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Model of growth for long-range chemically ordered compounds : application to quasicrystals

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Abstract. — We propose an electronic model for the growth of long-range chemically ordered binary compounds. By varying one parameter, we show that a specific concentration can be *dynamically* selected and the associated chemical order propagated during a *rapid* solidification. The basic assumptions of the model are: 1) the diffusion inside the growing structure is frozen out, and 2) the « chemical » reconstruction at its surface remains free to occur. In a first step, we study two one-dimensional models and show that both *periodic* and *quasi-periodic* structures can be built-up one atom at a time, using an energetic rule of growth. The first model is phenomenological and includes classical interactions between the atoms, the second is a tight-binding model including quantum effects. We next discuss the possible application to quasicrystals and argue — with energetical considerations — that one possibility for favoring systematically quasi-periodic structures is a growth mechanism which uses clusters preexisting in the liquid phase as building blocks of the solid phase.

1. Introduction.

The experimental discovery of quasicrystals (QC's) in Al-Mn alloys by Shechtman *et al.* [1] in 1984, opened up new experimental and theoretical problems in the field of condensed matter. Owing to their specific non periodic structures, the physical properties of these materials such as conductivity, phonon spectra and elastic properties, magnetic susceptibility, role of defects, etc., are difficult to understand. Two of the major unsolved problems remain: the origin of their stabilization and their mechanism of growth. The stabilization is generally discussed in terms of Hume-Rothery rules for alloys [2], but a theory of stabilization by entropy (the « random tiling model ») has been also proposed [3]. Concerning the growth, Penrose [4] pointed out from the beginning that these materials are concerned with a « non-local growth problem » owing to their quasi-periodicity. Up to now, only theories of tiling patterns have been developed to clarify the propagation of such order [5]. These geometrical mechanisms always

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contain *ad hoc* rules, called matching rules, which allow the growth of QC's. However they do not include any energetical considerations, and this is clearly a weakness of these theories.

For real materials, there are mainly two kinds of quasicrystals: the usual icosahedral phase (*i*-phase) which is quasi-periodic in the three directions of space, and the dodecahedral phase which is quasi-periodic in only two directions. However, compounds with quasi-periodicity in only one direction have been reported for several alloys as in Al-Pd-Fe [6] and Al-Co-Cu-Si [7] alloys. In that one-dimensional case, it becomes difficult to understand how geometrical mechanisms of growth allow the propagation of quasi-periodicity. This remark is also supported by the existence of another family of ordered alloys presenting one-dimensional antiphase boundaries (AB) with long-periods. These complicated structures can be found in Au-Cu alloys — the most famous example — but also in A_3B type compounds like Ag_3Mg , Cu_3Pt , Au_3X with $X = Mn, Cd, Zn$ [8], which present a rich variety of phases with long periods. In $Ti_{1+x}Al_{3-x}$ alloys, Loiseau *et al.* [9] reported a Devil's staircase structure for a part of the phase diagram, with periodic structures varying with the concentration. The length of the period in these alloys can be large, but never becomes infinite in contrast with QC's.

The aim of this paper is to put in light a new path in the understanding of the growth for these complicated ordered intermetallic compounds. Within the context of a simple *one dimensional* model for binary alloys, we propose a mechanism based on purely energetical considerations for the growth of long-range chemically ordered (LRCO) structures. The central point of the theory is that the electronic structure of a *growing* structure can select *dynamically* a specific concentration — varying with some parameters of the model — and drive the propagation of the associated chemical order for both *periodic* and *quasi-periodic* structures, as soon as there is more than one chemical species in the alloy. These structures are built up one atom at a times without global reorganization of the growing structure. However, as we will see, the growth mechanism using single atoms as building blocks do not favor the formation of quasi-periodic structures. For that reason, we extend this mechanism to the case where the building blocks for the growth are not single atoms, but small metallic clusters which maintain their pristine geometry in the solid. We show that, owing to their specific electronic structures, the binding of such clusters could favor systematically quasi-periodicity during the growth.

Although the model is based on a very simple idea (as we will see in Sect. 2), the results are not trivial and could explain simply the propagation of any complicated chemical order (periodic or not) during growth. It is however clear that the weakness of the model for its applicability to real materials (and in particular for QC's) is the dimensionality. This point is discussed in section 3, but additional studies will be necessary to extent the qualitative results of this paper.

Concerning the metallurgy of QC's, it is interesting to note some general features. All these compounds are found in the region of the phase diagram surrounding a peritectic point or line of successive peritectic points. That means physically that the different chemical species mix to give various ordered intermetallic compounds with different chemical compositions. Among these intermetallic phases, we find the QC phase(s) but also periodic phases with different chemical compositions. All these QC's can be obtained by *rapid solidification*, by quenching the alloy. With these rapidly quenched alloys, two kinds of QC's are obtained: *metastable* QC's as in Al-Mn alloys and *stable* in ternary alloys such as Al-Cu-Fe, Al-Ni-Cu, Al-Pd-Fe, Al-Cu-Li, ... Metastable means that the QC phase separates into several periodic phases with different chemical composition by annealing them and cooling down again. Conversely, *stable* QC can be annealed at high temperature with the elimination of defects with respect to the « perfect » QC structure. These stable QC's can be also solidified by slow solidification, as with usual crystals, by taking the *exact* chemical composition of the specific QC. This criticality of the chemical composition is one of the important feature of the metallurgy of

QC's. As noted earlier by Schaeffer and Benderski [10], the rapid solidification of QC's is also contrasted drastically with the case of metallic glasses which occur close to eutectics. Around an eutectic point, the phase separation is favored and the glass is produced only if the solidification is sufficiently rapid. The glassy structures have no long-range order, and can be viewed — in a simple way — as a frozen configuration of the liquid state. There is no nucleation and no growth process during their solidification, which is in contrast with the case of QC for which there is a nucleation and a growth. Furthermore, a very high rate of nucleation has been established for QC and Schaeffer and Benderski [10] argued that it is the higher rate of nucleation of QC compared to the competing periodic phases which favors them. In view of these conditions of rapid solidification, it remains difficult to understand why we do not obtain a glass instead of a QC phase.

To simulate this rapid solidification, we have assumed in this paper that 1) the diffusion inside the growing structure remains frozen during the growth, and 2) the reconstruction at its surface is allowed. We develop these considerations in the context of two particular models. One includes only classical interactions between the atoms, the second is purely electronic and includes quantum effects. The detailed rule of growth is developed in section 2. We apply this rule to the classical model in section 3, for which exact results can be given. The results for the electronic model are numerical and exposed in section 4. Both models give rise to qualitatively similar results. The extension to a growth mechanism using clusters as building blocks is also discussed in section 4, including remarks for real QC's.

2. Description of the model of growth.

The comparison between the growth conditions for obtaining metallic glasses and quasi-crystals noted in the introduction gives us a simple starting point for the model. The two basic assumptions are: 1) the diffusion inside the growing structure is frozen out, and 2) the reconstruction is allowed at the surface. If we now describe the solidification process as a succession of chemical reactions, we obtain for a monoatomic compound (atom X) a cluster of size $n + 1$ from a cluster of size n by the following chemical reaction:

where M_n and M_{n+1} denote the cluster of size n and $n + 1$. The chemical reconstruction in that case has no importance since we have only one kind of atom. But the situation is quite different if we take a binary alloy composed of atom A and B. In that case, we have a competition between two chemical reactions which are written as:

where $M_n A$ ($M_n B$) denotes the cluster of size $n + 1$ with an atom A (respectively B) bound at the surface. The reactions can be rewritten in only one:

The diagram of energy for this reaction is sketched in figure 1. The activation energies $E_n^{(1,2)}$ drive the kinetics of the reaction, and the difference of energy ΔE_n between the two possible configurations $M_n A + B$ or $M_n B + A$ drives the thermodynamical properties.

The results obtained in this paper will show that this local chemical competition is a good « driving force » for generating periodic or quasi-periodic structures during growth. In order to

Fig. 1. — Diagram of energetics for the chemical reaction (2.3). M_n denotes the cluster of size n , $M_n A$ and $M_n B$ are the clusters of size $n + 1$, with an atom A or an atom B bound to the cluster M_n . The activation energies $E_n^{(1)}$ and $E_n^{(2)}$ drive the kinetics of the reaction. ΔE_n drives the thermodynamical equilibrium. The growth mechanism proposed in this paper is based on the energetical balance ΔE_n between both configurations $M_n A + B$ and $M_n B + A$.

put clear the effects of this chemical competition and to have a well-defined problem, we will assume the different following approximations:

First, we suppose that the entropic part of the free energy doesn't play a crucial role at the quenching temperature, so that only the energies ΔE_n will be taken into account (in some sense, it is a growth at zero temperature). Moreover, we assume that the system has always the time to visit both configurations and selects the best situation for its energy, i.e. we neglect the effects of the kinetics.

Second, we neglect the problem of the nucleation process. It is known that the nucleation of a crystal occurs at finite temperature only if the fluctuation of density yields clusters of size $n > n_c$. This is due to the competition between two terms in the free enthalpy of a cluster: the energy of the bulk which is negative below the melting point and proportional to n , where n is the number of atoms in the cluster, and a second positive term which is due to the surface tension and proportional (in 3D) to $n^{2/3}$, such that the total enthalpy is negative only for cluster of size $n > n_c$ [11]. In this paper, we neglect completely this problem and suppose that the critical size of nucleation is 1. In the conclusion we will return to this important problem in connection with QC's.

