Abstract. Structural arguments are proposed that support the hypothesis that the equilibrium 5f-surfaces of \( i \)-AlPdMn icosahedral alloys are actual cuts of the bulk structure with almost pure Al termination planes \([1, 2]\) corresponding to actual bulk properties with no need for possible Al segregation on the surface. Most of the 5f termination planes in \( i \)-AlPdMn are made of two close planes containing essentially Al at the upper one and Al and Pd at the second one (see for instance \([3]\)). Here, perfect unrelaxed structural models that differ only in the chemical distribution of the atomic species are devised, close to the description proposed in \([4]\). Once compared to experimental X-rays data \([5]\), the calculations show that although the chemical decoration has a rather limited influence on the global \( R \)-factor, there is a clear tendency toward favoring models with almost pure Al on the atomic surface located on the node \( n \), in excellent agreement with the surface studies.

1. Introduction
The \( i \)-AlPdMn phase is one of the most studied systems among the quasicrystals. Especially, their fivefold surface has been investigated by various surface sensitive techniques \([1, 2, 6, 7, 8]\). The interest to their surface has arisen from interesting surface properties such as good oxidation resistance and low friction (see, for instance \([9]\)).

Surface studies of sputter-annealed 5f-surfaces of \( i \)-AlPdMn possesses a step-terrace morphology \([3, 6, 7, 10]\). The structural nature of the terraces has been explored by many techniques, among them low energy electron diffraction analysis of intensity-voltage curves (LEED-IV) where Gierer \textit{et al.} \([1, 2]\) noticed that two types of closely spaced, dense planes form the terminating layers, from among the large ensemble of non-identical planes which forms the bulk structure. In other words, the bulk structure can be classified into groups of self-similar planes, and one of these groups was the most likely candidate for the surface structure. Very similar observations were reported in X-ray photoelectron diffraction (XPD) studies \([11]\). However, at present, there is a debate as to which group of planes is favored \([12, 13, 14, 15]\).

The chemical decoration of the terminating layers has been investigated by LEED-IV technique \([1, 2]\). The best fit of the data to the Boudard model \([5]\) revealed that the planes
containing 93 at.% Al and 7 at.% Mn on average are the top planes in the terminating layers while Pd is restricted to the second plane. Very similar results were obtained by low energy ion scattering (LEIS) [8]. To be specific, both techniques indicated that all Pd resides only in the second plane; the top plane is free of Pd. Regarding the top plane Mn content, LEIS set the upper limit in one study as 6.3 at.%. A later LEIS study indicated that the top planes contain almost pure Al with 1 at.% Mn [8]. LEED-IV data analysis set an upper limit of 10 at.%. It is worth noting that, unlike LEED-IV, LEIS technique does not require a structural model: data analysis is model independent. Recent STM studies for film nucleation, especially Si [16] and Bi [17], suggest that the topmost surface plane contains some Mn: the average Mn concentration in the topmost plane is between 0 and 10 at.%, and our recent bulk structural model analysis [3], suggests that it is most probably less than 4 at.% [3].

Our present goal is the following. We shall first set up a simple but realistic model that allows for large chemical variations while keeping constant the overall stoichiometry and all other diffraction parameters and check the theoretical X-rays diffraction spectra against the experimental ones for bulk i-AlPdMn. We will then analyze the variations of the $R$-factors as a function of specific occupancy factors to check the consistency between the rich Al planes as observed by surface studies and the predictions of the bulk models.

2. The atomic model

The geometrical fact that makes the present work possible for a valuable test for consistency, is that each of the dense 5f-planes is generated by one unique AS, either $n$ or $n'$ according to the stacking [10, 18]. The consequence is that the composition of these termination planes is dictated by the nature of the atomic species attached to one AS only. Based on the most recent analyzes [3] from the actual structural models, an agreement has emerged that the $n$ ASs generate the termination upper planes.

We therefore designed a generic model of i-AlPdMn, characterized by two independent parameters $0 \leq x \leq 1$ and $0 \leq y \leq 1$ representing the occupation factors of the atomic species Pd and Mn on the ASs $n$ and $n'$, in a way that keeps constant both the overall composition, and the shape and volume of the relevant chemical cells in perpendicular space. The model is used to study the variations of $R$-factor as a function of $x$ and $y$ obtained from the comparison with the experimental X-rays diffraction data collected by M. Boudard et al. [5]. The idea is to progressively modify the chemical decorations between $n$ and $n'$ with no change in the shapes of the cells nor in the overall composition: then, the variations in diffraction intensities are exclusively due to the sole chemical contrast.

