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Unique six-dimensional structural model for Al-Pd-Mn and Al-Cu-Fe icosahedral phases

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A simple unique 6D atomic structural model for both *i*-AlPdMn and *i*-AlCuFe is proposed that is built with an unique and simple set of atomic surfaces and chemical subcells. The model has accurate compositions with respect to the best experimental estimates of both structures and fit reasonably well the experimental diffraction data of x-rays and neutrons spectra with no fitting parameters. It presents a surprisingly small number of chemical configurations for the basic *B* (Bergman) and *M* (Mackay) type clusters as compared to what could be expected for quasiperiodic ternary systems. Finally, because of its relative simplicity, the present model is well adapted for being used in discussing the physical properties of either *i*-AlPdMn or *i*-AlCuFe that are essentially dependent on the local atomic arrangements of the various chemical species.

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I. INTRODUCTION

Search for precise atomic descriptions of real quasicrystals has been one of the most puzzling problems from the very beginning after their discovery.[1] Very substantial progresse has been made from the firsts attempts (see for instance, Refs. 2–4) of structure determination in the framework of the *N*-dim crystallography.[5–8]

The most sophisticated presently available atomic models are those of the decagonal[9] and icosahedral phases.[10] They show diffraction diagrams that compare to the experimental diffraction data as accurately as those of usual refined periodic structures. However, these sophisticated optimized models are based on relatively complex networks of intricate atomic clusters that are rather difficult to visualize and to use for correlating atomic structures and physical properties. Moreover, they are described using more than hundreds of fit parameters that make the uniqueness of the final structure essentially impossible to assert and thus weakens somehow the physical pertinence and usefulness of these models.

Our present goal is to take another point of view, complementary to the modern crystallographic approaches of structural determination, in constructing an ideally quasiperiodic atomic model with *no fitting parameters*, that is as simple as possible and exhibits *a minimum number of different chemical configurations* for the main atomic aggregates encountered in these kind of structures, i.e., the *B* (Bergman) and *M* (Mackay) type clusters.

The validation of our model is based on the standard quantitative comparisons between model and experiment on chemical compositions, density, and, of course, neutrons and x rays diffraction results. We extracted the diffraction files from the experiments of. Cornier-Quiquandon *et al.*[3] for *i*-AlCuFe and of Boudard *et al.*[4] for *i*-AlPdMn. Validation criteria have been considered as satisfactory using the following figures: it should reproduce the experimental composition and density in a range better than 1% and should fit neutron and x-ray-diffraction data with a reliability factor R_I (defined later in the paper) not larger than 7% remembering that we use no adjustable parameters. Beyond these structural figures of merit, we shall assess the plausibility of our model in inferring some of its physical properties as compared to the well-established experimental magnetic properties of these alloys.[11–14]

II. SIX-DIMENSIONAL MODEL

The many attempts made during this work for constructing plausible atomic structures have all been rejected on the basis of at least one unsatisfactory criterion as previously defined. One unique structural model came out that fitted all the criteria for both *i*-AlCuFe and *i*-AlPdMn and turned out to be, in fact, the simplest by far, of all tested models.

A. Structural characteristics

The model is a chemical decoration of an overall skeleton of three main atomic surfaces (AS) as proposed[15] in 1995 by Katz and one of us (D.G.) designated here as KG model. It is based on the cell decomposition for the four *B*, *B′* and *M*, *M′* basic clusters that have been recently extensively discussed.[16,17] These four clusters represent 97.61% of the atoms of the structure in the sense that any randomly picked atom of the structure has 97.61% probability to belong to at least one of those clusters. The interatomic distances are computed for the *i*-AlPdMn phase on the basis of a primitive six-dimensional (6D)-lattice parameter[4] $A=0.6451$ nm; they are given in parentheses for *i*-AlCuFe with a primitive 6D-lattice parameter[3] $A=0.631\,46$ nm.

The basic clusters are defined as follows:

(i) the $M(M')$ cluster has 50 atoms: a center (1 atom), an inner dodecahedron partially occupied (7 atoms on 20 sites) of radius 0.2567 (0.2513) nm, a complete outer icosahedron (12 atoms) of radius 0.4561 (0.4465) nm, and a complete outer icosidodecahedron (30 atoms) of radius 0.4796 (0.4695) nm.

(ii) the *B* cluster has 33 atoms: a center (1 atom) surrounded by a complete icosahedron (12 atoms) of radius 0.2819 (0.2760) nm and a complete dodecahedron (20 atoms) of radius 0.4154 (0.4066) nm;

(iii) the *B′* cluster has 32 atoms: an empty center, a first partial icosahedron (3 atoms on 12 sites) of radius 0.1742 (0.1706) nm completed by a second partial icosahedron (9 atoms on 12 sites) of radius 0.2819 (0.2760) nm and a com-

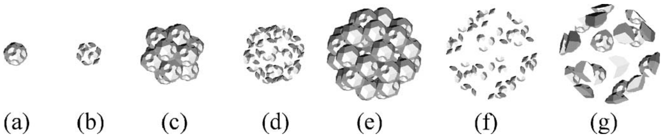

FIG. 1. The seven cells of the decomposition of the n AS for the $M(M')$ clusters. See Table I for the corresponding atomic configurations.

plete dodecahedron (20 atoms) of radius 0.4154 (0.4066) nm.