Finally we neglect the effect of the atomic concentration in the liquid phase. This is clearly incorrect in the sense that if the concentration of atoms A is much higher than the concentration of B, the probability of occurrence of reaction (2.2b) is negligible with respect to reaction (2.2a). However we will let the crystal select its concentration during the growth, supposing that we have an infinite reservoir of A and B. The effect of the concentration could be taken into account by adding an other parameter. This would complicate the task, but would not change *qualitatively* the results of the model.

Using these assumptions, the growth mechanism is based on the simple energetical balance of reaction (2.3). We start from one atom A or B, which schematically represents the cluster M_1 and make at each step the following evaluation of the energetics:

$$\begin{aligned}\Delta E_n &= E(M_n B + A) - E(M_n A + B) \\ \Delta E_n &= [E(M_n B) - E(M_n A)] - [E_\ell(B) - E_\ell(A)].\end{aligned}\tag{2.4}$$

In this formula, $E(M_n A)$ and $E(M_n B)$ denote the energy of the clusters of size $n + 1$, one with atom A at the « surface » and the other with atom B. The energy of the atoms A and B in the liquid phase is represented by $E_\ell(A)$ and $E_\ell(B)$. It is possible to write —

at least formally — the energies of the clusters as:

$$\begin{aligned} E(M_n B) &= E(M_n) + \delta I(B, M_n) \\ E(M_n A) &= E(M_n) + \delta I(A, M_n). \end{aligned} \quad (2.5)$$

In this notation $\delta I(A, M_n)$ (or $\delta I(B, M_n)$) denotes the energy of interaction of the atom A (or B) bound at the surface with all the other atoms of the cluster, such that the difference of energy ΔE_n can be rewritten now as follow:

$$\Delta E_n = [E_t(A) - \delta I(A, M_n)] - [E_t(B) - \delta I(B, M_n)] \quad (2.6)$$

and appears as the difference of *binding* energy at the surface between the atom A and B. From the energetics point of view, it appears clearly that the growth is not driven by the minimization of the energy of the cluster, but by the energy gain obtained by binding, to the cluster, one atom (A or B) from the liquid phase.

At each step of the growth, the energy ΔE_n with formula (2.4) will be calculated. If this energy is negative, an atom B will be selected (since it is energetically favored), and the cluster of size $n + 1$ is $M_{n+1} = M_n B$. If it is positive, we have the reverse situation and $M_{n+1} = M_n A$. This describes a complete dynamical procedure which determines the succession of atoms in the cluster. Importantly, since we have assumed from the beginning that the diffusion is frozen out, the order obtained remains unchanged during the growth.

Starting from these considerations, we have selected two models to calculate the different energies contained in ΔE_n , the difficult part being the energies of the clusters with successive size n . These models are treated in sections 3 and 4 respectively and show qualitatively similar results.

3. Application to a phenomenological Ising model.

In this section, we apply the mechanism explained above to a one-dimensional classical model. For the purpose of clarifying the basic growth mechanism, the Ising model that we take is phenomenological. Its interest is not to describe correctly an experimental case, but rather to allow the obtention of exact results and a complete understanding of the mechanism of growth. Similar effects occurring for this simple Ising model will appear in more complicated model as we will see in section 4.

Let us consider a cluster (a chain) of size n , so that its sites are labelled by an index i varying from 1 to n . To each site, we assign a pseudo-spin variable σ_i . Pseudo-spin means that σ_i can take only two values, one corresponding to the situation where there is an atom A at site i , and the other to the situation where there is an atom B. The series $\{\sigma_i\}$ thus denotes the chemical order in the cluster. We will consider *repulsive* interactions between atoms A in the cluster as a function of their distance, and no interaction in any other case (between atom B or between A and B). So we assign a value $\sigma_i = 1$ if atom A is at site i , and $\sigma_i = 0$ if we have an atom B. The energy of atom A or B in the solid phase is noted $E_s(A)$ and $E_s(B)$. In that simple case the energy of the cluster can be written as:

$$E(M_n) = \sum_{i=1}^{n-1} \sum_{p=1}^{n-i} J(p) \sigma_i \sigma_{i+p} + \sum_{i=1}^n E_s(A) \sigma_i + E_s(B)(1 - \sigma_i) \quad (3.1)$$

where $J(p)$ is the (positive) energy of interaction between two atoms A at distance p in the cluster. An equivalent model is to take as values of the pseudo-spin $\sigma'_i = \pm 1$, which represents attractive interaction between atoms of different nature and repulsive interaction in the other case. The equivalency can be seen by the transformation $\sigma'_i = (2\sigma_i - 1)$, which yields a renormalization of $E_s(A)$, $E_s(B)$ and $J(n)$. It is important to note that we do not search

the ground-state of (3.1) with n tending to infinity (problem which has been solved elsewhere-[12]), but we apply the growth process explained above which is a quite different problem.

Taking advantage now that $\sigma_{n+1} = 1$ if we add an atom A to the cluster M_n and $\sigma_{n+1} = 0$ in the other case, the values of ΔE_n that we defined with formula (2.4) can be calculated:

$$\begin{aligned} E(M_n B) &= E(M_n) + E_s(B) \\ E(M_n A) &= E(M_n) + E_s(A) + \sum_{p=0}^{n-1} J(p+1) \sigma_{n-p} \end{aligned} \quad (3.2)$$

and thus we obtain

$$\Delta E_n = \delta\mu - \sum_{p=0}^{n-1} J(p+1) \sigma_{n-p} \quad (3.3)$$

the two parameters of the model being the interaction that we take of the following form:

$$J(p) = J(|p|) = \eta |p| \rightarrow 0 \leq \eta \leq 1 \quad (3.4)$$

and the difference

$$\delta\mu = (E_s(B) - E_f(B)) - (E_s(A) - E_f(A)). \quad (3.5)$$

In the following discussion, we start from one atom A, but the results are not changed if we start from B. This is obvious in that case since $\sigma_1 = 0$ implies that there is no interaction between this first atom (B) and the others. The successive order is obtained by considering the sign of ΔE_n and we have:

$$\begin{aligned} \text{if } \Delta E_n < 0 &\rightarrow \sigma_{n+1} = 0 \quad (\text{atom B}) \\ \text{if } \Delta E_n > 0 &\rightarrow \sigma_{n+1} = 1 \quad (\text{atom A}) \end{aligned} \quad (3.6)$$

such that

$$\sigma_{n+1} = \frac{1}{2} (1 + \text{sign}(\Delta E_n)). \quad (3.7)$$

Next, ΔE_{n+1} is calculated and this determines σ_{n+2} , and the procedure is continued. The formula (3.3) and (3.7) can be put in a condensed way, such that the $(n+1)$ -th term is expressed as a function of the n -th term (see appendix), and we have:

$$\begin{aligned} \Delta E_{n+1} &= f(\Delta E_n) \\ f(x) &= (1 - \eta) \delta\mu - \frac{\eta}{2} + \eta x - \frac{\eta}{2} \text{sign}(x) \end{aligned} \quad (3.8)$$

with the obvious notation: $\text{sign}(x) = 1$ if $x > 0$ and $\text{sign}(x) = -1$ if $x < 0$. The formula (3.8) defines formally a *discrete dynamical system* (with the discrete « time » n) [26]. As we will see, it presents some *attractors* which evolve with the parameter $\delta\mu$. The existence of such attractors is the reason for which the growth process converge to periodic or quasi-periodic structures. This point is central for the understanding of the model and will be extensively used for the proof, reported in the appendix, of the results that we will now expose.

3.1 UNIFORM ONE-DIMENSIONAL STRUCTURES. — Before applying the growth process to this model, we first look at the structures which are stabilized by the interactions $J(n)$. Let's consider an infinite chain with a fixed density of spin $\langle \sigma_i \rangle_i = c$, with $0 \leq c \leq 1$. The question is, which order minimizes the energy of interaction? This problem has been previously solved

by Hubbard [12] in the context of one-dimensional Wigner crystals. If we have a density $c = 1/s$, where s is an integer, due to the convexity of the interactions ($J(n+1) + J(n-1) - 2J(n) > 0$) [12], the structure which minimizes the energy consists to take one spin $\sigma_i = 1$ over all the s sites, and the others equal to zero. Thus the structure $c = 1/2$ is given by 1010.., $c = 1/4$ by 10001000... If now c takes more complicated values $c = r/s$ where r and s are two irreducible integers, the mean distance between two consecutive spins 1 is still $d = 1/c = s/r$. But this time, since we have an underlying lattice, it is impossible to take the distances between two spins 1 equal to d (d is not integral), and the frustration induced yields more complicated structures. The general formula which gives the value of the spins minimizing the energy of interaction is given by [12, 13]:

$$\sigma_n = [nc + \alpha] - [(n-1)c + \alpha] \quad (3.9)$$

where α is a phase which is the same for all the system (that we can take equal to zero), and $[x]$ means integer part of x . The distance between two spins 1 is exactly $[s/r]$ or $[s/r] + 1$. The structure is *uniformly* ordered and is periodic with a period length equal to s . This formula extended to irrational value of c gives quasi-periodic structure. For instance, if we take the Golden mean $c = \frac{\sqrt{5}-1}{2}$, the formula (3.9) generates the usual Fibonacci chain [14]. The term uniform is used [8] because the fluctuations of density of atom A with respect to B is « minimal » for the structure described by (3.9). As examples, the unit cells for some specific values of c are given:

$$\begin{aligned} c = 1/3 & \quad 100 \\ c = 3/5 & \quad 10101 \\ c = 3/7 & \quad 1001010. \end{aligned}$$

As we will see in the next subsections, these uniform structures — stabilized by the interactions — can be build up one atom at a time, starting from one atom and using the rule of growth explained in section 2.

