Covering Cluster Description of Octagonal MnSiAl Quasicrystals

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A likely mechanism for the formation of quasicrystals is by maximally covering space with overlapping, stable atomic clusters. This notion is here applied to the experimentally determined layered structure of octagonal MnSiAl quasicrystals, which can be described in terms of a decoration of the octagonal Ammann-Beenker tiling. This decoration is abstractly represented by a novel, two-color version of the tiling. The covering cluster of the quasicrystal corresponds to an octagonal covering patch of the colored tiling. This covering patch appears in two variants with complementary colors. The 3D quasicrystal has a centered octagonal translation module, and its space group is $I8_4/mcm$.

I. INTRODUCTION

Clusters have long been suspected to play an important role in the formation and stabilization of quasicrystals. Jeong and Steinhardt[1] have argued that *overlapping clusters* could generate order through constraints on the possible overlaps. Overlapping clusters share certain atoms, and so they must agree in the overlap, which reduces the types of overlap to a small number of possibilities. Jeong and Steinhardt could show that such constraints can lead to perfectly ordered, quasicrystalline structures, for instance the Penrose tiling. The key principle is the maximization of a small number of well chosen clusters, which asks for overlaps and therefore creates correlation and order. Such an approach could successfully be applied also to the octagonal Ammann-Beenker tiling.[2]

Independently of this, similar questions had been studied also from a purely geometric viewpoint. Gummelt[3,4] found a suitably decorated decagon with the property that every structure completely covered by it is equivalent to a perfect Penrose tiling. It is again the restricted number of possible overlaps which is responsible for the creation of order. Jeong and Steinhardt[5] could extend this result by showing that the perfect Penrose tilings have the highest density of Gummelt's decagon among all tilings, irrespective of whether they are covered or not. A similar result could be obtained also for the octagonal Ammann-Beenker tiling,[6] although so far no formal proof has been found which extends to tilings which are not completely covered.

So far, this cluster approach had only been worked out for tilings, and the application to actual atomic structures had remained on a rather abstract level. Only very recently, Steinhardt et al.[7] succeeded to apply it to a particular instance of a decagonal quasicrystal, $Al_{72}Ni_{20}Co_8$. In this case, the experimentally determined atomic cluster suggests constraints of overlap which eventually enforce the formation of a perfect quasicrystal. It is the purpose of this paper to present such a covering cluster for octagonal MnSiAl quasicrystals.

Octagonal quasicrystals had first been observed by Wang, Chen and Kuo[8] in CrNiSi and VNiSi alloys. They are periodic along one direction, and quasiperiodic and eightfold symmetric in the plane perpendicular to the periodic direction. Their structure is closely related to the β-manganese type tetragonal structures in the same alloy systems. Later, the octagonal quasicrystal phase was found, with improved quality, also in the MnSiAl alloy system.[9] Huang and Hovmöller[10] put forward a structure model for this octagonal MnSiAl phase, which was later improved and further corroborated by Jiang, Hovmöller and Zou.[11] It is this latter, improved structure model of octagonal MnSiAl on which our paper is based.

We shall present a cluster C which completely covers the MnSiAl quasicrystal structure, and the overlaps which this cluster admits are such that among all structures covered by the cluster, the octagonal quasicrystal has the highest cluster density. Maximization of this cluster therefore appears as the natural ordering principle leading to the formation of octagonal quasicrystals.

It is not our intention to argue that the formation and stabilization of *every* quasicrystal is governed by such a cluster maximization principle. Our example shows, however, that there are cases where such an interpretation is indeed very tempting. Nevertheless, other mechanism might contribute to the stabilization of the quasicrystalline phase also in this case.

In the remainder of this paper we first analyze the structure model of octagonal quasicrystals (Section II). The results of this analysis allow for a thorough discussion of the space group symmetry (Section III). In Section IV we proceed to the heart of the paper, by describing how the quasicrystal structure can be regarded as being covered by copies of a single cluster C, and explaining how the maximization of the density of this cluster leads to a perfect quasicrystal. We finally conclude in Section V.

II. THE OCTAGONAL QUASICRYSTAL STRUCTURE

In this section we review the structure of octagonal MnSiAl quasicrystals as described in Ref. 11. This structure is a periodic stacking $\ldots AB'AB''\ldots$, where the layer A is eightfold symmetric, and the layers B are fourfold symmetric. The latter occur in two versions, B' and B'', rotated by 45° with respect to each other. All three layers can be described as decorations of the well-known Ammann-Beenker tiling,[12,13] consisting of squares and 45° rhombi. The decorations in the layers A and B' of an octagonal patch as given in Ref. 11 are shown in Figure 1. The decoration of layer B'' can be obtained by rotating the decoration of layer B' by 45°.

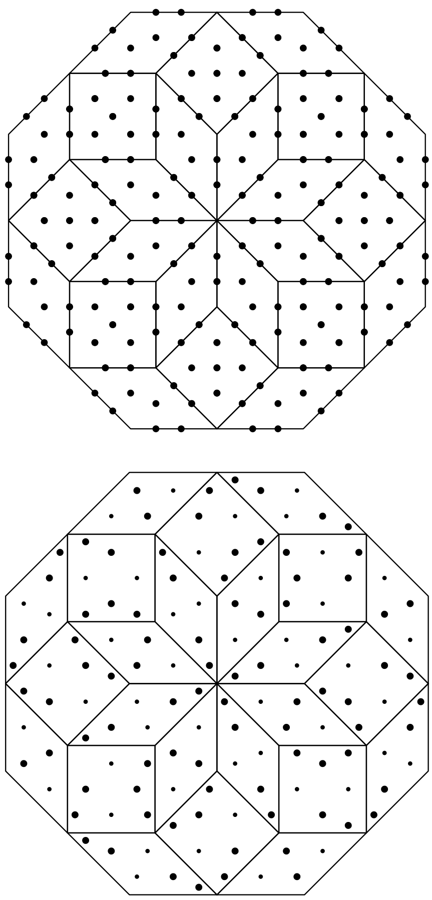

FIG. 1. Decoration of an eightfold symmetric patch, as given in Ref. 11. Only the decorations of layers A (top) and B' (bottom) are given. The decoration of layer B'' can be obtained by rotating the decoration of layer B' by 45°. Large dots denote Mn atoms, small dots Si or Al atoms.