The prototype is based on the simple heuristic idea that the atomic ordering should *minimize* the number of chemical configurations of the M and M' clusters. This is achieved by distributing the chemical species according to the cells of the geometrical decomposition of the $M(M')$ clusters shown in Fig. 1 and defined in Table I: four cells (a, c, e, g) are associated each to a single well-defined configuration whereas the three cells (b, d, and f) generate atomic sites that are common to two configurations (see Table I). Here, a decision must be taken of what atomic species to choose associated to either of these two involved configurations. As will be justified later, a convenient regrouping of the subcells is the following:

(i) the cells (c) and (d) form a cell noted $\alpha=(c)+(d)$ that collects all sites of the large outer icosahedra of either the M or M' clusters with the exception of those sites that are also centers of the other $M(M')$ cluster;

(ii) the cells (d), (e), and (f) form a cell noted $\beta=(d)+(e)+(f)$ that generates the complete orbit of the vertices of the icosidodecahedra of either M or M' clusters; because it contains the (d) subcell, the cell β cannot be located on the same node as α;

(iii) the last interesting cell is the cell (g) that we will note $\gamma=(g)$ and that represents the sites of the partially occupied (7/20) inner dodecahedron of one of the $M(M')$ clusters and that are not part of the icosidodecahedron of the other $M(M')$ cluster.

These three cells, α, β, and γ, are the *only ingredients* needed to describe the chemistry of both structures i-AlPdMn and i-AlCuFe.

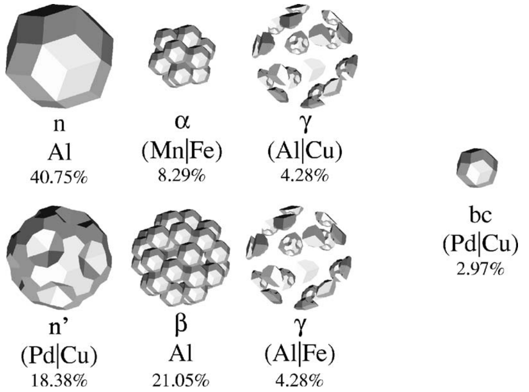

FIG. 2. The model (see Table II) is a chemical decoration of the three basic atomic surfaces of the KG model (Ref. 15) attached to, respectively, the even node $n=(0,0,0,0,0,0)$ and the odd node $n'=(1,0,0,0,0,0)$ and the (odd) body center $bc=(\bar{1},1,1,1,1,\bar{1})/2$. The decoration is performed with three subcells issued from the $M(M')$-cluster decomposition: α corresponds to the large icosahedron, β to the full icosidodecahedron, and γ to the partially occupied (7 atoms over 20) inner dodecahedron. The notation $(X|Y)$ of the chemical species means using X for modeling i-AlPdMn and Y for modeling i-AlCuFe.

Indeed, it must be observed that the optimum experimental compositions of the alloys proposed in, respectively, Refs. 18 and 19 are, respectively, $Al_{70.3}Pd_{21.4}Mn_{8.3}$ and $Al_{62}Cu_{25.5}Fe_{12.5}$, we note that the composition differences between the two alloys are very close to integer multiples of the atom fraction generated by the γ cell, $c_\gamma=4.28$ at. %: $\Delta c_{\mathrm{Al}}\approx 2c_\gamma$, $c_{\mathrm{Fe}}-c_{\mathrm{Mn}}\approx c_\gamma$, and $c_{\mathrm{Cu}}-c_{\mathrm{Pd}}\approx c_\gamma$. Hence a natural chemical decoration consists in distributing an α cell on n, a β cell on n', and a γ cell on each n and n' ASs as shown in Fig. 2. This leads to the model given in Table II and shown in Fig. 2, that is defined as follows:

(i) i-AlPdMn: the n AS is aluminium with the exception of the cell α that is associated to Mn; the n' AS is palladium with the exception of the cells β and γ that are both associated to Al; the bc AS is pure Pd;

(ii) i-AlCuFe: the n AS is aluminium with the exception of the cell α associated to Fe and the cell γ associated to Cu; the n' AS is copper with the exception of the cell β associ-

TABLE I. Cell decomposition of the n AS for the M (M') configurations. The cell decomposition for n' AS is the same by exchanging the role of M and M'. The cells (a) to (g) are shown in Fig. 1. The cells (b), (d), and (f) define atomic sites that are shared between M and M' clusters whereas the cells (a), (c), (e), and (g) correspond to atoms belonging to a single M or M' cluster.

Cell	Volume	Fraction % of n AS	Configuration
(a)	$-71+44\tau$	1.08	M center
(b)	$68-42\tau$	0.24	M center AND M' outer icosahedron
(c)	$-444+276\tau$	14.37	M' outer icosahedron
(d)	$340-210\tau$	1.18	M' outer icosahedron AND M icosidodecahedron
(e)	$-770+480\tau$	37.11	M icosidodecahedron
(f)	$340-210\tau$	1.18	M icosidodecahedron AND M' inner partial dodecahedron
(g)	$-361+224\tau$	8.03	M' inner partial dodecahedron

TABLE II. The distribution of the chemical cells shown in Fig. 2 defining the structural model. The model of *i*-AlPdMn has composition $Al_{70.35}Pd_{21.36}Mn_{8.29}$ (to be compared with the experimental one $Al_{70.3}Pd_{21.4}Mn_{8.3}$) and a density $\varrho=4.95$ g/cm^3. The model of *i*-AlCuFe has composition $Al_{61.80}Cu_{25.63}Fe_{12.57}$ (to be compared to the experimental value $Al_{62}Cu_{25.5}Fe_{12.5}$) and a density $\varrho=4.56$ g/cm^3.

