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Six-dimensional structure model for the icosahedral quasicrystal Al_6CuLi_3

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The structure of icosahedral quasicrystals can be described either by a quasiperiodic density function in three-dimensional (physical) space, or by a periodic density function in six-dimensional (6D) space. The real structure is obtained as a particular 3D section of the 6D density function. The 6D description involves 6D bodies, which on intersection by 3D space give rise to atoms in physical space. In this paper we derive all possible perpendicular-space shapes belonging to the 6D atoms, which arise for 6D structures describing any decoration of the 3D Penrose tiling. These results are applied to icosahedral Al_6CuLi_3, for which a 6D structure model is proposed. Refinement of this model on single-crystal x-ray-diffraction data shows the structure to be close to that of a decorated Penrose tiling. Unlike $Al_{73}Mn_{21}Si_6$, it is found that a perpendicular-space shape is necessary which has a lower internal symmetry than given by the icosahedral point group.

I. INTRODUCTION

Quasicrystals are characterized by their diffraction pattern having a so-called noncrystallographic point-group symmetry. Since the discovery in 1984 of icosahedral Al-Mn by Shechtman *et al.*,[1] many compounds with these characteristics (all of them alloys) have been synthesized. Among these are compounds with an octagonal, a decagonal, a dodecagonal, and an icosahedral symmetry of the diffraction pattern.[2]

A direct consequence of a diffraction pattern with a noncrystallographic symmetry is that the structure of these compounds cannot have translational symmetry in all three independent directions. For the icosahedral case the translational symmetry is completely lost. This led to two different approaches for describing the structure.

In the first approach one tries to describe the structure by specifying the atomic positions in three-dimensional (3D) space. This is mostly done by replacing the lattice, as is used for ordinary crystals, by the 3D Penrose tiling.[3] The two basic building blocks comprising the Penrose tiling are filled with atoms, thus leading to a so-called decorated Penrose model for the structure. The fundamental measure is the length of the edge of the building blocks, which is approximately 5 Å, dependent on the chemical composition. For Al_6CuLi_3 this approach proved to be successful, leading to the structure model given in Fig. 1.[4,5] For Al-Mn and $Al_{73}Mn_{21}Si_6$ no one has succeeded in designing a decorated Penrose model which adequately describes the observed diffraction intensities.[6]

The second approach uses the fact that the electronic or atomic density function can be obtained as a 3D section of a higher-dimensional density function. This latter function is periodic; thus only the density function in one unit cell of the 6D lattice needs to be specified. For icosahedral $Al_{73}Mn_{21}Si_6$ a good description of the diffraction data was obtained for a structural model consisting of "6D atoms" on the origin and on the body center of the 6D unit cell. The 6D atoms were found to be the convolution of an ordinary atomic electron density in physical space and spherical shells in perpendicular

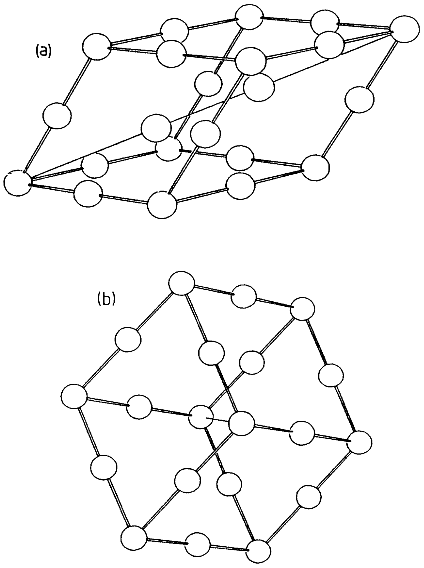

FIG. 1. Prolate and oblate rhombohedron comprising the 3D Penrose tiling. Decorating sites indicated are those corresponding to the structure model for Al_6CuLi_3 after Refs. 4 and 5. The occupation of the vertices is $0.69Al+0.22Cu+0.09Li$, of the midedge positions, $0.75Al+0.10Cu+0.15Li$, and of the long-body diagonal of the PR, $0.17Al+0.83Li$.

space.[7–10] Using powder neutron-diffraction data of a series of isomorphous substituted samples, direct experimental evidence for the perpendicular-space shape of these atoms was obtained.[11]

The fundamental problem with the 3D approach to the structure is that it is *a priori* unknown whether a 3D Penrose tiling or some other quasilattice should be selected, or whether the structure can be described by some quasilattice at all.[12] Even if the 3D Penrose tiling gives a good approximation to the structure, subsequently better approximations are given by decorations of inflated Penrose tilings. The original tiles are replaced by new ones, with their diameters a factor τ^3 larger, where $\tau \equiv (1+\sqrt{5})/2$ is the golden ratio. Very soon inflation leads to a number of atomic position parameters, which is too large to be determined by any experiment.

Clearly, these problems with the 3D approach are resolved by the higher-dimensional approach. For icosahedral quasicrystals the diffraction pattern can be considered as the projection from a 6D hypercubic reciprocal lattice.[13–15] Then the electron density is the 3D section of a periodic density function in 6D space. Consequently, its value in one unit cell of the 6D hypercubic lattice completely determines this function. However, there is still an infinite number of parameters to be determined: The shape of the 6D atoms is unknown. This means that one has the choice to use perpendicular-space shapes for the 6D atoms which correspond to any kind of 3D quasilattice or to no quasilattice at all.