3.2 CONDITIONS ON $\delta\mu$ TO OBTAIN PURE A OR B PHASE. — Turning back to the growth model, we will first describe simple cases that we can easily reach without complicated tools. In this subsection, we search the conditions to have pure phase of A or B. Pure « B » means that all the pseudo-spins (except the first one since we start with $\sigma_1 = 1$) take the value 0. For that we have the condition that for all size n , ΔE_n must be negative. Writting this condition for the step 1, we obtain:

$$\Delta E_1 = \delta\mu - J(1) < 0 \Rightarrow \sigma_2 = 0$$

and now, using the values $\sigma_2 = 0$ we calculate ΔE_2 :

$$\Delta E_2 = \delta\mu - J(2) < 0 \Rightarrow \sigma_3 = 0$$

and continue this procedure up to the infinity:

$$\left\{ \begin{array}{l} \Delta E_3 = \delta\mu - J(3) < 0 \Rightarrow \sigma_4 = 0 \\ \Delta E_4 = \delta\mu - J(4) < 0 \Rightarrow \sigma_5 = 0 \\ \dots \quad \dots \\ \Delta E_n = \delta\mu - J(n) < 0 \Rightarrow \sigma_{n+1} = 0 \\ \dots \quad \dots \\ \Delta E_\infty = \delta\mu - \lim_{n \rightarrow \infty} J(n) < 0. \end{array} \right.$$

The condition on $\delta\mu$ to obtain a pure B phase is thus

$$\delta\mu \leq \delta\mu_0 = \lim_{n \rightarrow \infty} J(n) = 0. \quad (3.10)$$

The same procedure can be applied to know the condition to have pure A phase. In that case, all successive pseudo-spins take the value 1, and thus $\Delta E_n > 0$ for all n . We obtain successively:

$$\Delta E_1 = \delta\mu - J(1) > 0 \Rightarrow \sigma_2 = 1$$

and taking the value $\sigma_2 = 1$, we can calculate the next energy

$$\Delta E_2 = \delta\mu - J(1) - J(2) > 0 \Rightarrow \sigma_3 = 1$$

and continue the procedure:

$$\left\{ \begin{array}{l} \Delta E_3 = \delta\mu - J(1) - J(2) - J(3) > 0 \Rightarrow \sigma_4 = 1 \\ \Delta E_4 = \delta\mu - J(1) - J(2) - J(3) - J(4) > 0 \Rightarrow \sigma_5 = 1 \\ \dots \dots \dots \\ \Delta E_n = \delta\mu - \sum_{i=1}^n J(i) > 0 \Rightarrow \sigma_{n+1} = 1 \\ \dots \dots \dots \\ \Delta E_\infty = \delta\mu - \sum_{n=1}^{\infty} J(n) > 0. \end{array} \right.$$

Thus we have the condition to have pure A phase:

$$\delta\mu \geq \delta\mu_1 = \sum_{n=1}^{\infty} J(n) = \frac{\eta}{1-\eta} \quad (3.11)$$

If we take as value of the parameter $\delta\mu$ one satisfying the conditions (3.10) or (3.11), the growth process yields pure B or A phase respectively. In the next subsection, we explain what happens if we take a value of $\delta\mu$ satisfying the condition:

$$\delta\mu_0 < \delta\mu < \delta\mu_1 \quad (3.12)$$

3.3 MIXED PHASES. — We now suppose that $\delta\mu$ satisfies the condition (3.12). Before giving the general results, let us take the specific value:

$$\delta\mu = \sum_{p=1}^{\infty} J(2p) = J(2) + J(4) + J(6) + \dots = \frac{\eta^2}{1-\eta^2}. \quad (3.13)$$

We can calculate the successive values of ΔE_n and the associated value of σ_{n+1} . For ΔE_1 we obtain:

$$\Delta E_1 = \delta\mu - J(1) < 0 \Rightarrow \sigma_2 = 0.$$

This condition is satisfied if

$$\begin{aligned} \frac{\eta^2}{1-\eta^2} - \eta &< 0 \\ \eta &< \frac{\sqrt{5}-1}{2} \approx 0.618. \end{aligned} \quad (3.14)$$

and with this condition, it is easy to follow the successive steps and verify:

$$\left\{ \begin{array}{l} \Delta E_2 = \delta \mu - J(2) > 0 \Rightarrow \sigma_3 = 1 \\ \Delta E_3 = \delta \mu - J(1) - J(3) < 0 \Rightarrow \sigma_4 = 0 \\ \Delta E_4 = \delta \mu - J(2) - J(4) > 0 \Rightarrow \sigma_5 = 1 \\ \dots \dots \dots \\ \Delta E_{2n} = \delta \mu - J(2) - J(4) - J(6) - \dots - J(2n) > 0 \Rightarrow \sigma_{2n+1} = 1 \\ \Delta E_{2n+1} = \delta \mu - J(1) - J(3) - J(5) - \dots - J(2n+1) < 0 \Rightarrow \sigma_{2n+2} = 0. \end{array} \right. \quad (3.15)$$

For this value of $\delta \mu$, and with the condition (3.14), we obtain the infinite succession (101010...) (or equivalently ABABAB..) so that the crystal obtained is a chemically ordered alloys with concentration $c = 1/2$. If the condition (3.14) is not fulfilled, the result *remains* true, but the infinite sequence 101010... will be produced above a finite critical value of $n > n_c(\eta)$ which depends on η (the proof is given in the appendix). For that reason, the ordered alloy $c = 1/2$ appears, in some sense, as an *attractor* of the dynamical system induced by the process of growth.

It can be seen from (3.15) that ΔE_{2n} tends to zero when n tend to the infinity. This means that if we decrease $\delta \mu$ from the value given by (3.13), some defects (spin « 0 » instead of spin « 1 » at some places) with respect to the 1/2 structure will appear in the sequence of spins. For that reason, the value $\delta \mu^-(1/2) = \sum_{p=1}^{\infty} J(2p)$ is the lowest value of $\delta \mu$ for which it is possible to built up a 1/2 structure. Reversely, if we increase by $\delta \varepsilon$ the value of $\delta \mu$ from the value (3.13), it exists, n_0 for which the value of ΔE_{2n_0+1} can become positive. This induces also a defect (but this time a spin « 1 » instead of spin « 0 » at some place) which will be found again at distance $4n_0, 6n_0, \dots$. To know to which value of $\delta \varepsilon$ the sequence 1/2 survives without any defect, we just write the condition that $2n_0$ must be infinite (which means that the defect « appears » at the infinity). Writing this condition, we obtain:

$$\delta \varepsilon \leq \sum_{n=1}^{\infty} J(2n-1) - \delta \mu^-(1/2) = \frac{\eta - \eta^2}{1 - \eta^2}. \quad (3.16)$$

This implies that for all values of $\delta \mu$ which satisfies the condition:

$$\delta \mu^-(1/2) = \sum_{p=1}^{\infty} J(2p) \leq \delta \mu \leq \delta \mu^+(1/2) = \sum_{p=1}^{\infty} J(2p) + \frac{\eta - \eta^2}{1 - \eta^2}. \quad (3.17)$$

The crystal obtained will be the chemically ordered alloy $A_{0.5}B_{0.5}$. It is now interesting to understand the structure of the ΔE_n . The important parameter is the minimum value that take the absolute value of ΔE_n during the growth:

$$\Delta(\delta \mu) = \min_n |\Delta E_n| \quad (3.18)$$

The physical meaning of this parameter is clear: it gives in some sense a measure of the *selectivity* and the stability of the growth process for the phase 1/2. At finite temperature, the growth process (determinist at zero temperature) becomes probabilistic. Thus if $\Delta(\delta \mu)$ is much lower than the temperature, the probability to fix an atom A at some place can become comparable to the probability to fix an atom B. This induces the presence of defects and the chemical order cannot be built up if these defects are randomly distributed. Reversely, if the ratio $\Delta(\delta \mu)/k_B T$ is much higher than 1, the process can select on an average the chemical

order with the concentration $c = 1/2$. The value of $\Delta(\delta\mu)$ can be easily calculated for the $1/2$ case. In equations (3.15), the absolute value of ΔE_{2n} becomes minimal when n tends to the infinity, so that we have simply $\min_n |\Delta E_{2n}| = \delta\mu - \delta\mu^-(1/2)$. For ΔE_{2n+1} , the minimum of

its absolute value is also reached at the infinity, so that we have $\min_n |\Delta E_{2n+1}| =$

$\delta\mu^+(1/2) - \delta\mu$, and finally:

$$\Delta(\delta\mu) = \min(\delta\mu - \delta\mu^-(1/2), \delta\mu^+(1/2) - \delta\mu). \quad (3.19)$$

This result is sketched in figure 2. The maximum of « selectivity » is obtained for $\delta\mu = (\delta\mu^-(1/2) + \delta\mu^+(1/2))/2$ and is equal to $(\delta\mu^+(1/2) - \delta\mu^-(1/2))/2$.

Fig. 2. — The minimum over n of the absolute value of ΔE_n as a function of $\delta\mu$ is drawn for the case $c = 1/2$. This minimum is a measure of the selectivity of the growth process. It is reached when n tends to the infinity and is non zero for $\delta\mu$ satisfying: $\delta\mu^-(1/2) < \delta\mu < \delta\mu^+(1/2)$ range over which the ordered alloy $A_{0.5}B_{0.5}$ is obtained.

All the results obtained for the specific case $1/2$ can be generalized to any value of the concentration. In the appendix, the proof of the following assertions is given. The numerical illustration of the results is sketched in figure 2 for two values of the parameter η .