Site	Cell	Volume	at. %	*i*-AlPdMn	*i*-AlCuFe
n	α	$-104+66\tau$	8.2913	Mn	Fe
	γ	$-361+224\tau$	4.2779	Al	Cu
	$T_n-\alpha-\gamma$	$470-282\tau$	40.7531	Al	Al
n'	β	$-90+60\tau$	21.0446	Al	Al
	γ	$-361+224\tau$	4.2779	Al	Fe
	$T_{n'}-\beta-\gamma$	$470-278\tau$	18.3836	Pd	Cu
bc	T_{bc}	1	2.9715	Pd	Cu

ated to Al and the cell γ associated to Fe; the *bc* AS is pure Cu.

Here, the two structures *i*-AlPdMn and *i*-AlCuFe differ only in the atomic species of the γ cells on n and n' that are pure Al in *i*-AlPdMn and become Cu and Fe in *i*-AlCuFe. The chemical compositions derived from this model are $Al_{70.35}Pd_{21.36}Mn_{8.29}$ and $Al_{61.80}Cu_{25.63}Fe_{12.57}$. These are astonishingly close to the optimal experimental ones of respectively $Al_{70.3}Pd_{21.4}Mn_{8.3}$ as reported by Quiquandon *et al.*[18] and $Al_{62}Cu_{25.5}Fe_{12.5}$ as reported in Ref. 19. This good agreement with the experimental compositions (and subsequent good fit with the densities) simultaneously for the two alloys is a strong argument in favor of the relevance of the chemical cells chosen in the present generic model.

As mentioned in the previous section, the diffraction spectra for neutrons and x rays radiations of the two models have been calculated and compared to the experimental data on single grains available in the literature. Our calculations are performed with an optimized computation of the form factor of the polyhedral cells obtained by summing the form factors of the convex polyhedra P_k that define these cells:

$$\hat{\chi}(q_\perp) = \sum_k \int_{P_k} e^{-2\pi i q_\perp x_\perp} dx_\perp . \qquad (1)$$

The computation is done using the very convenient analytical formula recently derived by Brandolini *et al.*[20] for convex polyhedra. Using the notations depicted in Fig. 3, this calculation is made in two steps:

$$\int_P e^{-2\pi i q_\perp x_\perp} dv_\perp = \sum_{k=1}^{p} \frac{i q_\perp v_k}{2\pi |q_\perp|^2} \int_{F_k} e^{-2\pi i q_\perp x_\perp} ds_\perp , \qquad (2)$$

where F_k is the kth face among p of the convex polyhedron P, v_k is the unit normal to that face pointing outwards, $dv_\perp$ and $ds_\perp$ are the differential elements for, respectively, the volume in P and the surface on F_k. The surface integration on the face F_k gives

$$\int_{F_k} e^{-2\pi i \xi x_\perp} ds_\perp = -\frac{1}{(2\pi|\xi|)^2} \sum_{j=1}^{n} (e^{-2\pi i \xi a_{j+1}} - e^{-2\pi i \xi a_j}) \frac{\xi w_j}{\xi \sigma_j}, \qquad (3)$$

where ξ is the component of $q_\perp$ in the plane of the face F_k, a_j is the m vertices of F_k counterclockwise oriented; the vector σ_j is the unit vector along the side $[a_j, a_{j+1}]$, and w_j is the outward unit normal to this side in the plane of the face F_k.

The experimental diffracted intensities for *i*-AlPdMn are those measured by Boudard *et al.*[4] for both neutrons [Fig. 4(a)] and x rays [Fig. 4(b)] spectra. On these figures, the sign of the diffracted amplitudes of the experimental data has been arbitrary given the ones of the theoretical amplitudes. The theoretical diffraction spectra have been calculated with a unique global scale parameter and an arbitrary fixed global Debye-Waller correction parameter $B_\parallel$ of 0.9 Å^2 (pure aluminium). It can be noted that the reliability factor[21] R_I is better in the case of the x rays diffraction (R_I^X=2.77% with 314 reflections) than in the case of the neutrons diffraction (R_I^N=4.55% with 221 reflections) although the x rays spec-

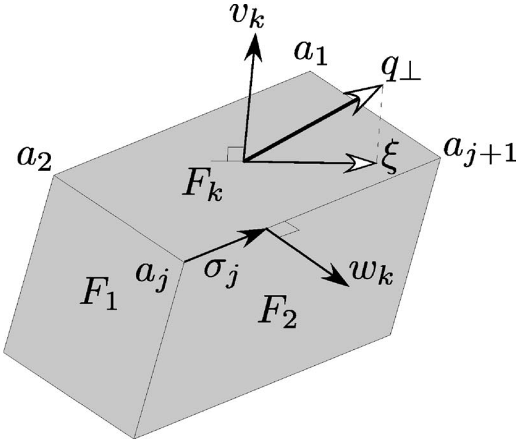

FIG. 3. Definition of the variables used in formula (1) and (2) for calculating the Fourier transform of a convex polyhedron [after Brandolini *et al.* (Ref. 20)].

