0	0.5	$x_{ic} = 0.3091$ $z_{ic} = 0.5$

tions [5]. Following the generalization of the Landau theory which has been recently proposed for reconstructive transitions of the displacive type [10], we will assume a transcendental dependence of  $\eta$  in functions of the displacements [10]. One finds here:

$$\eta = \eta_0 \left\{ \sin \left[ \frac{2\pi}{a} (x_i - x_j) - \frac{\pi}{2} \right] + \cos 2\frac{\pi}{\phi} \right\} \quad (1)$$

where  $\Delta x = x_i - x_j$  represents the distance between two antiparallel atoms (e.g. atoms 1 and 4 in Fig. 1a) pertaining to the same cluster.  $\phi$  is the golden mean. The form of the function (1), which holds for the whole set of displacements, is represented in figure 2. The points indicated on the curve of figure 2 correspond however to the specific displacements associated with the Al(7) atoms. Thus, for the specific displacements  $\Delta x = a\phi^{-1} + an$ , and  $a(\phi - 1)\phi^{-1} + an$  where  $n$  is an integer, the Al(7) atoms form two sets of icosahedral clusters which can be deduced one from another by a shifting of  $\frac{a}{2}$ ,  $\frac{a}{2}$ ,  $\frac{a}{2}$  and a rotation of  $90^\circ$  around the [001] cubic axis. For the specific displacements corresponding to such icosahedral domains, the point-group symmetry of the Al(7) sublattice increases from  $m\bar{3}$  to  $m\bar{3}5$ . As indicated in figure 2 it is the space-group symmetry of the sublattice which increases to  $Pm\bar{3}n$  and  $Pm\bar{3}m$  for the respective displacements  $\Delta x = (2n + 1)\frac{a}{2}$ , and  $na$ . For such virtual displacements the system acquire fourfold axes and its symmetry increases.

The thermodynamic stability of the icosahedral clusters can be verified by the introduction of (1) in the potential  $F$ , and by minimization of  $F$  with respect to the displacements [10]. One gets the equation of state:  $\eta(a + b\eta + c\eta^2) \frac{\partial \eta}{\partial \Delta x} = 0$ . The stable solution  $\eta = 0$  is obtained for  $\Delta x = a\phi^{-1} + an$ , or  $\Delta x = a(\phi - 1)\phi^{-1} + an$ , i.e. for the *icosahedral clusters*. This result is in agreement with the spirit of Landau's theory as a zero value of the order-parameter is associated with the *highest point-group symmetry* realized by the atomic clusters. The solution  $\eta = \{-b + (b^2 - 4ac)^{1/2}\} / 2c$  corresponds to general temperature dependent displacements  $\Delta x$  (Pm3 symmetry with cubic clusters), whereas  $\frac{\partial \eta}{\partial \Delta x} = 0$  is associated with the increased Pm3n and Pm3m symmetries.

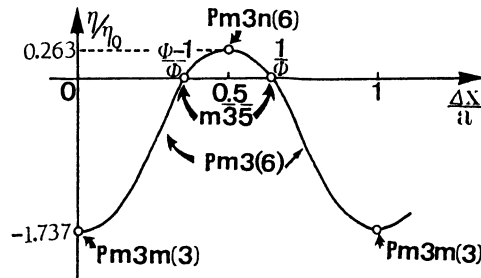


Fig. 2. — Periodic dependence of the order-parameter for the Pm3 (cubic clusters) to Pm3 (icosahedral clusters) transition. The number of atoms per unit-cell, pertaining to the Al(7) sublattice are indicated in brackets.

At this point it should be stressed that the assumed displacive field mechanism takes place *within* the initial cubic unit-cell, and thus must be complemented in order to *loose* the cubic periodicity and stabilize a three-dimensional *aperiodic* structure. A direct way for expressing the loss of cubic translational symmetry is to find, in the primitive cubic Brillouin-zone, a non-zero  $k$ -vector which creates an *icosahedral density wave*, resulting in an infinite quasi-crystalline diffraction pattern in the three-dimensional reciprocal space. On that goal let us consider the wave-vector:

$$\mathbf{k}_1 = \mu \left( \frac{2\pi}{a}, 0, 0 \right) \quad (2)$$

with  $\mu = \frac{5 - 3\phi}{2\phi} \sim 0.09$ .  $\mathbf{k}_1$  is an *incommensurate* wave-vector lying close to the center of the first Brillouin-zone. Its star  $k_1^*$  is formed by the six arms  $\mathbf{k}_{1,2} = \mu \left( \pm \frac{2\pi}{a}, 0, 0 \right)$ ,  $\mathbf{k}_{3,4} = \mu \left( 0, \pm \frac{2\pi}{a}, 0 \right)$ , and  $\mathbf{k}_{5,6} = \mu \left( 0, 0, \pm \frac{2\pi}{a} \right)$ .