The choice of spherical shells as perpendicular-space shapes is a good approximation for the $Al_{73}Mn_{21}Si_6$ quasicrystal.[7–11] In an alternative approach, based on arguments of dense packing, it was proposed that these spherical shapes should be replaced by certain polyhedron surfaces.[16] Diffraction data were not sufficient to discriminate between these two models. Alternatively, one can choose the atomic surfaces to correspond to a decoration of one particular quasilattice. For the 3D Penrose tiling, describing icosahedral quasicrystals, a partial approach has been made by Ishihara and Shingu[17] and by Yamamoto and Hiraga.[8] For the dodecagonal quasicrystals such perpendicular-space surfaces were derived by Gahler.[8]

In this paper we will derive all atomic surfaces corresponding to any decoration of the 3D Penrose tiling. The various special positions of the 6D icosahedral space group, belonging to the different decorating positions of the 3D Penrose tiling, are classified, and the corresponding perpendicular-space shapes are derived. Using the 6D space-group symmetry, it is shown which decorations in 3D space are compatible with the icosahedral symmetry.[19]

In the second part of the paper, we present single-crystal x-ray-diffraction results for icosahedral Al_6CuLi_3. Using the perpendicular-space shapes of the 6D atoms, a 6D structure model for Al_6CuLi_3 is proposed which corresponds to the decorated Penrose tiling model.[4,5] Structure refinements show that for Al_6CuLi_3 the perpendicular-space shapes derived for the decorated Penrose tiling give a better description of the x-ray data than a model with spheres as perpendicular-space shapes.

II. FUNDAMENTAL PERPENDICULAR-SPACE SHAPES

There are several ways to generate the vertices of a 3D Penrose tiling. Two of these are particularly interesting, since they start from a lattice in 6D space. In the cut and projection technique, all 6D lattice points within a volume, infinitely extended along physical space and bounded in perpendicular space, are projected onto physical space. The shape of the perpendicular-space section of this volume determines the precise distribution of points in physical space. The vertices of the Penrose tiling are obtained for that shape, being the triacontahedron (TR) as obtained by projection of the 6D unit cell onto perpendicular space.[20–22]

In the second approach, the points in physical space are obtained as the physical-space section of some function on 6D space. To obtain the vertices of the Penrose tiling, entities of the shape of the former mentioned TR in perpendicular space and of zero measure in physical space are positioned on each node of the 6D lattice.[23,24]

Up to this point, both methods are equivalent. However, the section approach allows for the interpretation that it provides a 6D periodic density function describing the structure of a quasicrystal. The entities of zero measure in physical space can be considered as the 6D equivalent of point atoms in physical space. These bodies are hereafter denoted as perpendicular-space shapes. Real atoms are obtained when the 6D atoms are defined as the convolution of a perpendicular-space shape and an ordinary electron density in physical space. (Note that the convolution of a perpendicular-space shape and a point is that shape itself.)

Decorated Penrose tilings, or any quasiperiodic structure, can be obtained by a filling of the 6D unit cell with these 6D atoms. Such a structure model was determined for icosahedral $Al_{73}Mn_{21}Si_6$, in which use was made of spherical shells as perpendicular-space shapes. In this section we will derive the five different perpendicular-space shapes which will produce different decorations of the 3D Penrose tiling, according to the procedure given by Ishihara and Shingu.[17]

From the above discussion it follows that the first fundamental perpendicular-space shape is the triacontahedron (TR). Placed on all vertices of the 6D lattice, it generates the vertices of the Penrose tiling, i.e., the most simple decoration.

To obtain the (point) atoms on the midpositions of all edges, it is realized that such an atom should be present exactly when both vertices are part of the Penrose tiling. That is, for the origin and point on $\mathbf{e}_{\parallel}^{1}$ to be part of the Penrose tiling, physical space should intersect with both the TR centered on the origin and the TR centered on $\mathbf{e}_1$. ($\mathbf{e}_i = \mathbf{e}_{\parallel}^{i} + \mathbf{e}_{\perp}^{i}$, $i = 1, 2, \ldots, 6$, as defined by Elser[21] is used.) In projection onto perpendicular space, this means that when physical space intersects both the TR and one translated over $\mathbf{e}_{\perp}^{1}$, it should also intersect with the midedge atom. The intersection of these two TR thus defines the perpendicular-space shape for the 6D atoms, giving rise to the midedge decorating position in the Penrose tiling. Since the TR has ten edges equal to $\mathbf{e}_{\perp}^{1}$, this intersection is easily recognized as the rhombic icosahedron (RI) with $\mathbf{e}_\perp^1$ as unique axis, a polyhedron of half the volume of the TR. The position in 6D space is given by $\mathbf{r}=\frac{1}{2}\mathbf{e}_1$ or, equivalently, $(\frac{1}{2},0,0,0,0,0)$. To generate atoms at the midpoints of all edges, equivalent, but differently oriented RI should be placed at the points obtained as permutations of $(\frac{1}{2},0,0,0,0,0)$. Note that these permutations are the same points as obtained by application of the 6D icosahedral space-group symmetry. The resulting structure thus has the required symmetry.

Analogously, decorating positions at the midpoints of the faces of the Penrose rhombs are obtained from perpendicular-space shapes defined as the intersection of three TR. For example, for the face spanned by the origin and $\mathbf{e}_\parallel^1$ and $\mathbf{e}_\parallel^2$, the intersection of a TR centered on the origin with one translated over $\mathbf{e}_\perp^1$ and one translated over $\mathbf{e}_\perp^2$ should be taken. The resulting shape is a rhombic dodecahedron (RD), a polyhedron of one-fifth of the volume of the TR. The perpendicular-space shape for an atom in the middle of the prolate rhombohedron is again a prolate rhombohedron (PR), and for an atom in the middle of the oblate rhombohedron it is an oblate rhombohedron (OR).

These five perpendicular-space shapes are given in Table I, together with their volume, position, multiplicity, and site symmetry in the 6D unit cell. They are called fundamental shapes, because together they comprise all possibilities for an atom being present in the Penrose tiling, whenever a particular vertex, edge, face, or cell is part of that tiling.

III. GENERAL PERPENDICULAR-SPACE SHAPES

The five fundamental perpendicular-space shapes as defined in Sec. II are sufficient to design a 6D structure model for a decorated 3D Penrose tiling with special decorating positions only, i.e., vertex, midedge, midface, and midcell positions. To describe general decorating positions, e.g., an atom somewhere in the PR, other shapes will occur. These additional bodies will be derived in this section.