For any rational value of the concentration $c = r/s$, there are two limiting values $\delta\mu^+(r/s)$ and $\delta\mu^-(r/s)$ given by

$$\begin{aligned} \delta\mu^-\left(\frac{r}{s}\right) &= \lim_{\varepsilon \rightarrow 0^-} \left(\left(\frac{1-\eta}{\eta} \right) \sum_{p=1}^{\infty} \eta^p \left[p \left(\frac{r}{s} + \varepsilon \right) \right] \right) \\ \delta\mu^+\left(\frac{r}{s}\right) &= \lim_{\varepsilon \rightarrow 0^+} \left(\left(\frac{1-\eta}{\eta} \right) \sum_{p=1}^{\infty} \eta^p \left[p \left(\frac{r}{s} + \varepsilon \right) \right] \right) \end{aligned} \quad (3.20)$$

($[x]$ denotes the integer part of x) for which the growth rule yields the periodic ordered alloy $A_c B_{1-c}$ (with the succession of spin given by (3.9)), under the condition that $\delta\mu$ satisfies $\delta\mu^-(r/s) \leq \delta\mu \leq \delta\mu^+(r/s)$.

The growth diagram sketched in figure 3 has a Devil's staircase structure [13b, 15] and presents a step for each (irreducible) rational value r/s of c . The width of the step is given by

$$\Delta\mu \left(\frac{r}{s} \right) = \delta\mu + \left(\frac{r}{s} \right) - \delta\mu - \left(\frac{r}{s} \right) = \left(\frac{1-\eta}{\eta} \right) \left(\frac{\eta^s}{1-\eta^s} \right) \quad (3.21)$$

and decreases exponentially with s . The parameter of selectivity decreases also exponentially with s . The curve $\min_n |\Delta E_n|$ as function of $\delta\mu$ is reported in figure 4.

The quasi-periodic structures are also found in this diagram as limiting sequence of a series of rational values of $c_m = r_m/s_m$ for which c_m tends to an irrational number when m tends to the infinity. However, at the same time, the series of the step widths $\Delta\mu(c_m)$ tends rapidly to zero with s_m , and it is the same for the parameter of selectivity. For these structures, the selectivity do not hold at large distance and only approximate structures of the quasi-periodic order can be obtained. The second reason is that nature should adjust the parameter $\delta\mu$ with an infinite precision to « good » values giving quasi-periodicity, which is clearly a nonphysical condition. However, it is interesting to note that the difference between quasi-periodic and periodic structures is not *qualitative* but rather *quantitative*, and the nature can use the same mechanism to built-up both. The problem is to understand how nature could stabilize the growth of such large periodic structures that it becomes experimentally impossible to make the difference with a quasi-periodic one. This problem will be studied in the context of the tight-binding model of section 4.

3.4 EXTENSION OF THE MODEL TO HIGHER DIMENSION. — The main result that we have shown up to now is that the local chemical competition occurring during the growth can drive the selection and the propagation of a specific chemical order at least in one dimension. The question is now, will that remain true for higher dimensions ? We have no simple response to that question, however some qualitative arguments can be given. First, it is clear that the energetical criterium is not the only one. If the atoms do not have the same size, the steric effects will have drastic consequences and modify the chemistry induced by the energetics. In particular, it can only select some particular concentrations compatible with both considerations: steric and energetical. Moreover, assuming equivalent sizes for the atoms, it is not clear if the growth can be viewed as a « dynamical system » with the ordered alloys as « attractors ». This depends essentially on the strategy used by nature to dispose the atoms. If this strategy is well defined, the extension of the one-dimensional result can be expected. If there is no well-defined strategy, this extension is more dubious. However, it is well known, that the growth of crystal occurs around a topological defect, as a screw defect, which propagates during the growth. From this point of view, the propagation of this defect defines a specific place for disposing one atom at each step. In that case, the choice of atom A or B is relevant from the energetics point of view and the chemical selection can hold.

4. Application to a tight-binding model for binary alloys.

The same procedure described in section 2 is now applied to a more realistic model for binary alloys. We will consider only electronic energies for the atoms. The atoms A and B are represented by an electronic level ϵ_A and ϵ_B and a valency v_A and v_B for each type of atoms. The energy of the atoms in the « liquid » phase — where they are not bound to the cluster — is thus:

$$\begin{aligned} E_l(A) &= v_A \epsilon_A \\ E_l(B) &= v_B \epsilon_B \end{aligned} \quad (4.1)$$

a)

b)

Fig. 3. — Growth diagram for the pseudo-spins model (3.1). The concentration of the ordered alloy obtained is shown as a function of $\delta\mu$. It is a Devil' staircase including periodic and quasi-periodic alloys. Some particular periodic structures are quoted. For a) $\eta = 0.85$ and for b) $\eta = 0.5$.

Fig. 4. — Minimum over n of the absolute value of ΔE_n as a function of $\delta\mu$ is represented. For each commensurability r/s (the specific case $1/2$ is drawn in Fig. 2), this minimum is non zero when $\delta\mu^-(r/s) < \delta\mu < \delta\mu^+(r/s)$. $\delta\mu^-(r/s)$ and $\delta\mu^+(r/s)$ are given by formula (3.20).

the difference of energy $\varepsilon_A - \varepsilon_B$ represents chemically the difference of electronegativity between the atom A and B. In the « solid » phase, the atoms share their electrons *via* the hopping terms of the kinetics energy of the electrons. For sake of simplicity — but as for the Ising model, any other model can be taken to apply the same procedure of growth — we will take only first neighbour hopping integrals $t = t_{i,j}$ with $(i - j) = \pm 1$. Moreover all the integrals between two successive atoms in the solid: AA, AB or BB are taken equal, so that we have: $t = t_{AA} = t_{AB} = t_{BB}$. The on-site energy of the electrons in the solid remains equal to ε_A or ε_B (in order to limit the number of parameters of the model) so that the eigenenergies and eigenwavefunctions of a cluster of size n obey the following tight-binding equations:

$$-t\Psi_{i+1}^{(\nu)} - t\Psi_{i-1}^{(\nu)} + \varepsilon_i\Psi_i^{(\nu)} = E_\nu\Psi_i^{(\nu)} \quad (4.2)$$

For all sites of the cluster $1 \leq i \leq n$. For the ends of the chain $i = 1$ or $i = n$, we have the choice to let them be free — as we made for the Ising model —, or to take cyclic boundary conditions which means that the $n + 1$ atom at the step n is the atom 1. In the last case, the successive steps of the growth consists of injecting atom $n + 1$ between the atom n and the atom 1. We performed both conditions and the results are not qualitatively changed, but the final structure is more easily identified with the second method in the sense that we don't need to go to a high number of atoms to mark the final period of the growing structure (in other words, the « attractor » of the dynamical process of growth is more rapidly reached using this boundary conditions).

The energy of a cluster of size n is given by its band energy:

$$E(M_n) = \sum_{i \text{ occup}} E_i \quad (4.3)$$

where the E_i are solutions of the equations (4.2) with the series $\{\varepsilon_i\}$ describing the chemical order of the cluster: $\varepsilon_i = \varepsilon_A$ or ε_B . The number of occupied states in (4.3) is given by the number of electrons $n_e(n)$ (note that we fill up the band by putting two electrons on the occupied states of the bands) and we have at each step n :

$$n_e(n) = v_A n_A(n) + v_B n_B(n) \quad (4.4)$$

where $n_A(n)$ is the number of atom A in the structure and $n_B(n)$ is the number of B.

The parameters of the model are the difference of on-site energy :

$$\delta\varepsilon = \frac{(\varepsilon_A - \varepsilon_B)}{t} \quad (4.5)$$

that we always take positive by convention, and the respective valencies v_A and v_B of the atoms.

This model is a charge-transfer model in the sense that the mixed phases and the binding between atoms A and B is due to the transfer of electrons from the species of highest energy level A towards B. For this reason, the model is slightly incorrect since any charge transfer induces automatically an increase of the coulombic energy that we do not take into account in the evaluation of the energies. This simplification is necessary because an Hartree-Fock calculation for the coulombic energy would cost too much numerical time for the growth process. As a first approximation, it is reasonable to consider that the coulombic interactions « renormalize » the difference of the on-site potentials $\delta\varepsilon$ and do not change qualitatively the results. Another simple model which would give similar results is to modulate, not the on-site energy, but the hopping integrals: $t_{AA} \neq t_{AB} \neq t_{BB}$. Both models yield to similar « chemical Peierls » effects, but we focus in this paper only on the first model.

4.1 INTEGRAL VALUES OF VALENCIES. — In this subsection, we fix the valencies of the atoms to simple integral values $v_A = 2$ and $v_B = 1$. The parameter $\delta\varepsilon$ can vary — at least formally — from zero to infinity, two limiting situations which correspond respectively to no difference of electronegativity, and a complete charge transfer from A towards B.

In the case where $\delta\varepsilon = 0$, there is no charge transfer, and the binding is purely covalent. In that case, whatever the chemical composition of the cluster is, the electronic energy is given by:

$$E_k = -2t \cos(k) \quad (4.6)$$

where k is the usual crystal momentum and the difference of energy ΔE_n which drives the growth depending on the difference of energy between the two competing configurations, the maximum gain of energy is obtained by minimizing the number of electrons in the structure. For that reason, since $v_B < v_A$, an atom B is bound to the structure at each step. The final structure is the pure B phase, that we note by definition the $\langle 0 \rangle$ phase. In the reverse case $\delta\varepsilon \gg 1$, the charge transfer between atoms A and B fully operates, and it is always favorable to bind an atom A to an atom B, since an electron from A is transferred to the atom B. There remains one electron on the atom A with an high energetic level. Thus, to complete the charge transfer, an atom B is added. In that case, the two electrons of A are transferred to the levels of the atoms B. The limiting phase obtained is the periodic alloys AB_2 that we refer hereafter as the $\langle 1 \rangle$ structure.