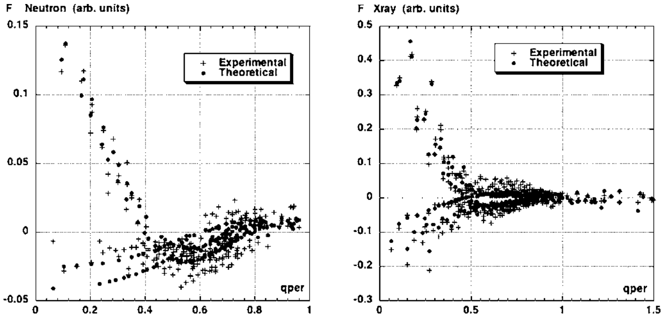

FIG. 4. Structure factors of *i*-AlPdMn obtained from neutrons (left) and x rays (right) diffractions as a function of $|Q_\perp|$ for both the experimental results of Boudard *et al.* (Ref. 4) and the present model. The reliability factors are $R_I^N=4.55\%$ for 221 reflections for neutrons and $R_I^X=2.77\%$ for 314 reflections for x rays.

trum presents a larger number of reflections. This could be the result of the fact that *the atomic positions of the model have not been relaxed* (no fit parameters of the positions) and x rays spectra, being governed by the electronic density, are less sensitive to small deviations of atomic positions, than neutron spectra that are directly correlated to the very positions of the nuclei of the atoms.

The experimental diffracted intensities for *i*-AlCuFe are the neutrons-diffraction data measured by Cornier-Quiquandon *et al.*[3] They are reported in Fig. 5 together with the theoretical values of the present model. The reliability factor is found to be $R_I^N=6.46\%$ for 626 reflections.

B. Chemical configurations of the main clusters

As shown in Table II, the atomic models of *i*-AlPdMn and *i*-AlCuFe are very similar using the usual chemical substitutions Mn with Fe and Pd with Cu: the only difference is the way the γ cells are occupied: Al for *i*-AlPdMn, but Fe and Cu for *i*-AlCuFe. These γ cells correspond to the atoms of the inner partially occupied (7/20) dodecahedra of M (if located on n') and M' (if located on n) clusters. This inner shell is pure Al for both M and M' clusters in *i*-AlPdMn whereas it is pure Fe on M and pure Cu on M' in *i*-AlCuFe.

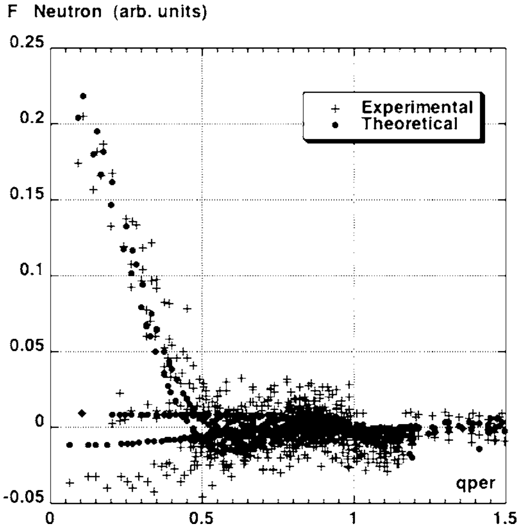

FIG. 5. Structure factors of *i*-AlCuFe obtained from neutrons diffraction as a function of $|Q_\perp|$ for the experimental results of Cornier-Quiquandon *et al.* (Ref. 3) and the present model. The reliability factor is $R_I^N=6.46\%$ for 626 reflections.

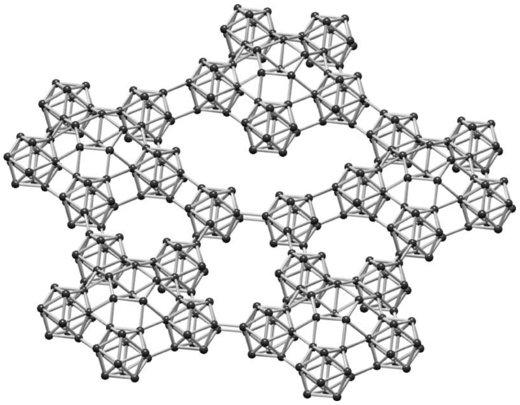

FIG. 6. Fraction of the (Mn|Fe) network of the model. It is made of a collection of large icosahedra connected by squares. Any two (Mn|Fe) atoms on this network are at a distance at least equal to 0.4796 (0.4695) nm. The notation $x(y)$ is used to specify the values in nanometers, respectively, for *i*-AlPdMn and *i*-AlCuFe.

In order to make the present discussion valid for both alloys we designate by $(X|Y)$ the chemical species associated to a given cell—if they are different between the two alloys—with the convention that X refers to the chemical species in *i*-AlPdMn and Y to the one in *i*-AlCuFe. For example, the cell α on the site n is occupied by (Mn|Fe), i.e., by Mn for *i*-AlPdMn and Fe for *i*-AlCuFe.