TABLE I. Perpendicular-space shapes and special positions of the 6D atoms. Shown are the decorating position in the 3D Penrose tiling; the perpendicular-space shape of the corresponding atom in 6D; the special position with respect to the 6D unit cell; site-symmetry group; multiplicity (mult.); and the relative volume of the perpendicular-space shape ($v_\perp$). The special positions incorporate shifts along the vectors $\mathbf{r}(51)=(0.5,\alpha_1,\alpha_1,\alpha_1,\alpha_1,\alpha_1)$, $\mathbf{r}(52)=(\alpha_1,0.5,\alpha_1,-\alpha_1,-\alpha_1,\alpha_1)$, $\mathbf{r}(53)=(\alpha_1,\alpha_1,0.5,\alpha_1,-\alpha_1,-\alpha_1)$, and $\mathbf{r}(54)=(\alpha_1,-\alpha_1,\alpha_1,0.5,\alpha_1,-\alpha_1)$, with $\alpha_1=1/(2\sqrt{5})$; along the vectors $\mathbf{r}(21)=(\alpha_2,\alpha_3,\alpha_3,0,0,\alpha_3)$ and $\mathbf{r}(22)=(\alpha_2,-\alpha_3,0,\alpha_2,\alpha_2,0)$, with $\alpha_2=1/(3-\tau)$ and $\alpha_3=\alpha_2/\tau$; and along the vectors $\mathbf{r}(31)=(\alpha_4,\alpha_4,\alpha_4,\alpha_5,-\alpha_5,\alpha_5)$ and $\mathbf{r}(32)=(\alpha_6,-\alpha_6,-\alpha_5,-\alpha_6,\alpha_5,\alpha_5)$, with $\alpha_4=1/\{1+[(\tau-1)/(\tau+1)]^2\}$, $\alpha_5=\alpha_4[(\tau-1)/(\tau+1)]$, and $\alpha_6=\alpha_4[(\tau-1)/(\tau+1)]^2$; $\tau\equiv(1+\sqrt{5})/2$. The values of the structural parameters x,y,z range from -0.5 to 0.5

Decorating position	Perpendicular-space shape	6D position	Site symmetry	mult.	$v_\perp$
Vertex	TR	(0,0,0,0,0,0)	$\overline{5}\overline{3}m$	1	1
Midedge	RI	(0.5,0,0,0,0,0)	$\overline{5}m$	6	$\frac{1}{2}$
Midface	RD	(0.5,0.5,0,0,0,0)	mmm	15	$\frac{1}{5}$
Mid-PR	PR	(0.5,0.5,0.5,0,0,0)	$\overline{3}m$	10	$1/(10\tau)$
Mid-OR	OR	$(0.5,-0.5,0,-0.5,0,0,)$	$\overline{3}m$	10	$1/(10\tau^2)$
Edge	$\frac{1}{2}$RI	(0.5,0,0,0,0,0) $+x\mathbf{r}(51)$	$5m$	12	$\frac{1}{4}$
Face-diagonal	$\frac{1}{2}$RD	(0.5,0.5,0,0,0,0) $+x\mathbf{r}(21)$	$mm2$	30	$\frac{1}{10}$
Face	$\frac{1}{4}$RD	(0.5,0.5,0,0,0,0) $+x\mathbf{r}(21)+y\mathbf{r}(22)$	m	60	$\frac{1}{20}$
PR-diagonal	$\frac{1}{2}$PR	(0.5,0.5,0.5,0,0,0) $+x\mathbf{r}(31)$	$3m$	20	$1/(20\tau)$
OR-diagonal	$\frac{1}{2}$OR	$(0.5,-0.5,0,-0.5,0,0)$ $+x\mathbf{r}(32)$	$3m$	20	$1/(20\tau^2)$
PR-mirror	$\frac{1}{6}$PR	(0.5,0.5,0.5,0,0,0) $+x\mathbf{r}(53)+y\mathbf{r}(21)$	m	60	$1/(60\tau)$
OR-mirror	$\frac{1}{6}$OR	$(0.5,-0.5,0,-0.5,0,0)$ $+x\mathbf{r}(54)+y\mathbf{r}(22)$	m	60	$1/(60\tau^2)$
PR	$\frac{1}{12}$PR	(0.5,0.5,0.5,0,0,0) $+x\mathbf{r}(51)+y\mathbf{r}(52)+z\mathbf{r}(53)$		120	$1/(120\tau)$
OR	$\frac{1}{12}$OR	$(0.5,-0.5,0,-0.5,0,0)$ $+x\mathbf{r}(51)-y\mathbf{r}(52)-z\mathbf{r}(54)$		120	$1/(120\tau^2)$

As an example, consider the decoration with an atom on the midpoint of an edge of the Penrose tiling, parallel to $\mathbf{e}_{\parallel}^{1}$. The corresponding 6D structure has a RI at the position $(\frac{1}{2},0,0,0,0,0)$ in the 6D unit cell. A shift of the 6D atom parallel to physical space does not change the condition relating the presence of this 3D atom with the presence of the vertices of the Penrose tiling. Its position in 3D space changes with that shift vector. Define the vector $\mathbf{r}_{51}$ in 6D space by $\mathbf{r}_{51}=\mathbf{e}_{\parallel}^{1}=(0.5,\alpha_1,\alpha_1,\alpha_1,\alpha_1,\alpha_1)$, with $\alpha_1=(\tau-1)/(\tau+1)$. Then a shift of the original 6D atom over $x\mathbf{r}_{51}$ will produce atoms in 3D space at the position $(0.5+x)\mathbf{e}_{\parallel}^{1}$ whenever this edge is part of the Penrose tiling. However, the 6D icosahedral space-group symmetry generates an equivalent atom shifted over $-x\mathbf{r}_{51}$ from the edge midpoint. Thus the decoration generated will have atoms at both positions $(0.5\pm x,0,0,0,0,0)$.

Instead of a RI at both positions $(\frac{1}{2}\mathbf{e}_1\pm x\mathbf{r}_{51})$, one can divide the RI in two halves, such that these halves are each other's image under the inversion operator at $0.5\mathbf{e}_1$. If one-half is placed at $(\frac{1}{2}\mathbf{e}_1+x\mathbf{r}_{51})$ and the other at $(\frac{1}{2}\mathbf{e}_1-x\mathbf{r}_{51})$, the icosahedral space-group symmetry is preserved. Furthermore, if the two new perpendicular-space shapes are chosen to add up to the RI in their common projection onto perpendicular space, the result is a decorated 3D Penrose tiling where for each edge precisely one of the positions $(0.5\pm x)\mathbf{e}_{\parallel}^{1}$ is occupied.