We have performed numerically the growth process by varying the values of $\delta\epsilon$, and the results are similar to the results of the Ising model. In particular, the results remain unchanged if we start from an initial atom A or B. All the structures found between the phase $\langle 0 \rangle$ and $\langle 1 \rangle$ can be described as an ordered mixing of the unit cells of these two limiting phases. To mark correctly the final period of the structure, we performed the calculation up to a size of cluster equal to 400 atoms. The two critical value for $\delta\epsilon$ are: $\delta\epsilon_0 = 0$ below which we obtain the phase $\langle 0 \rangle$, and $\delta\epsilon_1 = 1.23$ above which we obtain the phase $\langle 1 \rangle$. Between these two limiting phases, the growth process converges to periodic sequences which are uniform mixing of sequences BB (that we will note « 0 ») and ABB (noted « 1 »). The growth diagram as a function of $\delta\epsilon$ is sketched in figure 5. The phases are marked by $\langle p/q \rangle$, where p and q are two irreducible integers. Here, q denotes the total number of sequences BB and ABB in the period of the crystal and p denotes the number of ABB sequences. The period $\langle p/q \rangle$ contains exactly $N(p/q) = 3p + 2(q - p)$ atoms: p atoms A and $2q$ atoms B. The chemical order associated corresponding to the mixture of sequence ABB and BB is exactly the same as for the Ising model of section 3: the succession of « 0 » and « 1 » is given by the formula (3.9). As examples, we have:

$$\left\langle \frac{1}{3} \right\rangle = 100 = (\text{ABB}) (\text{BB}) (\text{BB}) = \text{ABBBBBB}$$

$$\left\langle \frac{3}{7} \right\rangle = 1001010 = (\text{ABB}) (\text{BB}) (\text{BB}) (\text{ABB}) (\text{BB}) (\text{ABB}) (\text{BB})$$

$$\left\langle \frac{5}{8} \right\rangle = 11010110 = (\text{ABB}) (\text{ABB}) (\text{BB}) (\text{ABB}) (\text{BB}) (\text{ABB}) (\text{ABB}) (\text{BB})$$

$$\langle 1 \rangle = 1 = \text{ABB}.$$

As for the Ising model, the growth diagram in a Devil's staircase. We found numerically commensurability with q of the order of 20, varying $\delta\epsilon$ elementary step of 10^{-3} . By taking more accurate variation for this parameter, it is possible to find commensurability with higher values of q .

The electronic structure of the alloys is easy to describe, and some examples are given in figure 6. Except the phase $\langle 0 \rangle$ which is metallic (no gap at the Fermi level), all the ordered alloy $\langle p/q \rangle$ are insulating. The alloy $\langle p/q \rangle$ contains $p + 2q$ bands. The number of electrons being $p\nu_A + (2q)\nu_B = 2(p + q)$ per period, the Fermi level always reaches the top of the $(p + q)$ -th bands. The ordered alloys obtained always correspond to the *complete* filling of bands. From this point of view, they can be classed among *closed electronic shell* systems and seen as one-dimensional Hume-Rothery alloys.

In this section we have shown that the results obtained for the phenomenological Ising model can be extended to more complicated model including quantum effects. We have treated the *simplest* tight-binding model that it is possible to do for a binary alloy, and the results show that it is possible to build, one atom at a time, periodic and quasi-periodic ordered alloys. However, for the same reasons as for the Ising model, we are not in a situation favoring the quasi-periodicity. This type of model can explain — at least in principle — the existence of a Devil's staircase structure for the phase diagram of $\text{Ti}_{1-x}\text{Al}_x$, by noting however that the number of steps in this real system remains finite and that real incommensurate structure is never reached (at zero temperature). This point is consistent with our results, and shows that to build-up a really quasi-periodic system or a periodic system that we cannot separate experimentally from an incommensurate one, as for QC's we need a new hypothesis associated to the basic mechanism of growth that we propose. Searching for generic conditions that systematically favor incommensurability will be discussed now.

Fig. 5. — The growth diagram for the tight-binding model is plotted. The valency of the atoms A and B has been fixed to 2 and 1 respectively. For each value of $\delta\epsilon$, the growth mechanism yields one periodic or quasi-periodic ordered alloy. This alloy is characterized by $\langle p/q \rangle$. The succession of sequence 1 = ABB and 0 = BB is given by formula (3.9) by taking $\epsilon = p/q$. Some particular periodic structures are quoted. The Devil's staircase structure is similar to that in figure 3.

4.2 CLUSTERS AS BUILDING BLOCKS: THE CASE OF QUASICRYSTALS ? — In our simplified model, we have supposed that only one orbital per atom participates to the chemical binding. In fact, for real atoms, the situation is more complicated since several orbitals and electrons per atom can be important for the chemical binding. This will have some consequences since the ordered alloy obtained by the growth always corresponds to a number of electrons per atom which fills up a finite number of the lowest electronic bands of the alloy. The number of electron per orbital of the atoms is thus an essential parameter for the growth. In *one direction*, one can take into account this parameter by taking for our « modeling » atoms an *effective valence* $v_A = r_A/s_A$ corresponding to the number of electrons (r_A) per orbitals (s_A), and one effective electronic level. As example, we have plotted in figure 7 the numerical results obtained for the valencies: $v_A = 3/2$ and $v_B = 1$. As for integral valencies, it has a Devil's staircase structure, corresponding to the ordered mixing of sequences 0 and sequences 1. What has been changed in the description of the structures is the elementary sequency « 1 ». The sequence 0 remains BB since the valency of B has not been changed. However, the sequence 1 corresponds to ABBAB. It is easy to understand this point by taking a very large value of $\delta\epsilon$ for which the charge transfer operates fully. If we make a periodic structure ABB, the electronic structure is made of three bands: two lower ones due to B, and one higher in energy due to A. Owing to the specific valencies of the atoms ($3/2$ and 1), the first lower band is full, and the second one is half-filled. To profit from the charge transfer, we can add one A in the period of the structure. In that case, we obtain four bands: two lower and two higher separated by an important gap. The two lowest are filled, but the first higher is half-filled. Thus to complete the charge transfer, we add one atom B. This time, we have five bands, three lower

a)

b)

Fig. 6. — The electronic dispersion of the ordered alloys obtained by the growth is plotted for two different cases. ϵ_B is taken as the origin of the energy, and ϵ_A is taken in the range giving rise to the specific alloy. In a) for the limiting phase $\langle 1 \rangle = ABB$. There are three bands, two filled and the other empty. In b) for the phase $\langle 2/3 \rangle = ABBABBBB$. There are height bands, five are filled.

Fig. 7. — The growth diagram is plotted for the case where the valency of the atoms have non integral values. For this diagram $v_A = 3/2$ and $v_B = 1$. As for integral values of the valency, the diagram is a Devil's staircase, and the mixing of sequence 1 and 0 is the same as for figure 5. However, the sequence 1 has changed, and is now $1 = \text{ABBAB}$.

which are filled, and two higher which are empty and thus the unit cell of the phase $\langle 1 \rangle$ effectively corresponds to ABBAB.

For single atoms, owing to the contraction of the orbitals of the core electrons, only the orbitals of the external shell participate to the chemical binding (basically s, p and/or d orbitals). In that case, the parameter $v_A = r_A/s_A$ in our model can take only simple values such as $s_A = 5$ and $r_A \leq 10$ for external d-electrons, $s_A = 1$ and $r_A \leq 2$ for s-electrons, $s_A = 3$ and $r_A \leq 6$ for p-electrons. This complicates the growth diagram by changing the elementary sequences with which the ordered alloys are build-up, but do not change *qualitatively* the things since the length of the elementary sequences of the phase $\langle 0 \rangle$ and $\langle 1 \rangle$ remain small (each one would contain a few number of atoms). However, this situation could be changed if these effective valencies could take complicated values. The aim of this section is to discuss this possibility for small metallic clusters, and show that this could favour systematically quasi-periodicity for the structures obtained by the growth model.