The α cell on AS n is entirely occupied by (Mn|Fe) atoms which therefore distribute on the *vertices of the external large icosahedra* of the M' clusters. They form a remarkable network of icosahedra that are connected together by bridges in the form of squares as shown in Fig. 6. The average number of Mn atom neighbors to a Mn is $Z_{\mathrm{Mn}}=(15+2\tau)/3=6.078\ldots$ that distributes according to $Z_{\mathrm{Mn}}=5$ with frequency $(-6+5\tau)/6=0.3484$, $Z_{\mathrm{Mn}}=6$ with frequency $(12-7\tau)/3=0.225\,46$, and $Z_{\mathrm{Mn}}=7$ with frequency $(-4+3\tau)/2=0.4270$. The network has *one unique first neighbor distance* equal to 0.4796 nm for *i*-AlPdMn (0.4695 nm for *i*-AlCuFe). Hence any two (Mn|Fe) atoms are far away from each other as soon as the (Mn|Fe) composition is smaller or equal to 8.29 at. %. Beyond this composition, a few magnetic atoms can be closer to each other and can thus generate magnetic coupling effects. This is the case for the remaining 4.28 at. % of Fe atoms in *i*-AlCuFe that distribute on the inner partially occupied dodecahedra of the M clusters. This could be the origin of the substantial differences between these two alloys regarding the macroscopic magnetic properties.

The β cell on n' is occupied by aluminium atoms for both alloys. This implies that the sites of the icosidodecahedra of the M' clusters are pure Al in both cases. The same holds almost exactly for the M cluster [with the minor difference of the (d) subcell that is the overlapping between α and β located on n] with the icosidodecahedron mostly occupied by

TABLE III. Chemical configurations of M, M' and B, B' clusters in the *i*-AlPdMn and *i*-AlCuFe structures. Each configuration is described using the following sequences: (a) M (M') clusters: center (1), inner dodecahedron (7/20), outer icosahedron (12), icosidodecahedron (30), see Fig. 7; (b) B clusters: center (1), icosahedron (12), dodecahedron (20), see Fig. 8; (c) B' clusters: first inner icosahedron (3/12), second inner icosahedron (9/12), dodecahedron (20), see Fig. 9.

	Cell	Frequency (%)	Chemical composition
(a)	M_1	81.97	1Al, 7(Al|Fe), 12(Pd|Cu), 30Al
(a)	M_2	18.03	1 Al, 2(Al|Fe)-5Al, 7(Pd|Cu)-5Al, 5(Mn|Fe) -25Al
(a)	M'_1	81.97	1(Pd|Cu), 7(Al|Cu), 12(Mn|Fe), 30Al
(a)	M'_2	18.03	1(Pd|Cu), 2(Al|Cu)-5Al, 11(Mn|Fe)-1Al; 30Al
(b)	B_1	30.81	1(Pd|Cu), 1(Mn|Fe)-11Al, 13(Pd|Cu)-5Al -2(Al|Fe)
(b)	B_2	30.18	1(Pd|Cu), 3(Mn|Fe)-9Al, 4(Pd|Cu)-15Al -1(Al|Fe)
(b)	B_3	24.30	1(Pd|Cu), 2(Mn|Fe)-10Al, 8(Pd|Cu)-10Al -2(Al|Fe)
(b)	B_4	10.14	1(Pd|Cu), 3(Mn|Fe)-9Al, 5(Pd|Cu)-15Al
(b)	B_5	2.01	1(Pd|Cu), 1(Mn|Fe)-11Al, 14(Pd|Cu)-5Al -1(Al|Fe)
(b)	B_6	1.55	1(Pd|Cu), 2(Mn|Fe)-10Al, 9(Pd|Cu)-10Al -1(Al|Fe)
(b)	B_7	0.62	1(Pd|Cu), 1(Mn|Fe)-11Al, 15(Pd|Cu)-5Al
(b)	B_8	0.38	1(Pd|Cu), 2(Mn|Fe)-10Al, 10(Pd|Cu)-10Al
(c)	B'_1	55.11	3Al, 3(Pd|Cu)-6Al, 6(Mn|Fe)-12Al-2(Al|Cu)
(c)	B'_2	21.29	3Al, 3(Pd|Cu)-6Al, 6(Mn|Fe)-13Al-1(Al|Cu)
(c)	B'_3	12.46	3Al, 6(Pd|Cu)-3Al, 3(Mn|Fe)-16Al-1(Al|Cu)
(c)	B'_4	11.15	3Al, 9(Pd|Cu), 20Al

Al. For the same reason, the (Pd|Cu) sites being defined complementary to the Al ones in the n' AS, the α cell located on n' is mostly (Pd|Cu), implying thus that the vertices of the external icosahedra of the M clusters are mostly occupied by (Pd|Cu) atoms. Finally, the centers of the B' clusters are empty, the centers of the B clusters are (Pd|Cu) atoms, those of the M clusters are Al atoms, and those of M' clusters are (Pd|Cu) atoms.

The complete chemical configurations of the B- and M-type clusters have been computed and are shown in Table III. There are remarkably few different configurations for quasiperiodic ternary alloys: the M and M' clusters have only two chemical configurations each, with only one major configuration ($\approx 82\%$) for each. The B cluster splits into eight different chemical configurations in which four have a probability equal or smaller than 2% and three have a frequency larger than 20%. Among the four configurations of the B' cluster there are only two major configurations (representing $\approx 76\%$). All together, this leads to a cluster description with primarily $1M+1M'+3B+2B'$, hence only seven major types of chemically ordered clusters the frequency of which is larger than 20%.