We thus find a new perpendicular-space shape as a half RI, with a corresponding position in 6D space of $(0.5(1+x), x\alpha_1, x\alpha_1, x\alpha_1, x\alpha_1, x\alpha_1)$, for $-0.5\leq x\leq 0.5$. The only requirement is that the face dividing the original RI has a symmetry according to the site symmetry of the original position $\bar{5}m$. This does not determine the $\frac{1}{2}$RI completely, but it does ensure that the RI will be divided into equal parts.

Generally, the procedure for obtaining the perpendicular-space shapes for general decorating positions is as follows. Consider one of the fundamental perpendicular-space shapes and its position in the 6D unit cell. The 6D position corresponding to a more general decorating position in the Penrose tiling is obtained by application of a shift vector parallel to physical space. The new position in 6D space will be of lower symmetry; consequently, the 6D space group will generate a number of N equivalent positions, which replace the original special position. The new perpendicular-space shape is obtained from the original one through a set of cutting faces, with the only requirement being that this set has a symmetry according to the site-symmetry group of the original special position. The result is a new perpendicular-space shape of $1/N$ the volume of the fundamental shape and with internal symmetry according to the site symmetry of the new position. As a consequence, N of these new shapes adds up to give exactly the original perpendicular-space shape, thus producing a decorated Penrose tiling where in each edge, face, or cell only one of the N equivalent positions is occupied. Apparently, the icosahedral symmetry does not require the decoration to preserve the internal $\bar{3}m$ symmetry of the rhombohedra.

In Table I a complete list is given of all possibilities for the decorating position. Note that there is still freedom in the choice of the boundary face (cutting face) defining, for example, the $\frac{1}{2}$RI or the $\frac{1}{2}$PR.

IV. ATOMS IN 6D SPACE

A 6D atom can be defined as the convolution of the step function θ on a perpendicular-space shape and an ordinary atomic electronic density in physical space:

$$\theta(\mathbf{r})=\begin{cases}1 & \text{for } \mathbf{r} \text{ within the} \\ & \text{perpendicular-space shape,} \\ 0 & \text{otherwise ,}\end{cases} \tag{1}$$

and $\rho(\mathbf{r})$ is a 3D atomic density for $\mathbf{r}$ in physical space and is zero otherwise, with the density for the 6D atom given by

$$\rho_{6\mathrm{D}}(\mathbf{r})=\int \theta(\mathbf{r}')\rho(\mathbf{r}-\mathbf{r}')d\mathbf{r}' \ . \tag{2}$$

This definition produces one atom in 3D space for each 6D atom which is intersected by physical space. Thus it is the proper generalization to higher-dimensional space of the concept of an atom. Other, equivalent atoms will be present in the 6D unit cell when the 6D space-group symmetry is taken into account. The positions of this complete set of atoms constitute one orbit of the 6D space group (modulo the lattice translations). The number of positions in the unit cell multiplied by the order of the site-symmetry group is equal to the order of the factor group of the space group with its translation subgroup.

These notions lead to a different interpretation of the physical-space component of the perpendicular-space shapes.[25] A true physical-space component of the perpendicular-space shapes is obtained if the latter are changed such that they obtain a component along physical space proportional to, for example, the length of the perpendicular-space vector. Let $\mathbf{u}_{\parallel}$ be any fixed vector in physical space. Then the step function for a perpendicular-space shape with such a physical-space component becomes

$$\theta(\mathbf{r})\begin{cases}1 & \text{for } \mathbf{r}=\mathbf{r}_{\perp}+|\mathbf{r}_{\perp}|\mathbf{u}_{\parallel}, \text{ and } \mathbf{r}_{\perp} \text{ within the} \\ & \text{perpendicular-space shape,} \\ 0 & \text{otherwise}\end{cases} \ . \tag{3}$$

On the other hand, a physical-space component which is independent of the perpendicular-space position within a finite part of the perpendicular-space shape only defines a new 6D atom. Shifting the upper part of the perpendicular-space shape by $\mathbf{u}_{\parallel}$ and the lower part by $-\mathbf{u}_{\parallel}$ corresponds to the situation sketched in the previous sections, but does not constitute a true perpendicular-space component.[24] A new perpendicular-space shape is obtained from half the volume of the original one, and it is placed at a special position in the 6D unit cell with twice the multiplicity of the original one.

The perpendicular-space shapes, together with their special positions in the 6D unit cell (Table I), make it possible to describe any decoration of the 3D Penrose tiling. For the vertex, midedge, midface, and midrhomb positions, the position in the 6D unit cell is a special position of the 6D icosahedral space group which is completely fixed. This implies that these decorating positions are special positions determined by the icosahedral symmetry. The corresponding perpendicular-space shapes are completely determined by the requirement of obtaining a decorated Penrose tiling as 3D structure. On the other hand, the only requirement for the structure model seems to be the icosahedral symmetry of the corresponding 6D electron density. Then perpendicular-space shapes are possible which differ from the ones defined in Table I, but which still have to have internal symmetry according to the site symmetry of the special position they belong to. The effect for the structure in 3D space will be that some original decorating site will be empty, while at other positions additional atoms will occur. Without special care this will lead almost certainly to unreasonable short interatomic distances or to a structure with holes.[16]

For the general decorating positions, it is found that the icosahedral symmetry requires that only one of the positions of one orbit in the 6D unit cell lead to an atom in 3D space. For example, symmetry requires only one of the two positions $(0.5\pm x)$ on the long-body diagonal of the PR to be occupied. In particular, this implies that proper decorations of the Penrose tiling can be obtained, which destroy the internal symmetry of the constituting PR and OR, but which preserve the icosahedral symmetry.

The precise distribution defining which of the two (N) positions is occupied in which cell of the 3D Penrose tiling is given by the perpendicular-space shape. Because the latter is not completely determined, different distributions are possible, which are all proper decorations of the Penrose tiling.