It is well-known that the physical properties of small metallic clusters is governed by the shell structure of the valence electrons [16]. In a finite metallic cluster with an approximated spherical jellium square-well potential, they form an electronic shell with orbitals characterized by the angular momentum quantum number ℓ and a degeneracy given by $2(2\ell + 1)$ (the factor 2 is due to the spin degeneracy). One finds a succession of levels given by 1s, 1p, 1d, 2s, 1f, 2p, 1g for the lowest states [16]. The stability of some specific sizes N of clusters, experimentally observed [16], give rise to what has been called the *magic* numbers which correspond to the filling of the successive shells. For alkali metals — with one valence

electron — they are given by:

$$\begin{aligned}1s &\rightarrow N = 2 \\1p &\rightarrow N = 8 \\1d &\rightarrow N = 18 \\2s &\rightarrow N = 20 \\1f &\rightarrow N = 34 \\2p &\rightarrow N = 40 \\1g &\rightarrow N = 58\end{aligned}$$

The stability of these clusters coming from the closure of a specific subshell, their chemical reactivity can be expected to be poor since they behave in some sense as *giant* rare-gas-like atom, and the eventual binding of such rigid clusters would come from Van der Waals interactions. In fact, the situation is not so simple, and clusters with non closed subshell can be also stabilized (in that case, some subshells are filled and the last occupied one is not completely filled). These clusters correspond to the so-called Mac-Kay clusters [17]. Recently, Khanna and Jena [18] argued that the reactivity of such metallic clusters — considered as a whole — could be very important. They showed as example that an icosahedric aluminium cluster of aluminium Al_{13} behaves chemically as a *giant* chlore atom. This is due to the fact that it contains 39 electrons (3 for each aluminium atom), and to achieve the closure of the 2p shell, it misses 1 electron. The calculations showed that the binding between K and Al_{13} in KAl_{13} crystal should be *ionic*. The difference of electronegativity between Al_{13} and K is found to be of the same order than the difference between Cl and K, and the binding energy is about 5 eV per pair. Thus, although Al and K are both metallic and their difference of electronegativity is quite small, the presence of metallic clusters allows ionic binding between both ! The increasing of the electron affinity of Al_{13} with respect to the Al atom is essentially due to the delocalisation of the extra electron over the 13 atoms of aluminium. In the same way, Saito and Ohnishi [19] have shown that two Na_{19} clusters are able to be bound to form a *giant* dimer $(Na_{19})_2$. In that case, two electrons are put in common as in covalent bound between two atoms.

As pointed out by Khanna and Jenna [18], considering clusters as *giant* atoms with specific electronic shells give rise to a qualitative new chemistry. However, there is at least two important differences compared with the chemistry of single atoms. First, as noted above, only the external shell with a few number of orbitals (s p or d) comes into the chemical binding for single atoms. For the electronic shell of a cluster, the difference in energy between the lowest shell 1s and the highest occupied one (2p for example) is much smaller (few electron-volts) than for atoms, and all the orbitals have about the same extension in space. As consequences, all the electrons and orbitals of the electronic shells can be concerned in the binding between clusters. The second qualitative point is simply the fact that a cluster can be broken during a chemical reaction (or distorted from its original symmetry). Thus several energy scales are of importance : 1) the internal energy of binding of a given cluster and its resistance to eventual distortions, which in some sense characterize its metastability, and 2) the energy of binding between two different clusters.

After discussing briefly the possibility of connecting clusters to build-up structures, we study in the context of our simple model what is the main effect of such particular electronic structures for the basic building blocks. All the orbitals and electrons of a given cluster must be taken into account. Taking two different clusters, noted A and B, we will have r_A electrons for s_A orbitals for the cluster A, r_B and s_B for the cluster B. For these clusters of typical size 50-100 atoms, the parameters r_A , s_A , r_B , s_B , can take large values in contrast with single atoms. For one direction, as for single atom, we simulate the binding between clusters

by taking an effective level of energy ε_A and an effective valency $v_A = r_A/s_A$ for the cluster A, and ε_B , $v_B = r_B/s_B$ for the cluster B, and let t the hopping integral of electrons between clusters.

First, the valency v_A is varied, and let $v_B = 1$. As for the simple valency $v_A = 3/2$ discussed above, the procedure of growth yields a Devil's staircase structure by the same mechanism as before: we obtain periodic or quasi-periodic structures of sequences 0 and 1. The table I gives the different elementary sequences obtained by varying the parameter v_A . They have been marked numerically by taking high values of $\delta\varepsilon \gg 1$ for which we obtain the periodic phase $\langle 1 \rangle = 11111\dots$. For the successive valencies given in table I: $1 + 1$, $1 + 1/2$, $1 + 2/3$, $1 + 3/5$, $1 + 5/8$, $1 + 34/55$, the limiting sequence for a given valency is obtained by binding together the limiting sequences of the two preceding valencies. This is a reminiscence of their hierarchical structures (these particular structures correspond to the succession of approximate for the irrational number $v_A = (1 + \sqrt{5})/2$). For the case of $v_A = 1 + 34/55$ as example, the total number of clusters in the limiting phase $\langle 1 \rangle$ is found to be 144. For intermediate $\delta\varepsilon$ in the growth diagram, we have the usual ordered mixing of the 0 sequence (which remains BB since $v_B = 1$) and sequence 1 which contains 144 clusters. As example, for an ordered phase $\langle p/q \rangle = 8/21$, the periodic sequence will contain $8 \times 144 + 13 \times 2 = 1\,178$ clusters.

Table I. — The unit cell of the limiting phase $\langle 1 \rangle$ is given for various valency for the atom A. For B, the valency is let $v_B = 1$

$v_A = 1+1$	ABB
$v_A = 1+1/2$	ABBAB
$v_A = 1+2/3$	ABBABABB
$v_A = 1+3/5$	ABBABABBABBAB
$v_A = 1+5/8$	ABBABABBABBABABBABABB
$v_A = 1+8/13$	ABBABABBABBABABBABABBABBABABBABABB
$v_A = 1+13/21$	ABBABABBABBABABBABABBABBABABBABBABABBABBABABBABABBABABB

If we now vary both valencies v_A and v_B , the elementary period of the phase $\langle 1 \rangle$ will contain still larger number of clusters. This number can be calculated: let's us call N_A and N_B the number of clusters A and B in the period of $\langle 1 \rangle$. To satisfy the « charge-transfer » rule and achieve the closure of the B-bands, the total number of electrons must be equal to two times the number of B bands: $2 N_B$ (the factor two is due to the spin of the electrons). Thus we have the relation: $N_A(r_A/s_A) + N_B(r_B/s_B) = 2 N_B$, which yields: $N_A = (2 s_B - r_B) s_A$ and $N_B = r_A s_B$, if all the integers r_A , s_A , r_B , s_B are irreducible one with each others. A simple calculation can now be made. The typical size of clusters which can be

found in real QC's is about 50-100 atoms. Taking for examples the following valencies, $v_A = 86/55$ and $v_B = 35/47$, we obtain $N_A = 3\,245$ and $N_B = 4\,042$, and the total number of clusters in the limiting phase $\langle 1 \rangle$ is 7 245. A real cluster has roughly a size of 20 Å, so that the limiting sequence will have a size about 1.4×10^6 Å (0.14 mm !), which is large enough to consider the structure as quasi-periodic. The novelty here is that for these complicated *effective* valencies, the period of the structures in the phase diagram cannot be lower than about 7 000 clusters (for our specific example) whatever the value of $\delta\varepsilon$ is, and all the structures of the growth diagram can be considered as quasi-periodic. Then from the energetical criterium that we used, there is no way to restore a simple periodicity during the growth, unless to break the elementary building blocks in order to refine single atoms.

5. Conclusion.

Describing real QC's in terms of clusters has been made for several phases [20, 21]. In the icosahedral quasicrystal Al-Pd-Mn for example, two types of clusters have been experimentally observed [21, 22], and about 80 percent of the structure can be described with these two clusters. More recently, Janot and de Boissieu [22] have proposed, using diffraction data, a description of QC's as an hierarchy of clusters. Although their model is basically a theory of stabilization of QC's and not a theory of growth, it contains common features with our approach. First, the presence of small metallic clusters plays a central role, and second the electronic structure obtained is of the same type: closed electronic shell structures. Both models are coherent one to each other, but they contain also the same misleading: they describe structures with a gap at the Fermi level, which is not the case for real QC's (there is a pseudo-gap and the density of states at the Fermi level is roughly 1/3 to 1/10 — depending on the materials — the density of states of free electrons [23]). In our model, this comes obviously from the dimensionality, but we think that the tendency to produce a closed electronic shell during the growth should remain for higher dimension. An essential difference remains however between both models: in the present work, this is the competition between (at least) two types of clusters which propagates the quasi-periodicity, otherwise there is no way to do it. This crucial point does not appear in reference [22].

It is also well-known that assembling clusters do not make real QC's. This comes from the existence of atoms which do not belong to one of the two basic clusters of the structure. Some clusters can also share a few number of atoms and, in some sense, can overlap [24]. These points are indications for taking into account different scales of energy: the binding between clusters, but also the internal energy of such clusters including distortions, overlapping. For real QC's, we are probably in a situation where the growth process connects together small clusters, but also single atoms. This is clearly out of the possibilities of the present simple model.

Finally, there is one important kinetics argument in favor of clusters as essential building blocks of QC's. As noted in the introduction, QC's phases have a very high rate of nucleation with respect to the periodic competing phases. The presence of small icosahedral clusters in the liquid phase has been pointed out by Frank [25] for explaining the undercooling of alloys. To nucleate a periodic phase, these clusters — which have not the good symmetry for the periodic phase — must be destroyed or distorted, and an activation energy barrier must be overcome. This is not the case if these clusters are the building blocks of the solid phase, for which the nucleation could occur much more rapidly, as for QC's.

In this paper, we have first shown that the chemical competition occurring during a rapid solidification can drive the propagation of long-range periodic or quasi-periodic order. We have also shown (in the context of a tight-binding model) that the « effective valencies » of the building blocks of the structure must be close to an irrational number for the propagation of

very long periods (or quasi-periodic order). This notion has been earlier used by Sire [27] (called « filling factor » in this paper), by the present author [28], and took again in reference [22]. From the energetical point of view described in our paper, it is a natural way to introduce the necessity of clusters as *main* building blocks for quasicrystals. In that case, the dynamical process of growth invoked produces spontaneously quasi-periodic patterns with closed electronic shell structures. Although the one-dimensionality of the model remains its main limitation (and further studies are necessary) and develops for that reason an incomplete physical picture, this dynamical mechanism of growth could be one possible alternative to geometrical mechanisms [5] generally used for the understanding of growth of quasicrystals.

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Appendix.