The simplest chemical order is found on the $M(M')$ clusters: more than 80% of these clusters (configurations M_1 and M'_1 in Table III) follow the rule of *a same chemical species on all sites of a same geometrical orbit*. Hence the configuration M_1 is made of a central Al, 7(Al|Fe) on the inner dodecahedron, 12(Pd|Cu) on the outer icosahedron, and 30 Al on the icosidodecahedron. The M'_1 configuration follows the sequence 1(Pd|Cu), 7(Al|Cu), 12(Mn|Fe), and 30 Al. With the exception of the partial dodecahedral inner shell, these cluster configurations have the full $m35$ icosahedral symmetry. They have complete orbits of a same chemical species as shown in Fig. 7:

(i) the center is Al for M_1 and (Pd|Cu) for M'_1, the partial inner dodecahedron is pure (Al|Fe) for M_1 and pure (Al|Cu) for M'_1;

(ii) the large icosahedron is pure (Pd|Cu) for M_1 and pure (Mn|Fe) for M'_1;

(iii) the large icosidodecahedron is pure Al in both M_1 and M'_1.

The B and B' clusters are slightly more complicated than the previous ones with, respectively, eight and four configurations. They have low point symmetry and can be viewed as the clusters responsible for propagating the quasiperiodic order as symbolically exemplified by the matching rules for ideal tilings. The three main configurations B_1, B_2, and B_3 of the B cluster are displayed in Fig. 8. All have a (Pd|Cu) center, an icosahedron of a mixture of (Mn|Fe), and Al atoms with a major number of Al atoms and eventually a dodeca-

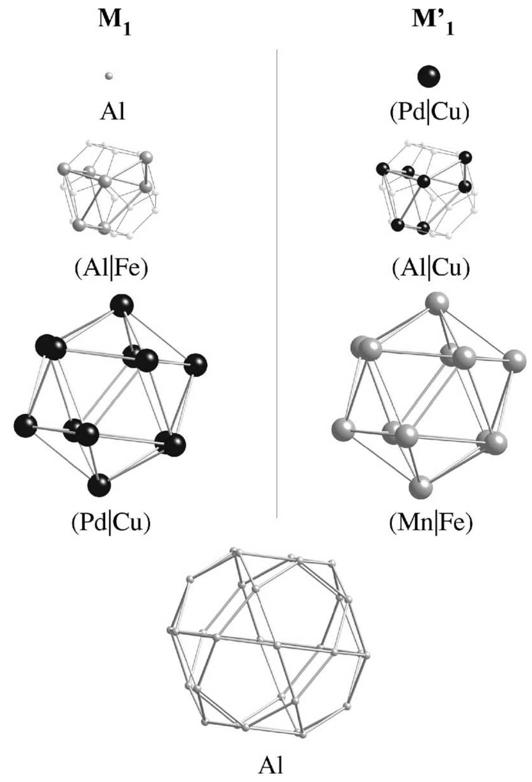

FIG. 7. The main configurations M_1 and M'_1 of the $M(M')$ clusters. Each shell is filled by one same atomic species noted $(X|Y)$ with X for i-AlPdMn and Y for i-AlCuFe. The sizes of the shells are characterized by the radius r of the polyhedra and the distance d between neighbor atoms on their vertices. The notation $x(y)$ is used to specify the values, in nanometers, respectively, for i-AlPdMn and i-AlCuFe: partially occupied inner dodecahedron $r=0.2567$ (0.2513), $d=0.2964$ (0.2902), icosahedron $r=0.4561$ (0.4465), $d=0.4796$ (0.4695), outer icosidodecahedron $r=0.4796$ (0.4695), $d=0.2964$ (0.2902). All vertices of the inner dodecahedra are drawn to help locate the only seven occupied.

hedron of a mixture of (Pd|Cu), Al, and (Al|Fe) atoms. The main configurations of the B' cluster are presented in Fig. 9. In these configurations B'_1 and B'_2 there is no central atom, three Al atoms are positioned on the first partial inner icosahedron, six Al and three (Pd|Cu) on the second partial icosahedron, and eventually a mixture of (Mn|Fe), Al, and (Al|Cu) on the outer full dodecahedron.

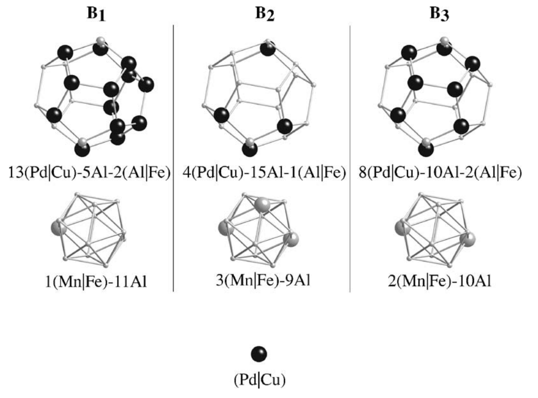

FIG. 8. The three main configurations B_1, B_2, and B_3 of the B cluster. The code is the same as in Fig. 7. The sizes of the polyhedra are icosahedron $r=0.2819$ (0.2760), $d=0.2964$ (0.2902), dodecahedron $r=0.4154$ (0.4066), $d=0.2964$ (0.2902).

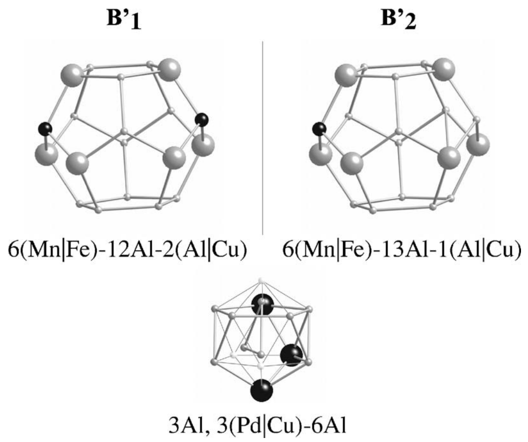

FIG. 9. The two main configurations B'_1 and B'_2 of the B' cluster. Compared to the B configurations, the inner icosahedra have an empty center and three atoms that are shrunk towards the center by a factor of τ. All polyhedron sizes are the same as those of the B configurations (see Fig. 8).