The skeleton of the atomic positions of the model in the real space is the usual simple one generated in 6D space by three AS located at respectively $n = (0, 0, 0, 0, 0, 0)$, $n' = (1, 0, 0, 0, 0, 0)$ and $bc = 1/2$ $(1, 1, 1, 1, 1, 1)$ as shown on figure 1.

The chemistry of the model is based on the cell decomposition of the $M$ and $M'$ clusters (pseudo-Mackay clusters) as discussed in previous model studies [4]. This cell decomposition is made of seven cells shown on figure 1:

- the central cell $\omega = c_1 \cup c_2$ is a small triacontahedron of volume $2\tau - 3$ located in the middle of the $n$ and $n'$ AS's. It generates the $M$ (if located on $n$) and $M'$ (if located on $n'$) centers.
- the cell noted $\alpha = c_2 \cup c_3 \cup c_4$ that generates the large icosahedra of the $M$ if on $n'$, or of the $M'$ if on $n$;
- the cell noted $\beta = c_4 \cup c_5 \cup c_6$ that generates the external icosidodecahedra of the $M$ if on $n$ or of the $M'$ if on $n'$;
- the cell noted $\gamma = c_6 \cup c_7$ that generates the partially occupied (7/20) inner dodecahedra of the $M$ if on $n'$, or $M'$ if on $n$. 


Figure 1. Top: the three main atomic surfaces of the models, from left to right, \( n \), \( n' \) and \( bc \). Middle: the cell decomposition in \( E_\perp \) of the geometric model for the \( M \) and \( M' \) clusters in \( E_\parallel \). Bottom: Definition of the model. The model depends on two independent occupancy parameters \( x \) and \( y \) that vary between 0 and 1 at constant stoichiometry \( \text{Al}_{68.83}\text{Pd}_{22.75}\text{Mn}_{8.42} \) (as compared with the experimental value \( \text{Al}_{70.3}\text{Pd}_{21.4}\text{Mn}_{8.3} \) in [19]) and density of 5.07. For \( x = 0, y = 0 \), the AS \( n \) is pure Al thus generating a structure where the dense 5f planes are occupied by pure Al. At the opposite extreme, values of \( x = 1 \) and \( y = 1 \) correspond to a model where the AS \( n \) is maximally charged in Pd and Mn atoms and \( n' \) is pure Al. Surfaces studies are in favor of the first case (\( x = y = 0 \)).
Table 1. Chemical decoration of \( M \) and \( M' \) clusters as a function of the \( x \) and \( y \) parameters. The centers and partial inner dodecahedra of \( M \) and \( M' \) are always occupied by Al.

| Model            | \( (x, y) \) | \( (0, 0) \) | \( (0, 1) \) | \( (1, 0) \) | \( (1, 1) \) |
|------------------|--------------|--------------|--------------|--------------|--------------|
| \( M \) cluster  |              |              |              |              |              |
| icosahedron      | \( 12y \text{Al} + 12(1 - y) \text{Mn} \) | \( 12 \text{Mn} \) | \( 12 \text{Al} \) | \( 12 \text{Mn} \) | \( 12 \text{Al} \) |
| icosidodecahedron| \( 30(1 - x) \text{Al} + 30x \text{Pd} \) | \( 30 \text{Al} \) | \( 30 \text{Al} \) | \( 30 \text{Pd} \) | \( 30 \text{Pd} \) |
| \( M' \) cluster |              |              |              |              |              |
| icosahedron      | \( 12(1 - y) \text{Al} + 12y \text{Mn} \) | \( 12 \text{Al} \) | \( 12 \text{Mn} \) | \( 12 \text{Al} \) | \( 12 \text{Mn} \) |
| icosidodecahedron| \( 30x \text{Al} + 30(1 - x) \text{Pd} \) | \( 30 \text{Pd} \) | \( 30 \text{Pd} \) | \( 30 \text{Al} \) | \( 30 \text{Al} \) |