V. PATTERSON FUNCTION ANALYSIS FOR Al_6CuLi_3

The Patterson function is defined as the Fourier transform of the diffraction intensities as obtained in a diffraction experiment:

$$P(\mathbf{r})=\sum_i I(\mathbf{S}_i)\exp(-2\pi i\mathbf{S}_i\cdot\mathbf{r})\ , \qquad (4)$$

where the summation is over all reflections i with scattering wave vector $\mathbf{S}_i$. It is the maximum amount of the information which can be obtained from an ordinary diffraction experiment without further assumptions, and it is therefore of particular interest.

The Patterson function can be regarded as the autocorrelation function of the electron density of a crystal:

$$P(\mathbf{r})=\int \rho(\mathbf{r}')\rho(\mathbf{r}+\mathbf{r}')d\mathbf{r}'\ . \qquad (5)$$

It thus gives information about the interatomic distances as well as about the direction of the interatomic vectors.

The calculation according to Eq. (4) can be done in physical space. This results in an aperiodic function $P(\mathbf{r})$, which for a structure according to a decorated 3D Penrose model consists of peaks at the positions of the vertices and decorating positions of eight interpenetrating Penrose tilings.[26] For $Al_{73}Mn_{21}Si_6$ this calculation showed peaks at the vertices of eight Penrose tilings, but also gave peaks which cannot be interpreted as due to a decoration of the Penrose tiling.[7,27] For Al_6CuLi_3 all peaks of the Patterson function (Fig. 2) could be interpreted as due to the decoration given in Fig. 1.[26]

The integer indexing of the diffraction peaks makes it possible to assign the measured intensities to the corresponding reciprocal lattice points in higher-dimensional space. Calculation of the higher-dimensional Patterson function [Eq. (4)] then gives the autocorrelation function of the electron density in higher-dimensional space.[28] For quasicrystals this was first done by Gratias, Cahn, and Mozer for $Al_{73}Mn_{21}Si_6$.[10] Their results showed two peaks, one at the origin and one at the body center of the 6D unit cell. The shape was that of an ordinary Patterson function peak in the physical-space section and that of the autocorrelation function of a sphere in perpendicular space, which had about the size of the TR as defined in Table I. The body-center position is not one of the positions in the 6D unit cell which occur for decorations of the 3D Penrose tiling. Therefore, the 6D approach shows directly that the 3D Penrose tiling gives an invalid description of the structure of icosahedral $Al_{73}Mn_{21}Si_6$.

For Al_6CuLi_3 the sections of the 6D Patterson function given in Figs. 3 and 4 show the 6D Patterson function to have peaks at the origin, at $(\frac{1}{2},0,0,0,0,0)$, at $(\frac{1}{2},\frac{1}{2},0,0,0,0)$, and their symmetry equivalents.[19,25,29] These peaks can be interpreted as being due to atoms at the lattice points and on the midpoints of the edges of the 6D unit cell. Comparison with Table I shows that these

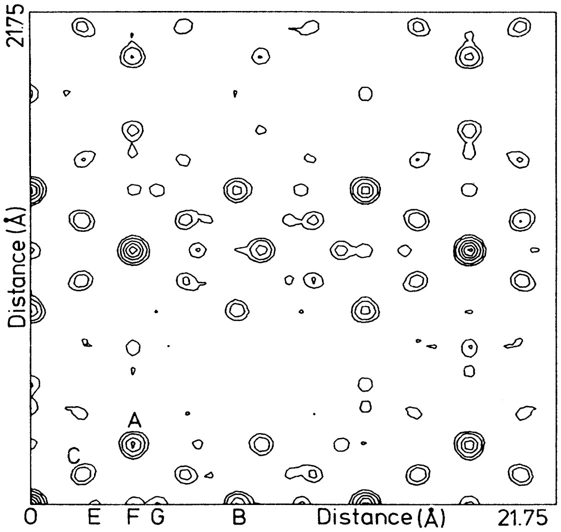

FIG. 2. Section of the 3D Patterson function for icosahedral Al_6CuLi_3, obtained by Fourier transformation of the measured x-ray-diffraction intensities (after Ref. 26). The two coordinate axes are twofold symmetry axes. The peaks O, A, B, and G are obtained for atoms on the vertices of a Penrose tiling. The peaks C, E, and F can be explained by assuming both the vertices and midedge positions to be decorated by atoms.

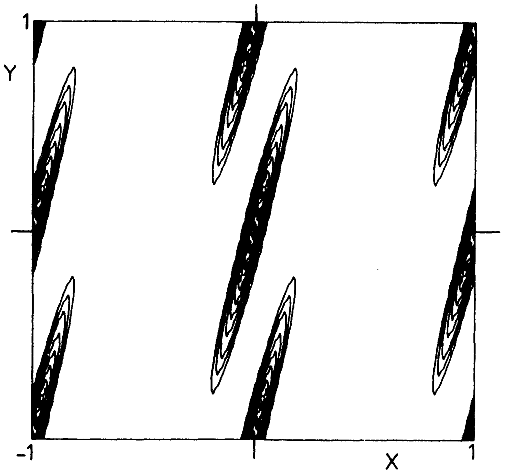

FIG. 3. Section of the 6D Patterson function for icosahedral Al_6CuLi_3, obtained by Fourier transformation of the measured x-ray-diffraction intensities, based on $|e_\parallel^*| = 0.099\,22$ Å^{-1}. Contour lines are drawn at intervals of 10% of the maximum value. The origin corresponds to the center of the figure. The values for x and y range from -1 to 1 and represent vectors along $(e_1+e_2+e_3)$ and $(-e_4+e_5-e_6)$, respectively. Both perpendicular space and physical space are interested in a line of threefold symmetry.