C. Extended $M(M')$-clusters

As demonstrated by Duneau a few years ago,[22,23] B- and M-type clusters can be extended to form larger aggregates with a reasonably small number of different geometrical and chemical configurations. For example, taking into account only the geometry of the atomic sites, a very large cluster M_{ext} of 551 sites of radius 1.1229 nm can be found generated by a small triacontahedron—linearly τ times smaller than the triacontahedron (a)+(b) of Fig. 1—of volume $13-8\tau$ centered at n sites and another cluster M'_{ext} of 454 sites of radius 1.1634 nm generated by the same small triacontahedron but centered at n'. These exceptionally large objects split in numerous different chemical configurations but astonishingly enough a large cluster of radius 0.881 16 nm containing 207 atoms still survives with a *unique chemical configuration* in the decorated model for the same acceptance volume at the node n and an other one of radius 0.722 47 nm containing 121 atoms at the node n'.

III. DISCUSSION

The present work is an attempt to rationally construct a simple synthetic structural solution for a perfectly ordered atomic distribution on an ideal quasiperiodic framework of both i-AlPdMn and i-AlCuFe alloys that are well known to be experimentally very similar. Such an attempt has already been proposed several years ago in a very elegant way by Elser[24,25] based on the Bergman subcell decomposition of a basic KG skeleton. Explicit deterministic illustration of the corresponding atomic surfaces has then been given by Kramer *et al.*[26] and Papadopolos *et al.*[27] Beyond its simplicity, Elser's model introduces occupancy probabilities on some cells for adjusting the stoichiometry and has unfortunately not been tested with respect to the experimental diffraction sets. Our present model is in the very continuation of Elser's approach but keeping a fully deterministic point of view.

First of all, it is worth mentioning that none of these kinds of simple models can successfully compete, as is, with respect to the reliability factors obtained by comparison with the experimental diffraction data, with the crystallographic models implying several hundreds of fit parameters. However, introducing partial occupancy factors on larger ASs and relaxing the atomic positions from the ideal $\mathbb{Z}$ module should certainly improve the diffraction data, but it would not make our understanding of these kinds of structures significantly better.

The similarities between the two structures *i*-AlPdMn and *i*-AlCuFe are made fully explicit in the present model: the two structures are similar in all respects except for the chemical occupation of the two γ cells: pure Al in *i*-AlPdMn and Cu and Fe in *i*-AlCuFe. Thus a synthetic way of noting the stoichiometry of these two structures is given by the general chemical formula $Al_{61.8}(Pd|Cu)_{21.35}(Mn|Fe)_{8.29}(Al|Fe)_{4.28}(Al|Cu)_{4.28}$ that suggests that some compositions obtained by mixing together all or part of these chemical species in quaternary or quinary systems could exhibit icosahedral symmetry. It is interesting to notice that several multicomponent alloys have indeed been obtained by substituting a fraction of Al by similar species in proportions close to those that are expected from the present model. This is the case for the quaternary alloy elaborated by Fisher *et al.*[28] with composition $Al_{67}Ga_4Pd_{21}Mn_8$ that compares very well with the composition expected by the present model that is $Al_{66.08}Ga_{4.28}Pd_{21.35}Mn_{8.29}$.

A. Comparison with existing models of the *i* phases

Quite several atomic models have been proposed—especially for *i*-AlPdMn—that deserve being compared to the present one. They are all based on three main ASs (at least) as those initially proposed by M. Cornier-Quiquandon *et al.*,[3] two large ASs at n, n' and a small AS on one only of the two bc sites of the face centered 6D-lattice. These four sites are the special points of the F-lattice of highest symmetry $m35$. Because of the fact these all models present three ASs at the same positions in 6D space and have comparable volumes, they give diffraction patterns that are very close to each other—in particular for the fundamental strong reflections—thus making it very hard to classify the models on the sole basis of the diffraction data.

If the question of the relative volumes of the ASs is well answered and common to all, the question of which of the two bc sites is used is not yet totally clear between the various authors. A simple rule is that, because of obvious steric reasons, the occupied bc site must be the one that has the same parity (odd or even sum $s=\Sigma_i n_i$ of the indices of the site) as the site n or n' that is occupied by the smallest of the two large ASs. In the present case, the smallest AS is the large truncated triacontahedron located on $n' = (1,0,0,0,0,0)$, an odd site, that implies the correctly occupied bc site to be $(\bar{1},1,1,1,1,\bar{1})/2$ that is also an odd site ($s=1$). The recent refined models studied by the group of Yamamoto include a small additional AS at the middle edge $(1,0,0,0,0,0)/2$ of the elementary vector of the underlying P 6D lattice. This is indeed known as an efficient way of replacing the inner partially (7/20) dodecahedra of the $M(M')$ clusters by icosahedra. This requires removing from the large ASs the cells (f)+(g) of Table I responsible for the sites of the inner dodecahedra together with removing the cells (a)+(b) to make all $M(M')$ centers empty as they should in real Mackay clusters. These geometrical refinements have also been investigated and tested in our models. They are not presented here because they do not bring any other significant changes in the atomic structures than those just reported here.