The aim of this appendix is to show that for any value of η ($0 < \eta < 1$) and for any concentration $0 \leq c = r/s \leq 1$, with r and s irreducible integers, it exists a range of $\delta\mu$:

$$\delta\mu^-(r/s) \leq \delta\mu \leq \delta\mu^+(r/s) \quad (\text{A.1})$$

for which the growth process yields the ordered alloy $A_c B_{1-c}$, with the succession of atoms A and B given by:

$$\sigma_n = \left[n \frac{r}{s} \right] - \left[(n-1) \frac{r}{s} \right]. \quad (\text{A.2})$$

For the simplicity of the notation, we will note now $x_n = \Delta E_n$. The formula (3.2) in the text becomes:

$$x_n = \delta\mu - \sum_{p=0}^{n-1} J(p+1) \sigma_{n-p} \quad (\text{A.3})$$

the term $n+1$ of the series can be written as a function of the n -th term:

$$x_{n+1} = \delta\mu - \sum_{p=0}^n J(p+1) \sigma_{n+1-p} \quad (\text{A.4})$$

and obtain:

$$x_{n+1} = \delta\mu (1 - \eta) + \eta x_n - \eta \sigma_{n+1} \quad (\text{A.5})$$

using

$$\sigma_{n+1} = \frac{1}{2} (1 + \text{sign}(x_n))$$

we have

$$\begin{cases} x_{n+1} = f(x_n) \\ f(x) = (1 - \eta) \delta\mu - \frac{\eta}{2} - \eta x - \frac{\eta}{2} \text{sign}(x) \end{cases} \quad (\text{A.6})$$

The formula (A.6) defines formally a *discrete dynamical system* [26], with « discrete time » n . The general scheme of the demonstration consists to prove that for any periodic series of spins given by (A.2) with period s , and $\delta\mu$ satisfying (A-1), it exists s points $x_1^*, x_2^*, x_3^*, \dots, x_{s-1}^*, x_s^*$ which are the *stable fixed points* of the function $f^s(x)$, defined by:

$$f^s(x) = \underbrace{f[f[f[\dots[f(x)]]]]}_{s \text{ times}} \quad (\text{A.7})$$

where the function f has been applied s times. These fixed points satisfy $f^s(x_m^*) = x_m^*$ and are transformed into one another by the function f . We have:

$$\begin{cases} x_2^* = f(x_1^*) \\ x_3^* = f(x_2^*) \\ \vdots \\ x_s^* = f(x_{s-1}^*) \\ x_1^* = f(x_s^*) \end{cases} \quad (\text{A.8})$$

and with the conditions on the signs:

$$\forall m, \quad 1 \leq m \leq s \quad \text{sign}(x_m^*) = 2\sigma_m - 1. \quad (\text{A.9})$$

This defines a s -cycle of the function f . The slope of the f^s function for all these points is lower than 1:

$$(f^s)'(x_m^*) = f'(x_1^*) \times f'(x_2^*) \times f'(x_3^*) \cdot \dots \times f'(x_{s-1}^*) \times f'(x_s^*) = \eta^s < 1 \quad (\text{A.10})$$

As consequence, the s -cycle defines an *attractor* of the dynamical system defined by (A.6) [26]. Starting from any initial conditions on x_0 belonging to the basin of attraction of this s -cycle, the iterative procedure will converge to it. Thus, for all i (with $1 \leq i \leq s$), it exists $n_0 > 0$ depending on η and $\delta\mu$, such that the series x_{n_0+m+p} converges to x_m^* when p tends to the infinity, and such that for all p we have $\text{sign}(x_{n_0+m+p}) = \text{sign}(x_m^*)$. The unit cell of the growing structure given by the $\text{sign}(x_m^*)$, is thus repeated *ad infinitum* during the growth above the critical « time » $n > n_0$.

First, we treat the particular phases $c = 1/s$ which is easy to understand, and next treat the general case $c = r/s$, for all irreducible integers r and s .

Particular case : $c = 1/s$.

What are the conditions on $\delta\mu$ for obtaining the ordered alloy $c = 1/s$ with the unit cell of spins 100...0 with $(s-1)$ zero repeated *ad infinitum*? In that case, the function f must have a s -cycle

period, and f^s have s fixed points noted $x_1^*, x_2^*, \dots, x_s^*$, and we have:

$$\begin{cases} x_2^* = \delta\mu(1-\eta) + \eta x_1^* - \eta\sigma_1 \\ x_3^* = \delta\mu(1-\eta) + \eta x_2^* - \eta\sigma_2 \\ x_4^* = \delta\mu(1-\eta) + \eta x_3^* - \eta\sigma_3 \\ \vdots \\ x_s^* = \delta\mu(1-\eta) + \eta x_{s-1}^* - n\sigma_{s-1} \\ x_1^* = \delta\mu(1-\eta) + \eta x_s^* - n\sigma_s \end{cases} \quad (\text{A.11})$$

Taking for convention that $\sigma_1 = 1$ and $\sigma_i = 0$ for $2 \leq i \leq s$, and solving the linear equations (A.11), we obtain:

$$\begin{cases} x_1^* = \delta\mu - \frac{\eta^s}{1-\eta^s} > 0 \\ x_2^* = \delta\mu - \frac{\eta}{1-\eta^s} < 0 \\ x_3^* = \delta\mu - \frac{\eta^2}{1-\eta^s} < 0 \\ \vdots \\ x_{s-1}^* = \delta\mu - \frac{\eta^{s-2}}{1-\eta^s} < 0 \\ x_s^* = \delta\mu - \frac{\eta^{s-1}}{1-\eta^s} < 0 \end{cases} \quad (\text{A.12})$$

the condition on the sign of each point is taken to be consistent with the convention that we took (the spin $\sigma_1 = 1$ and all the other equal to zero). Thus, we obtain the condition on $\delta\mu$ (using $0 < \eta < 1$):

$$\delta\mu^-(1/s) = \frac{\eta^s}{1-\eta^s} < \delta\mu < \delta\mu^+(1/s) = \frac{\eta^{s-1}}{1-\eta^s} \quad (\text{A.13})$$

this formula applied for $1/s = 1/2$ gives

$$\delta\mu^-(1/2) = \frac{\eta^2}{1-\eta^2} < \delta\mu < \delta\mu^+(1/2) = \frac{\eta}{1-\eta^2} \quad (\text{A.14})$$

which is the result calculated in section (3) for this specific concentration (formula (3.17)). We have sketched in figure A.1, the function f with a 1-cycle corresponding to the pure $\langle 1 \rangle$, and a 2-cycle corresponding to the phase $\langle 1/2 \rangle$.

General case $c = r/s$.

We search now the general case: conditions on $\delta\mu$ to have the ordered alloy with the spin given by (A.2). The s fixed points of $f^s(x)$ must verify the equations (A.8) (or equivalently (A.11)), with the conditions on the sign given by (A.8).

Solving the linear equations (A.11) for this general case, one obtains:

$$x_m^* = \delta\mu - \frac{1}{1-\eta^s} \sum_{p=1}^s \eta^p \sigma_{m-p} \quad (\text{A.15})$$

a)

b)

Fig. A1. — The function $f(x)$ is shown, and the iterative process $x_{n+1} = f(x_n)$ is sketched for two different cases. In a), the function f has a stable fixed point x^* , and the growth yields the pure phase $\langle 1 \rangle$. We are in the condition $\delta\mu > \delta\mu_1$. In b), the function f presents a stable 2-cycle (equivalently f^2 has two stable fixed points), and the growth yields the ordered alloy $A_{0.5}B_{0.5}$. In that case, $\delta\mu$ satisfies the condition (A.13).

and using (A.2), this can be rewritten as:

$$x_m^* = \delta\mu - \left(\frac{\eta - 1}{\eta} \right) \sum_{p=1}^{\infty} \eta^p \left[(m-p) \frac{r}{s} \right] - \left[(m-1) \frac{r}{s} \right] \quad (\text{A.16})$$

and now we define the two functions $g(z)$ and $S(z)$ of the real variable z :

$$\begin{aligned} g(z) &= \left(\frac{\eta - 1}{\eta} \right) \sum_{p=1}^{\infty} \eta^p \left[z - p \frac{r}{s} \right] + \left[z - \frac{r}{s} \right] \\ S(z) &= 2 \left([z] - \left[z - \frac{r}{s} \right] \right) - 1 \end{aligned} \quad (\text{A.17})$$

It can be easily check that both functions are periodic in z , with period 1:

$$\begin{aligned} g(z+1) &= g(z) \\ S(z+1) &= S(z) \end{aligned} \quad (\text{A.18})$$

and we have for all values of m (with $1 \leq m \leq s$):

$$\begin{aligned} x_m^* &= \delta\mu - g\left(m \frac{r}{s}\right) \\ S\left(m \frac{r}{s}\right) &= 2 \sigma_{m-1}. \end{aligned} \quad (\text{A.19})$$

The point is to fix the value of the parameter $\delta\mu$, such that for all z , we have:

$$S(z) = \text{sign}(\delta\mu - g(z)). \quad (\text{A.20})$$

If this condition occurs, we have the same for all the particular values of z , given by $z = mr/s$, and in that case, the equations (A.11) and (A.9) are satisfied. For that reason, we demonstrate the following assertion:

Proposition: It $\delta\mu$ satisfies $\delta\mu^-(r/s) < \delta\mu < \delta\mu^+(r/s)$, with

$$\begin{aligned} \delta\mu^-\left(\frac{r}{s}\right) &= \lim_{z \rightarrow 0^+} g(z) \\ \delta\mu^+\left(\frac{r}{s}\right) &= \lim_{z \rightarrow 0^-} g(z) \end{aligned} \quad (\text{A.21})$$

we have for all real value of z : $S(z) = \text{sign}(\delta\mu - g(z))$.