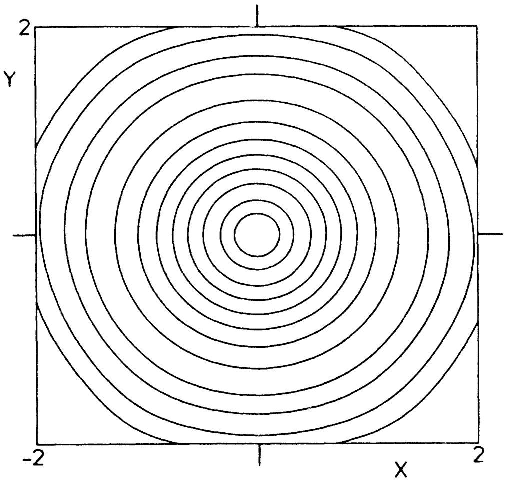

FIG. 5. Perpendicular-space section of the 6D Patterson function, centered on the origin. Coordinate axes are $xe_\perp^1$ and $yv_\perp^1$, with x and y ranging from -2 to 2. The vector $v_\perp^1$ is perpendicular to $e_\perp^1$ and is defined by $v_\perp^1 = (1/\tau)(e_\perp^4 - e_\perp^3) + (1/2\tau^2)(e_\perp^5 - e_\perp^6)$. This figure shows the perpendicular-space shape of the origin peak of the 6D Patterson function.

positions correspond with the vertex and midedge decorating positions of the 3D Penrose tiling, in accordance with the previously determined 3D structure model.[4,5]

In Figs. 5 and 6 sections of the 6D Patterson function are given which lie entirely in perpendicular space: They give the perpendicular-space shape of the Patterson peaks. Because the Patterson function has icosahedral symmetry, the origin peak has icosahedral internal symmetry. However, the internal symmetry of the peaks at $(\frac{1}{2},0,0,0,0,0)$ and at $(\frac{1}{2},\frac{1}{2},0,0,0,0)$ can be lower, $5m$ and mmm, respectively.

For the origin peak the results show no structure beyond spherical symmetry (Fig. 5). Note that the origin peak is the superposition of $[\rho(\mathbf{r})^2]$ integrated over all atoms in the 6D unit cell. Therefore, it is very difficult to relate its shape to the perpendicular-space shapes of the 6D atoms.

The major contribution to the peak at $(\frac{1}{2},0,0,0,0,0)$

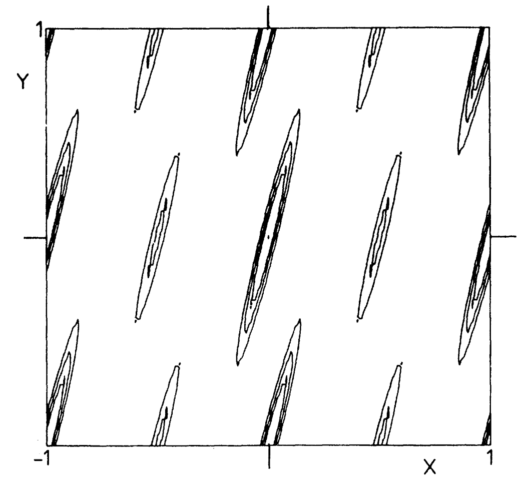

FIG. 4. Same as Fig. 3, but now with the point $M = (0.5,0,0,0,0,0)$ in the center of the figure.

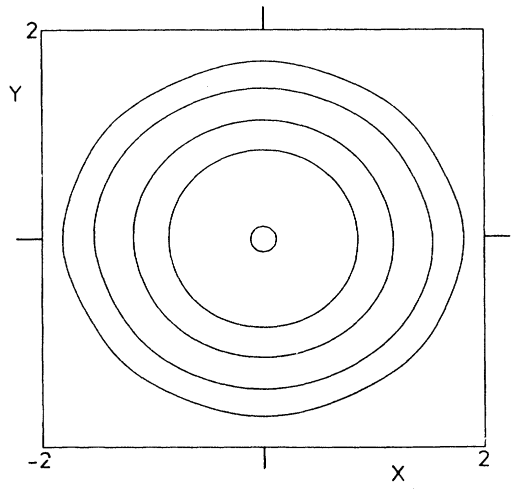

FIG. 6. Same as Fig. 5, but now around the point $M = \frac{1}{2}e_1$. This figure shows the perpendicular-space shape of the peak at $\frac{1}{2}e_1$ of the 6D Patterson function.

comes from the product of the density of the atom at the origin and the atom at the midedge position. For the 6D structure corresponding to a 3D Penrose tiling, the latter atom is a RI, with a diameter along the fivefold axis of $\tau|\mathbf{e}_\perp|=1.618|\mathbf{e}_\perp|$ and a diameter along the twofold axes of $\sqrt{(2\tau+1)/(2\tau-1)}|\mathbf{e}_\perp|=2.753|\mathbf{e}_\perp|$. For the TR the corresponding diameters are $3.236|\mathbf{e}_\perp|$ and $2.753|\mathbf{e}_\perp|$, respectively. Thus the eccentricity is found to be 0.588 for the RI and 1.175 for the ratio of the corresponding axes of the TR. For the boundary of the Patterson peak, one finds a maximum and minimum diameter of $4.854|\mathbf{e}_\perp|$ along the fivefold axis and $5.506|\mathbf{e}_\perp|$ along the twofold axes. This gives an expected eccentricity for the Patterson peak of 0.88, much closer to unity than the eccentricity of the RI. Furthermore, it can be shown that equal intensity contours of higher intensity, i.e., smaller diameter, are even closer to unity. The observed eccentricity at a diameter of about $4|\mathbf{e}_\perp|$ is 0.94 (Fig. 5), in accordance with the RI shape of the atoms at $(\frac{1}{2},0,0,0,0,0)$.

The conclusion is that the 6D Patterson function shows peaks at the positions corresponding the decorated Penrose tiling model. The perpendicular-space shape of the Patterson peaks is in accordance with the decorated Penrose model, although the differences between Patterson peaks for spherical atoms and Penrose-tiling-like atoms are very small.