These four major cells intersect two by two by \( c_2 \), \( c_4 \) and \( c_6 \). The decision has been made here to build the chemical order using the cells \( \omega \), \( \alpha \), \( \beta \) and \( \gamma \). The small AS at \( bc \) is always filled with Pd (see for instance [5]). The ASs at \( n \) and \( n' \) are decomposed using \( \beta \) and \( \alpha \) cells. The chemical distribution is done the following way (see figure 1). We first assign Al to both \( n \) and \( n' \) and then replace \( x \) percent of the volume of \( \beta_n \) by Pd and \( y \) percent of the volume of \( \alpha_n \) by Mn. Correlatively, to insure constant composition, we replace \( 1 - x \) percent of the volume of \( \beta_{n'} \) by Pd and \( 1 - y \) percent of the volume of \( \alpha_{n'} \) by Mn. The chemical decoration of the model is therefore entirely defined by the pair \( (x, y) \) varying in the domain \( x, y \in \{ (0,0), (1,0), (1,1), (0,1) \} \). These four corners correspond to \( M \) and \( M' \) clusters decorated with Al, Pd and Mn atoms as described on table 1. Finally, since \( \omega \) and \( \gamma \) are embedded in larger cells corresponding to Al species, the \( M \) and \( M' \) centers and inner partial dodecahedra are invariably occupied by Al atoms. Exchanging \( x \) and \( y \) with their complements to 1 results in exchanging the chemical distributions on the external icosahedra and the icosidodecahedra of the \( M \) and \( M' \) clusters. Hence, the \( (0,0) \) model corresponds to pure Al on \( n \) and all Pd and Mn on \( n' \), whereas its complementary model \( (1,1) \) corresponds to pure Al on \( n' \) and all Pd and Mn on \( n \).

The model is compared to the actual structure by calculating the theoretical diffraction intensities and comparing them to the experimental data collected by Boudard et al. [5] using the reliability factors, noted here \( R \)-factors, expressed in \( \% \) and defined by \( R_n = \frac{\sum |a_{\text{exp}} - a_{\text{theo}}|^2}{\sum a_{\text{exp}}^2} \) where \( a_{\text{exp}} \) and \( a_{\text{theo}} \) are the absolute values of the experimental and theoretical structure factors of the observed reflections. These reliability factors \( R(x, y) \) for X-rays data are plotted as 2D surfaces on figure 2.

The first point to be noted is that the \( R \)-factors vary between 6.51 \( \% \) for model \( (0, 0) \) to 16.56 \( \% \) for model \( (1, 1) \). This difference in the \( R \)-factors, of 10\( \% \), is relatively small given that the difference between the two models is a large change in the chemical decoration, \( i.e. \) complete exchange in the chemistry of \( M \) and \( M' \) clusters. This relative weak influence of the chemistry on the overall diffraction data could be the origin of the multiplication of different atomic models of \( i-AlPdMn \) concerning the chemical order. The difference in \( R \)-factors of 10\( \% \) between the extreme situations of having Pd and Mn atoms located on \( n' \) for model \( (0,0) \) and on \( n \) for model \( (1,1) \) establishes a relative scale for judging the effects of other aspects of chemical order.

The second point to be noted is that the surface \( R(x, y) \) shows little change with respect to \( y \) but a significant one with respect to \( x \). From models \( (0,0) \) and \( (1,0) \) where Mn atoms are on the icosahedra of the \( M \) clusters, to the \( (0,1) \) and \( (1,1) \) models where Mn atoms are on the icosahedra of the \( M' \) clusters, the variation in \( R \)-factors is only \( 8.89 - 6.51 = 2.38 \% \) and

\(^1\) Actually because of very small overlaps between \( \omega \), \( \alpha \), \( \beta \) and \( \gamma \), we use in the computations the two cells \( c_5 \) and \( c_1 \) in place of respectively \( \beta \) and \( \omega \); this insures perfect chemical distribution and generates no pertinent differences in our context.
Figure 2. Values $R(x, y)$ of the $R$-factor as a function of the two variables $(x, y)$ for X-rays diffraction data with 314 beams. Values of the $R$-factor at the four extreme $(x, y)$ points are: $(0,0) 6.51$, $(0,1) 8.89$, $(1,0) 15.87$ and $(1,1) 16.56$.

16.56 $-$ 15.87 = 0.69%, respectively. Although the smallest $R$-factor, 6.51%, is obtained for Mn atoms located on $n'$ (Mn on the icosahedra of the $M$ clusters), transferring some Mn to $n$ (at the expense of Al) has a very small impact on the $R$-factor. In other words, the X-ray diffraction data are not well-suited to showing the Mn/Al ordering on either $M$ or $M'$. On the contrary, the $R$-factor changes strongly from models (1,0) and (1,1) to models (0,0) and (0,1). The changes in $R$-factors along $x$ (exchanging Pd / Al between the $M$ and $M'$ icosidodecahedra) are 15.87 $-$ 6.51 = 9.36% and 16.56 $-$ 8.89 = 7.67%, respectively. The minimum $R$-factor of 6.51% is clearly in favor of locating all Pd atoms on $n'$.

These results are nicely consistent with the surface analysis data that show almost pure Al termination 5f-planes with a small amount of Mn.

In the simplest scheme of AS $n$ being pure aluminum ($x = y = 0$), $M$ clusters have Al at the center, on the inner partial dodecahedron and on the icosidodecahedron, and Mn atoms on the icosahedron. $M'$ clusters have Al at the center, on the inner partial dodecahedron and on the icosahedron, and Pd atoms on the icosidodecahedron.