Proof: Owing to the integer part functions coming in its definition, the function g is a staircase function which varies by a jump for each value of $z = \ell/s$ (with ℓ integers). The s jumps between two successive steps in the interval $[0, 1]$ is always *negative*, except for $z = r/s$ for which the jump is *positive*. If we call by definition: $\delta g(\ell/s) = \lim_{z \rightarrow \ell/s^+} g(z) - \lim_{z \rightarrow \ell/s^-} g(z)$, we have successively: for $\ell = r$, the jump is the sum of a

positive one equal to 1, coming from $[x - r/s]$ in the definition of $g(z)$, and a negative one coming from the summation over p in $g(z)$:

$$\delta g(r/s) = - \left(\frac{1-\eta}{\eta} \right) \frac{\eta}{1-\eta^s} + 1 = 1 - \left(\frac{1-\eta}{1-\eta^s} \right) > 0$$

for $\ell \neq r$, we have only the jump coming from the summation which is negative. This come from the integer part function which have a positive or zero jump for all value of p , and since $(\eta - 1)$ is negative, the total jump for the summation over all p is negative or zero. For all values of ℓ , it exists at least one value of p , such that the integer part $[x - pr/s]$ increases by plus one at point ℓ/s . Thus the summation is strictly negative, and we

have:

$$\forall \ell \neq r \quad \delta g\left(\frac{\ell}{s}\right) < 0.$$

Taking into account the 1-periodicity of the function g and the results on its variation, we can easily sketch this function (in Fig. A2): we start at point $x = 0$ from $\lim_{z \rightarrow 0^+} g(z)$, and next it has

$(r-1)$ negative jumps up to r/s . At this point, the function has a positive jump, and next $(s-r-1)$ negative one up to 1. The jump between 0^- and 0^+ is the same at 1^- and 1^+ (owing to the periodicity), and is negative. Thus, if we choose, $\delta\mu$ satisfying (A.21), we have:

$$\begin{aligned} 0 \leq z < \frac{r}{s} \quad \text{sign}(\delta\mu - g(z)) &= 1 \\ \frac{r}{s} \leq z < 1 \quad \text{sign}(\delta\mu - g(z)) &= -1. \end{aligned} \quad (\text{A.22})$$

If we now look at the function $S(z)$, it is easy to check that:

$$\begin{aligned} 0 \leq z < \frac{r}{s} \quad S(z) &= 1 \\ \frac{r}{s} \leq z < 1 \quad S(z) &= -1 \end{aligned} \quad (\text{A.23})$$

Fig. A2. — The function $g(z)$ is plotted for the case $r/s = 5/8$, and $\eta = 0.9$. The range of $\delta\mu$ over which the growth of this structure is stabilized is shown on the diagram. The two limiting values $\delta\mu^-(r/s)$ and $\delta\mu^+(r/s)$ are also marked.

and thus (A.22) and (A.23) together yield,

$$\forall z, \quad S(z) = \text{sign}(\delta\mu - g(z))$$

which achieves the proof of the proposition.

The conditions on $\delta\mu$ given by (A.21) can be rewritten in different way:

$$\begin{aligned} \delta\mu^-\left(\frac{r}{s}\right) &= \left(\frac{\eta-1}{\eta}\right) \lim_{\varepsilon \rightarrow 0^+} \left(\sum_{p=1}^{\infty} \eta^p \left[z - p \frac{r}{s} \right] \right) - 1 = \\ &= \left(\frac{1-\eta}{\eta}\right) = \lim_{\varepsilon \rightarrow 0^-} \left(\sum_{p=1}^{\infty} \eta^p \left[p \frac{r}{s} + \varepsilon \right] \right) \\ \delta\mu^+\left(\frac{r}{s}\right) &= \left(\frac{1-\eta}{\eta}\right) \lim_{\varepsilon \rightarrow 0^+} \left(\sum_{p=1}^{\infty} \eta^p \left[p \frac{r}{s} + \varepsilon \right] \right) \end{aligned} \quad (\text{A.24})$$

which is the result of formula (3.20) in the main text. The function:

$$\delta\mu(c) = \left(\frac{1-\eta}{\eta}\right) \sum_{p=1}^{\infty} \eta^p [pc] \quad (\text{A.25})$$

is an increasing function of c , which varies by discontinuities for each rational values of $c = r/s$, with the values of the discontinuities at these points given by (A.24). Thus, it is inversible, and the reverse function $c(\delta\mu)$ present a step for each rational values of c (this type of function is called a devil's staircase [13b]). It is complete, which means that the variation of $\delta\mu$ comes only from the discontinuities at the rational points. It comes out for the growth model that for each value of $\delta\mu$, it exists a unique ordered alloy with concentration c given by $c(\delta\mu)$ which is obtained during the growth. This alloy is periodic if c is rational, and quasi-periodic if c is irrational.

References

- [1] Shechtman D., Blech I., Gratias D., Cahn J. W., *Phys. Rev. Lett.* **53** (1984) 1951.
- [2] Friedel J., Denoyer F., *C. R. Acad. Sci. Paris Serie II* **305** (1987) 171.
- [3] Elser V., Proc. 15th Intern. Coll. on group theoretical methods in Physics, Vol. 1, R. Gilmore and D. D. Feng Eds. (World Scientific, 1987).
- [4] Penrose R., « Introduction to the mathematics of Quasicrystals » Aperiodicity and order, vol. 2, M. V. Jaric Ed. (Academic Press Inc., 1989).
- [5] a) Penrose R., *Bull. Inst. Math. Appl.* **10** (1974) 266;
b) Onoda G. Y., Steinhard P. J., DiVicenzo D. P. and Socolar J. E. S., *Phys. Rev. Lett.* **60** (1988) 25 2653; In the reference b), the authors add new « matching rules » in order to complete the rules earlier proposed by Penrose to produce a perfect 2D Penrose tiling. They interpret these *ad hoc* matching rules as short range interactions between atomic clusters, but they do not precise which interactions and from where they come (electronic? elastic? for which Hamiltonian?).
- [6] Tsai A. P., Masumoto T., Yamamoto A., *Philos. Mag. Lett.* **66** (1992) 4 203.
- [7] Daulton T. L., Kelton K. F., *Philos. Mag. Lett.* **63** (1991) 5 257.
- [8] Ducastelle F., « Order and phase Stability in Alloys », Cohesion and structure, Vol. 3, F. R. de Boer and D. G. Pettifor Eds. (North-Holland, 1991)
- [9] Loiseau A., Van Tendeloo G., Portier R., Ducastelle F., *J. Phys. France* **46** (1985) 595.

- [10] Schaeffer R. J., Bendersky L. A., « Introduction to Quasicrystals » M. V. Jaric Ed. (Academic press Inc., 1988).
- [11] Kelton K. F., *Solid State Phys* **45** (1991) 75.
- [12] Hubbard J., *Phys. Rev. B* **17** (1978) 494.
- [13] a) Pokrovsky V. L. and Uimin G. V., *J. Phys. C* **11** (1978) 3535;
b) Aubry S., *J. Phys. C* **16** (1983) 2497.
- [14] For a review on the theory of approximants, see Duneau M., « Approximant Phases of quasicrystals » Ecole d'Hiver sur les Quasicristaux, Gdr5-CNRS, Aussois, France (1994), to be published.
- [15] For a clear and simple review on Devil staircase's and related problems, see R. B. Griffiths, « Fundamental problems in Statistical Mechanics VII » H. Van Beijeren Ed. (Elsevier Science Pub. B.V. 1990).
- [16] de Heer W. A., Knight W. D., Chou M. Y. and Cohen M. L., *Solid State Phys.* **40** (1987) 93.
- [17] Mac Kay A. L., *Acta Cryst* **15** (1962) 916.
- [18] Khanna S. N. and Jena P., *Phys. Rev. Lett* **69** (1994) 11, 1664.
- [19] Saito S. and Ohnishi S., *Phys. Rev. Lett* **59** (1990) 190.
- [20] Guyot P., Audier M. and de Boissieu M., « Physics and Chemistry of finite systems: from Clusters to Crystals », Vol. 1, 49, P. Jena, S. N. Khanna and B. K. Rao Eds., Nato Asi Series (Kluwer Academic Publishers, 1990).
- [21] Boudard M., de Boissieu M., Janot C., Beeli G. H., Nissen H. U., Vincent H., Ibberson R. and Dubois J. M., *J. Phys. Condens. Matter* (1992);
Boudard M., *Thesis*, Grenoble (1993) unpublished.
- [22] Janot C. and de Boissieu M., *Phys. Rev. Lett* **72** (1994) 11 1674.
- [23] Mayou D. and Berger C., « Electronic Properties of Quasicrystals », Ecole d'Hiver sur les Quasicristaux, Gdr5-CNRS, Aussois, France (1994) to be published.
- [24] Kelton K. F., *Int. Mater. Rev* **38** (1993) 3 105.
- [25] Frank F. C., *Proc. R. Soc. London A* **215** (1952) 43.
- [26] Feigenbaum, *Physica* **7D** (1983) 16-39.
- [27] Sire C., *J. Phys. A. Math. Gen* **24** (1991) 5137.
- [28] Quémerais P., Réunion annuelle du groupe français d'étude des quasicristaux (livret de résumés 2, p. 42), C. Janot Ed., Institut Laue-Langevin, Grenoble (June 1993).