VI. STRUCTURE REFINEMENT

The decorated Penrose tiling model for the structure can now be translated into a 6D structure model. For atoms on the vertices, midpoints of the edges and on the long-body diagonal of the PR, the 6D structure model given in Table II is obtained. Note that the disorderly occupation of the 3D decorating positions translates directly into a disorderly occupation of the atomic sites in the 6D unit cell. A refinement on this model could be made by allowing for shell-like perpendicular-space shapes, adding up to form the complete perpendicular-space shape as defined in Table I. Although such shell-like atoms were necessary to describe the structure of $Al_{73}Mn_{21}Si_6$,[7,11] such an ordering is not necessary to obtain a good fit to the diffraction data of Al_6CuLi_3. Disordered occupation was also found in contrast-variation neutron-diffraction experiments.[30]

TABLE II. 6D structure model for icosahedral Al_6CuLi_3. Atoms are found on three special positions in the 6D unit cell. The values for the occupation probability (P_μ) are those obtained with the 6D refinement program. $\mathbf{r}(31)$ is defined in Table I. The value for x was found as 0.1234 after refinement. The value for the temperature factor B^μ for $\mu=$Al was found as 0.133.

6D atom	P_μ	Position
(Al,TR)	0.72	(0,0,0,0,0,0)
(Cu,TR)	0.19	(0,0,0,0,0,0)
(Li,TR)	0.09	(0,0,0,0,0,0)
(Al,RI)	0.75	(0.5,0,0,0,0,0)
(Cu,RI)	0.11	(0.5,0,0,0,0,0)
(Li,RI)	0.14	(0.5,0,0,0,0,0)
(Al,PR)	0.15	$(0.5,0.5,0.5,0,0,0)-x\mathbf{r}(31)$
(Cu,PR)	0.01	$(0.5,0.5,0.5,0,0,0)-x\mathbf{r}(31)$
(Li,PR)	0.84	$(0.5,0.5,0.5,0,0,0)-x\mathbf{r}(31)$

One advantage of the description of the structure in 6D space is that a closed, analytical expression is obtained for the structure factor. For 6D atoms defined as the convolution of a perpendicular-space shape and the density of an ordinary atom in physical space, atomic scattering factors are obtained as the product of an ordinary atomic scattering factor and the Fourier transform of the perpendicular-space shape. The former, $f_\parallel^\mu(|\mathbf{S}_\parallel|)$, is only a function of the physical-space component of the scattering vector, whereas the latter is a function of the perpendicular-space component of $\mathbf{S}$:

$$f_\perp^\mu(\mathbf{S}_\perp)=\int \theta^\mu(\mathbf{r})e^{2\pi i\mathbf{S}\cdot\mathbf{r}}\,d\mathbf{r}\ . \tag{6}$$

For nonzero values of $\theta^\mu(\mathbf{r})$ confined to $\mathbf{r}=\mathbf{r}_\perp$ entirely in perpendicular space, the dot product $\mathbf{S}\cdot\mathbf{r}$ is equal to $\mathbf{S}\cdot\mathbf{r}_\perp=\mathbf{S}_\perp\cdot\mathbf{r}_\perp$, i.e., is dependent on $\mathbf{S}_\perp$ only.

The complete expression for the structure factor is[8,17]

$$F(\mathbf{S})=\sum_\mu\sum_{(R|\tau)} f_\parallel^\mu(|\mathbf{S}_\parallel|)f_\perp^\mu(\mathbf{S}_\perp R)\times\exp[2\pi i\mathbf{S}\cdot(R\mathbf{r}^\mu+\tau)]\times\exp(-\tfrac{1}{4}B^\mu|\mathbf{S}_\parallel|^2)\ , \tag{7}$$

where the summation is over all independent atoms μ in the 6D unit cell and over all symmetry operators $(R|\tau)$ of the 6D space group modulo the translation group. For the icosahedral group describing the symmetry of Al_6CuLi_3, the translation part τ is zero for all operators. The factor involving B^μ describes the effect of atomic vibrations. In the present approach the effect of phasons is left out. Note that for perpendicular-space shapes of spherical or icosahedral symmetry, the atomic form factor $f_\perp^\mu(\mathbf{S}_\perp R)$ is independent of R. For perpendicular-space shapes of lower symmetry, the atomic form factor does depend on the symmetry operator, i.e., on the orientation of this atom.

The advantage of the expression Eq. (7) is that it is not only valid for structure models corresponding to the decorated 3D Penrose tiling, but that it allows for a variation of the perpendicular-space shape of these atoms. Alternative expressions for the structure factor for decorated Penrose tilings only have also been formulated.[21,31,32]

For spherical perpendicular-space shapes, the perpendicular-space atomic scattering factor is easily calculated.[7,8] For the general perpendicular-space shapes, the Fourier integral can be worked out using the rhombohedral dissection of these bodies.[17,33] These expressions were implemented in a computer program which calculates the structure factor according to Eq. (7).

Refinements were performed using the 37 independent reflections obtained in single-crystal x-ray diffraction as described earlier.[5,26] Only one B parameter was refined, with, for each atom, B^μ taken to be proportional to the inverse mass. An equally good fit was obtained as for the direct Fourier transform of the decorated 3D Penrose tiling, with about the same values for the occupation probabilities. The final fit gave a weighted R factor, $wR_{F^2}=(\sum w(|F_0|-|F_c|)^2/\sum w|F_0|^2)^{1/2}$, of 0.05, using weights w equal to the square root of the inverse of the standard deviation ($R_{F^2}=0.07$, using unit weights). The resulting values of the parameters are given in Table II.

To test the validity of the Penrose-tiling model, the perpendicular-space shapes as given in Table II were replaced by spheres. First, only the TR was replaced by a sphere of equal volume. No significant effect on the other atomic parameters or on the R factor was found, thus showing both the TR and a sphere to give a good description of the diffraction data. Replacing the RI by an equal volume sphere resulted in a much worse fit, with $wR_{F^2}=0.10$ ($R_{F^2}=0.11$). This proves that the RI, defining a 6D structure describing a decorated Penrose tiling, gives a better description than a sphere. It can be concluded that the structure of Al_6CuLi_3, unlike that of $Al_{73}Mn_{21}Si_6$, is indeed described by a decorated Penrose tiling in good approximation.