Historically, the first comparison to be made concerns the model of Cornier-Quiquandon *et al.*[3] proposed in 1991 for *i*-AlCuFe. Their basic ASs are very close, in shape and volume, to those used here, the chemical order was given only by global average values on each of the three ASs: Cu was found to be mostly located on n' and bc whereas the n AS was expected to be mostly occupied by Al. These average values are consistent with our present model of *i*-AlCuFe.

The second important comparison is with the model proposed by de Boissieu *et al.*[29] in 1994, a refinement of the first atomic model for *i*-AlPdMn proposed by Boudard *et al.*[4] Here the ASs are spheres and the chemical order is represented by concentric spherical shells. The sphere n is occupied by Mn at the center surrounded by a large shell of Al; n' is occupied by Mn at the center, then an intermediate shell of Pd surrounded by an external shell Al at the periphery. The site bc is occupied by a small sphere of Pd with the possible addition of a tiny sphere of Al at the bc'. Our model compares rather well with this spherical version: the site n is also a mixture of Al and Mn but distributed in a very precise geometrical way on the α cell—a small cell confined near the center—for the Mn atoms to distribute on the large icosahedra of the M' clusters. The site n' is also globally similar with the external Al spherical shell that is to be compared with the β cell corresponding to the icosidodecahedron of the M' cluster and the γ cell corresponding to the partial inner dodecahedron of the M cluster, both being pure Al. The bc site is definitely similar to the one of our present model, but, because of irreducible steric reasons, no AS is allowed in our model at the bc' site.

Concerning the recent model of Yamamoto *et al.*,[10] the comparison is much more difficult since this model is tuned by about hundred of fit parameters including partial occupancy factors at almost all cells for all atomic species. A result of atoms having partial occupancies is that the global ASs of the model are significantly larger than in the previous cases and in our model. However, the global tendencies show that the n AS has roughly the same kind of chemical distribution as in the Boudard *et al.* model, with a majority of Mn in the center and a majority of Al everywhere else. The n' AS is empty on the center and has then an intricate set of polyhedral shells containing in increasing radius Mn, Pd, and finally Al. These authors use the bc AS filled by Pd and finally introduce a small additional AS at $(1,0,0,0,0,0)/2$. This all is consistent with our deterministic model with the only difference of replacing the partially occupied sites of the inner dodecahedron of the M clusters of our model by an inner icosahedron generated by the small additional ASs located at $(1,0,0,0,0,0)/2$. This is consistent with their n' AS having an empty space in the middle and being truncated along the threefold axes. Without this structural difference, the model of Yamamoto *et al.* roughly resembles the one of Boudard *et al.*—and therefore ours—but with well defined polyhedral cells used for describing the chemical order that is only partial.

B. Some expected physical properties

The very main result of the present study is that a unique framework can be used that describes the chemical order of ideal *i*-AlCuFe and *i*-AlPdMn equally well. The model suggests that the two alloys are close to isomorphic by substituting Mn with Fe and Pd with Cu with the exception of the partially occupied inner dodecahedra of the M and M' clusters that are pure Al in *i*-AlPdMn but Cu (M') and Fe (M) in *i*-AlCuFe. This makes a substantial difference in the way the magnetic atoms (Mn|Fe) distribute in the bulk material.

In the case of *i*-AlPdMn the Mn atoms are at a minimum distance of 0.48 nm from each other up to a concentration of 8.29 at. %. At higher composition, the magnetic atoms necessarily show much shorter neighbor distances thus inducing macroscopic effect of ferromagnetism (see, for instance, Refs. 11–14). This feature seems to be in good agreement with both the experimental measurements of magnetic properties[11–14] and theoretical considerations[30] that suggest the value of 0.48 nm between neighbor Mn atoms to be an optimum distance between Mn atoms in the bulk quasicrystal. In the case of *i*-AlCuFe, the Fe concentration being substantially larger than 8.29 at. %, there are numerous close neighbor Fe sites at 0.29 nm from each others that can be responsible for the ferromagnetism observed in this alloy.

IV. CONCLUSION

We propose a simple chemically ordered 6D model valid for both *i*-AlPdMn and *i*-AlCuFe based on the Katz-Gratias skeleton. It has the advantage of giving a unified and synthetic description of the two alloys and should be viewed as an ideally simple and perfectly ordered atomic structural model of the icosahedral *i*-AlCuFe and *i*-AlPdMn types of phases. It uses only three prototypical subcells of the $M(M')$-cluster configurations and gives good compositions, densities, and satisfactory diffraction intensities simultaneously for both alloys *with no adjustable parameters*. The model is globally consistent with the chemical order obtained in previous structural investigations of these alloys. This chemical ordering generates a surprisingly small number of different configurations of the basic clusters for such quasiperiodic ternary alloys. The $M(M')$ clusters have one major high symmetry configuration each with a frequency larger than 80%. The B clusters split into eight chemical configurations, half of which only with a frequency larger than 10%. These last clusters have low point symmetries as expected for clusters that are responsible for the propagation of the quasiperiodic order. Finally, it would certainly be very interesting to check the present model with respect to electronic structures as initiated by Krajci and Hafner[31] and Zijlstra *et al.*[32]

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