In order to allow comparison with experiment, let us calculate the displacements associated with the preceding star and corresponding to the Mn sublattices. The eigen displacements related to the six branches of  $\mathbf{k}_1^*$  can be respectively expressed by the six density waves:

$$\begin{aligned} \psi_1 &= \cos [2\pi(3x + 5y)], \quad \psi_2 = \cos [2\pi(5x + 3z)], \quad \psi_3 = \cos [2\pi(3y + 5z)], \\ \psi_4 &= \cos [2\pi(-3x + 5y)], \quad \psi_5 = \cos [2\pi(5x - 3z)], \quad \psi_6 = \cos [2\pi(-3y + 5z)] \end{aligned} \quad (3)$$

in which only the two first Fibonacci numbers 3 and 5 have been considered as an approximation of the golden mean  $\phi$ . Minimization of the total density wave  $\psi = \sum \psi_i$  with respect to space coordinates yields the function which provides the displacements of the Mn atoms from their initial position in the cubic cell to their final position in the icosahedral structure. The corresponding diffraction pattern is shown in figure 3a. It displays typical fivefold symmetry axes. An additional verification of the consistency of the assumed mechanism is given in figure 3b where the calculated icosahedral positions are superposed on the high-resolution TEM micrograph obtained by Audier and Guyot [13]. The squares on the micrograph denote the projections of the vertices of the initial cubic lattice.

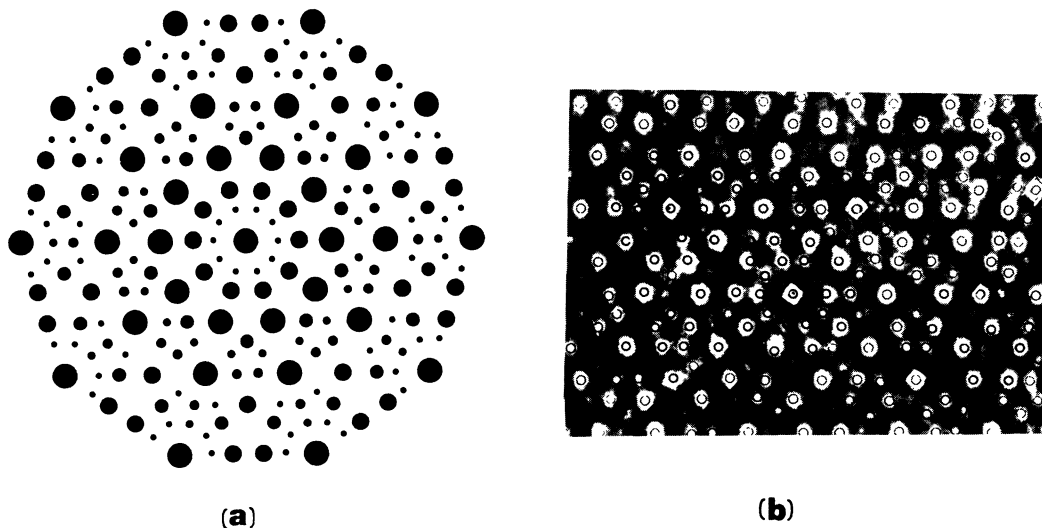


Fig. 3. — (a) Projection on the plane perpendicular to a five-fold axis of the calculated electronic diffraction pattern for the AlMnSi structure, when taking into account the total displacive mechanism assumed in our model (formation of icosahedral clusters *plus* the incommensurate density waves). Six hundred unit-cells have been used for the computer simulation. (b) Superposition of the calculated electronic diffraction pattern for the Mn quasilattice on a high-resolution TEM micrograph obtained by Audier and Guyot [13] along the five-fold axis. The dots represent the positions of the calculated projections in column approximation. With the exception of a small number of defects, denoted by black dots a very good coincidence can be verified. The squares indicate the projections of the vertices of the initial cubic lattice. The size of the smaller icosahedra correspond to the Mn(1) sublattices.

In summary, we have shown on the example of AlMnSi that the formation of icosahedral quasicrystal phases could be understood as resulting from the coupling of two independent mechanisms: 1) a displacement field which transforms groups of atoms, initially in cubic positions, into icosahedral clusters within a cubic unit cell; 2) an incommensurate propagation of density waves. The fact that the two assumed mechanisms are phenomenologically independent suggests that their experimental realization in Nature should not be necessarily correlated. Actually there exist a large number of well-known structures which concretize only the first mechanism, i.e. crystal structures in which near or ideal icosahedral clusters coexist with a three dimensional periodicity, namely in  $\beta$ -Mn, B<sub>12</sub>, UH<sub>3</sub>, MgZn<sub>2</sub>, Mg<sub>2</sub>Zn<sub>11</sub>, Cr<sub>3</sub>Si, CaCu<sub>5</sub> [14], the Frank-Kasper [15] or some of the AlLiCu alloys [16].