Peaks in the Patterson function corresponding to the atoms at $(\frac{1}{2},\frac{1}{2},\frac{1}{2},0,0,0)$ are not observed. This can be explained by the fact that lithium is a weak scatterer for x rays and therefore does not contribute much to either the Patterson or structure factors. This also implies that the position as well as the occupation factors for lithium are determined with less accuracy than the other atoms. Another possibility for the Li position was proposed to be at the body center of the 6D unit cell. We did not find peaks in the Patterson function for this position either. It is interesting to note that the body-center position in the 6D unit cell generates atoms which are sometimes on the long-body diagonal of the PR, at about the same position as obtained previously (Table II).[5]

New diffraction experiments were performed on a new single crystal of a volume of about 10 times the previous one.[26] For the 37 reflections with $I>2\sigma(I)$ as measured on the first crystal, the intensities obtained with the second crystal are the same, albeit with smaller standard deviations. In addition, 60 new reflections with $I>2\sigma(I)$ were obtained, which were all weak compared to the former set of 37 reflections. Refinements on the larger set of reflections showed that the model given in Table II cannot explain these new, weak reflections. Further refinements of the model, e.g., the use of a split PR atom, are the subject of future research.

VII. INFLATION

One property of the 3D Penrose tiling is that the tiles can be replaced by congruent tiles with edges τ^3 times as large, such that the new quasilattice points are a subset of the old ones. The choice for Al_6CuLi_3 of an edge of 5.039 Å is the minimum one to give reasonable atomic distances for a decorated Penrose tiling as a structure model.

Increasing the direct quasilattice vectors $\mathbf{e}_{\parallel}^i$ by a factor of τ^3, but maintaining a 6D hypercubic lattice and the relation $\mathbf{e}_i=\mathbf{e}_{\parallel}^i+\mathbf{e}_{\perp}^i$, means that the length of the basis vectors of the 6D direct lattice is increased by τ^3 also. The relation between the old and new 6D basis vectors is

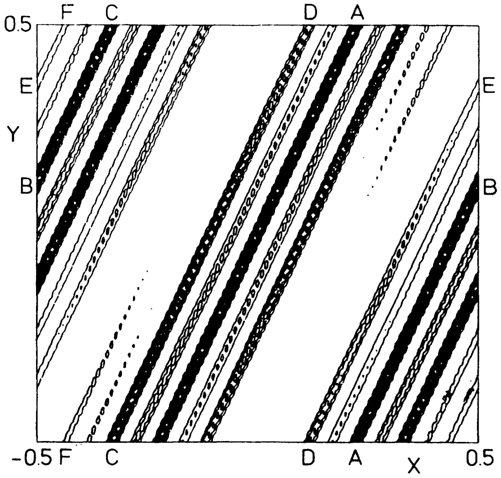

FIG. 7. Section of the 6D Patterson function obtained by Fourier transformation of the measured x-ray-diffraction data, based on $|\mathbf{e}_{\parallel}^*|=0.099\,22/\tau^3$ Å^{-1}$=2.342\times10^{-2}$ Å^{-1}. By following $A\rightarrow B\rightarrow\cdots\rightarrow F$, and matching equal letters, one sees that there is a single peak, centered on the origin and extending over about four unit cells in either direction. Note that the 6D lattice constant now is τ^3 times the lattice constant in Figs. 3–6.

$$\mathbf{E}_1=2\mathbf{e}_1+\mathbf{e}_2+\mathbf{e}_3+\mathbf{e}_4+\mathbf{e}_5+\mathbf{e}_6\ ,$$

and similar for the other basis vectors.

A decorated Penrose tiling can be described by a 6D structure model involving atoms which are congruent to the ones derived in Secs. II and III, but now with edges equal to the new, enlarged perpendicular space part $|\mathbf{e}_{\perp}|$ of the 6D lattice constant. Positioning such a TR on the nodes of the 6D lattice then leads to a vertex decoration of the inflated Penrose tiling, i.e., to a 3D structure which is $(\tau^3)^3$ less dense. To recover the original structure, 6D atoms are needed which have a perpendicular-space shape with a τ^3 larger diameter. In Fig. 7 one section of the experimental Patterson function of Al_6CuLi_3 is given for a τ^3 inflated indexing of the diffraction pattern. Indeed, it follows that the size of the origin peak is now approximately $5|\mathbf{e}_{\perp}|$, instead of $|\mathbf{e}_{\perp}|$ itself as for the original indexing (Fig. 2).

A complication for the structure of Al_6CuLi_3 is that applying the inflation once changes the positions of the atoms at the midedge positions in the 6D unit cell to the midpositions of the 5D hyperplanes $(0,\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2})$.

VIII. CONCLUSIONS

In this paper we have derived the set of perpendicular-space shapes of the 6D atoms, which are necessary to define a 6D structure model for all possible decorations of a 3D Penrose tiling (Table I). The vertex positions are generated by a triacontahedron (TR) as perpendicular-space shape, that is, by a body with the full icosahedral point group as internal symmetry. For other decorating sites other perpendicular-space shapes are derived, which have a lower internal symmetry. Consequently, these bodies are found at special positions in the 6D unit cell of site symmetry lower than icosahedral.

The 6D description shows that in physical space only one of the set of symmetry-equivalent positions need be decorated, while preserving the 6D icosahedral space-group symmetry. In physical space this means that the internal, $\bar{3}m$, symmetry of the PR and OR need not be present in the decorated tiling. Furthermore, perpendicular-space shapes are found which can continuously be varied within certain boundary conditions. The implication for the structure in physical space is that the choice of which one of the symmetry-equivalent positions is occupied in each rhombohedron can be made in many different ways. Each distribution derives from a 6D structure with icosahedral symmetry and gives rise to an icosahedral diffraction pattern.

For the icosahedral quasicrystal Al_6CuLi_3, a 6D structure model is proposed. Structure refinements show it to match the intensities of a single-crystal x-ray-diffraction experiment very well. In particular, it is found that the model with a rhombic icosahedron (RI) as the perpendicular-space shape gives a better fit than the model with a sphere as the perpendicular-space shape. This shows that the structure of Al_6CuLi_3 is indeed close to that of a decorated Penrose tiling. It is explained that the differences between a RI and a sphere as the perpendicular-space shape have only a marginal effect on the shape of the peaks in the 6D Patterson function.

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