3. Conclusion
The present numerical explorations on plausible sets of perfect unrelaxed chemical models of icosahedral $i$-AlPdMn structures show that the chemical decoration has a rather limited influence on the global $R$-factor for models that differ only in the way the chemical species are distributed between the $n$ and $n'$ ASs: this explains why it is so difficult to assert which model is best with respect to chemical distribution.

Irrespective of these restrictions, it is clear that the structural models that are in best agreement with the experimental X-rays results are those with parameters $(x, y)$ close to values $\{(0,0) \rightarrow (0,1)\}$. As a consequence, models having pure Al plus possibly some Mn on the $n$ AS with Pd confined on $n'$ and bc are the best candidates for a simple structural description consistent with both the bulk diffraction data and surface analyses as discussed in reference [3].

These results enforce the idea that 5-f termination planes do indeed correspond to actual cuts of the bulk structures, irrespective of the tiny contractions of the interplanar distances between the two last planes. Furthermore, observed local features, as dark stars, in STM images are
formed by $M, M'$ clusters since placing Pd on $n'$ eliminates the $B$ clusters being the candidates for them [20].

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References
[1] Gierer M, Van Hove M A, Goldman A I, Shen Z, Chang S-L, Jenks C J, Zhang C M and Thiel P A, *Phys. Rev. Lett.* **78**, 467 (1998).
[2] Gierer M, Van Hove M A, Goldman A I, Shen Z, Chang S-L, Pinhero P J, Jenks C J, Anderegg J W, Zhang C M and Thiel P A, *Phys. Rev., B* **57**, 7628 (1998).
[3] Unal B, Jenks C J and Thiel P A, *Phys. Rev., B* **77** 195419-1–10 (2008).
[4] Quiquandon M and Gratias D, *Phys. Rev. B* **74** 214205–1–9 (2006).
[5] Boudard M, de Boissieu M, Janot C, Heger G, Beeli C, Nissen H-U, Vincent H, Ibberson R, Audier M and Dubois J-M, *J. Phys.: Condens. Matter* **4** 10149–10168 (1992).
[6] Schaub T M, Bürgler D E, Güntherodt H-J, Suck J-B and Audier M, *Appl. Phys. A* **61**, 491 (1995).
[7] McGrath R, Leung L, Barrett S D and Ledieu J, *Proc. Royal Microscopical Society* **40**, 215 (2005).
[8] Jenks C J, Ross A R, Lograsso T A, Whaley J A and Bastasz R, *Surf. Sci.* **521**, 34 (2002).
[9] Dubois J-M, *Useful Quasicrystals*. First ed. World Scientific.Singapore: (2005).
[10] Barbier L, Le Floc'h D, Calvayrac Y and Gratias D, *Phys. Rev. Lett.* **88**, 085506 (2002).
[11] Zheng J-C, Huan C H A, Wei A T S, Van Hove M A, Fadley C S, Shi F J, Rotenberg E, Barman S R, Paggel J J, Horn K, Ebert P, and Urban K, *Phys. Rev. B* **69**, 134107 (2004).
[12] Papadopolos Z, Kasner G, Ledieu J, Cox E J, Richardson N V, Chen Q, Diehl R D, Lograsso T A, Ross A R, and McGrath R, *Phys. Rev. B* **66**, 184207 (2002).
[13] Papadopolos Z, Gröning O, and Widmer R, in *Models, Mysteries and Magic of Molecules*, edited by Boeyens J C A and Ogilvie J F, Springer, New York, (2008).
[14] Krajci M, Hafner J, Ledieu J, and McGrath R, *Phys. Rev. B* **73**, 024202 (2006).
[15] Ledieu J and McGrath R, *J. Phys.: Condens. Matter* **15**, S3113 (2003).
[16] Ledieu J, Unsworth P, Lograsso T A, Ross A R and McGrath R, *Phys. Rev. B* **73**, 012204/1 (2006).
[17] Smerdon J A, Sharma H R, Ledieu J and McGrath R, *J. Phys.: Condens. Matter*. **20**, 314005 (2008).
[18] Barbier L and Gratias D, *Progress in Surface Science* **75** 177-189 (2004).
[19] Quiquandon M, Calvayrac Y, Quivy A, Faudot F and Gratias D, in *MRS Symposium Proceedings: Quasicrystals* edited by Dubois J-M, Thiel P A, Tsai A-P and Urban K (MRS, Warrendale, 1999) pp. 95–106 (1999).
[20] Unal B, Jenks C J and Thiel P A, *J. Phys.: Condens. Matter* **21**, 55009 (2009).