The effectivity of the second mechanism assumed in our model, the existence of an incommensurate density wave, received recently two independent possible confirmations in AlCuFe alloys [17, 18] namely 1) the observation of soft phason modes at the icosahedral to crystal 670° C transition, which is interpreted by Bancel [17] as an elastic instability, in agreement with our prediction that such an instability should occur close to the center of the Brillouin-zone; 2) the existence in the phase diagram of such alloys of an intermediate phase interpreted as an incommensurate structure [18]. An additional illustration of the basic idea underlying our model, i.e. that the icosahedral phase results from a solid state transformation, was also suggested in AlCuFe alloys, in which Dubois *et al.* [19] showed that the icosahedral phase transforms reversibly at 747 °C into a closely related rhombohedral modification of symmetry  $R\bar{3}m$ . Although the preceding results require to be confirmed experimentally they show indeed that the icosahedral phase should be inserted in a more complex phase diagram than the current liquid-to-icosahedral model initially proposed [1-4]. In this respect, let us emphasize that the choice of the Pm3 group as the parent symmetry in our model is specific to the case of AlMnSi. We have verified that one could obtain icosahedral structures from a number of different initial space-groups, i.e. Im3, Fm3m, Pm3n,  $P6_3/mcm$ , or  $R\bar{3}m$ . Even for AlMnSi the Im3 ( $Z = 138$ ) or Im3m ( $Z = 69$ ) structures, which can be deduced from the Pm3 structure by small displacements, could have been used as parent phases.

The wave-vector (2) has been selected as the more adapted to the AlMnSi structure, but there exist other wave-vectors, adapted to different structures, that may create icosahedral density waves. The stars of such vectors must fulfil the two *necessary* conditions 1) to be formed by at least six independent arms, and 2) to allow construction of twelve vectors pointing towards the vertices of a regular icosahedron, by combinations with the reciprocal lattice basic vectors. For example, the wave-vector  $\mathbf{k}_2 = \left(2\mu_1 \frac{\pi}{a}, 0, 2\mu_2 \frac{\pi}{2a}\right)$  with  $\frac{\mu_1}{\mu_2} = \phi$  fulfil the *sufficient* condition to possess a twelve arms star which span a regular icosahedron. The zone boundary wave-vector  $\mathbf{k}_3 = \left(\phi \frac{\pi}{a}, 0, \frac{\pi}{a}\right)$  the star of which has six arms also fulfils the preceding condition.

The generality of our approach to quasicrystals can also be found in the fact that it allows to describe the variety of one or two-dimensional quasiperiodic structures that have been found experimentally. Thus, we were able to show that providing different sets of atomic positions and stars  $\mathbf{k}^*$  decagonal [20], dodecagonal [21], and octagonal [22] 2-d quasicrystals could be obtained as the result of a solid-state transformation, the incommensurate modulation being restricted to a plane.

To complete our model let us work out the theoretical phase diagram corresponding to the set of stable phases. The order-parameter associated with  $\mathbf{k}_1^*$  has six components, denoted  $\zeta_i$ . Observation of equal diffraction intensities in the icosahedral phase require the equilibrium conditions  $\zeta_i = \zeta$  for all  $i$ . One can thus write the order-parameter expansion under the effective form:  $F'(\zeta) = F'_0 + \frac{a'}{2} \zeta^2 + \frac{c'}{4} \zeta^4$ . Accordingly the whole transition mechanism from the cubic to the quasicrystal phase, i.e. the formation of icosahedral clusters *plus* the incommensurate density wave can be accounted by the two-order parameter potential:  $F(\eta, \zeta) = F(\eta) + F'(\zeta) + d\eta\zeta^2$ , which corresponds to the theoretical phase diagrams represented in figure 4. Among the various interesting features of these diagrams let us note the *second order transition line* which separates the Ic phase from a cubic phase with icosahedral clusters.

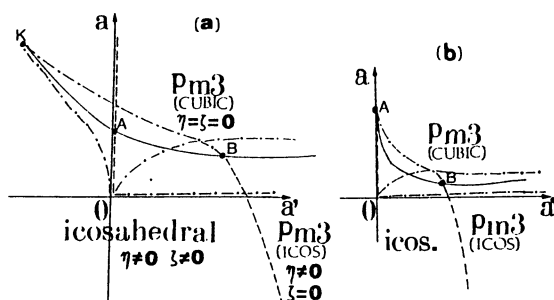


Fig. 4. — Phase diagram representing the potential  $F(\eta, \zeta)$  for  $bd < 0$  (Fig. 4a), and  $bd > 0$  (Fig. 4b) respectively. Solid, dashed and mixed lines are first-order transition lines, second-order transition lines, and limit of stability lines respectively. AK is an isostructural transition line which ends at the critical point K. The A and B multicritical points are at the crossing of a first and second-order transition lines.

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