To analyze the structure in more detail, let us have a closer look at a smaller, but very important motif, decorating an octagonal patch of two squares and four rhombi (note that in the following, we shall consistently write "patch" for a patch of tiles, and "cluster" for a cluster of atoms). The decoration of this patch in all three layers is shown in Figure 2. We first observe that the decoration of the tile edges in layer A is not symmetric. That is best seen by looking at the square with horizontal and vertical edges in Figure 2c. The five atoms in the interior of that square form a smaller square, with one atom at the center. This smaller square is obviously centered inside the tile. If we compare the positions of the corners of that square with the positions of the atoms on the edges of the tile, it is obvious that the edges are asymmetrically decorated. The edges are therefore *oriented*.

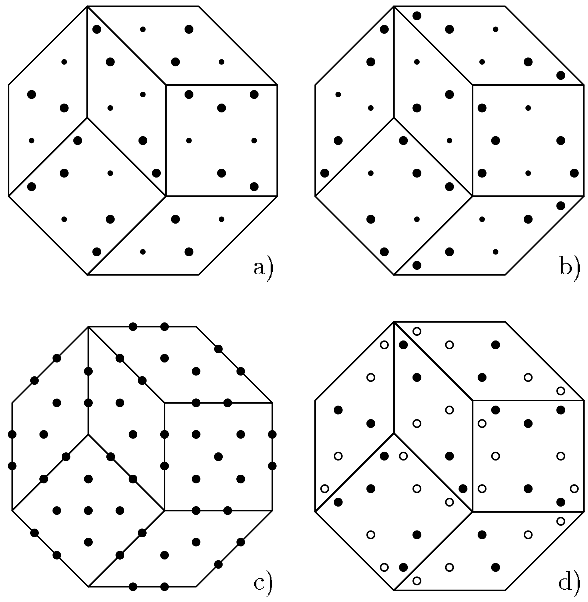

FIG. 2. Decoration of a small octagon patch. a) layer B', b) layer B'', c) layer A, and d) layers B' and B'' together. Large dots denote Mn atoms, small dots Si or Al atoms. In d), only Mn atoms are shown; atoms from the B' layer are shown as full dots, and atoms from the B'' layer as open dots.

While the A layer decoration of the interior of the tiles is symmetric, this is not the case for the decoration of the B-type layers. There are two possible decorations of the rhombus, and two possible decorations of the square. All these decorations occur in both the B' and the B'' layers. The two decorations of the square are mirror images of each other with respect to one of the diagonals of the square. A key observation is that if a tile has one of the two decorations in layer B', it has the other decoration in layer B'', and vice versa. This can best be seen in Figure 2d (where for simplicity we show only Mn atoms). The mirror line along the vertical diagonal of the square standing on its corner maps full dots (atoms from layer B') to open dots (atoms form layer B''), and vice versa. Incidentally, the same holds true for the two rhombi adjacent to that mirror line. Of course, all these properties hold for the decorations of all tiles in the structure, not only for the octagonal patch.

We are now ready to introduce an abstract representation of the tiles decorated with atoms. To represent the asymmetry of the tile edges, and also the asymmetry of the interior of the squares, we put arrows on the tile edges. Such arrows are commonly used to formulate matching rules for the Ammann-Beenker tiling.[14,13,15,16] Here, they arise naturally through the asymmetry of the decoration. To distinguish between the two possible decorations of the interior of the tiles, we use a coloring with two colors. A tile is painted in one color, if it has the first of the two possible decorations in layer B', and the second decoration in layer B'', and it is painted in the other color, if it has the second decoration in layer B' and the first decoration in layer B''. The squares are regarded here as being composed of two half-squares, devided along the diagonal symmetry axis of the decorated square. The two halves are then painted in two different colors. We should emphasize that every tile actually represents an entire, infinite prism in the quasicrystal. Two tiles which agree in shape, orientation and arrowing, but have different colors, represent the same prism; one of them is only translated by half a lattice period in the z-direction (perpendicular to the basal plane) with respect to the other.

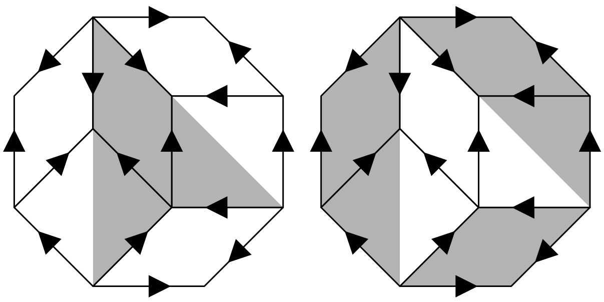

FIG. 3. Abstract representation of the two possible decorations of the octagon patch. For explanation, see text.

Our choice of the colors is shown in Figure 3. If an octagonal prism has in the B' layers the decoration shown in Figure 2a , and in the B'' layers the decoration shown on in Figure 2b, we represent it by the abstract tile patch shown on the left of Figure 3. If, on the other hand, the decorations of the B' and B'' layers are exchanged, we represent the prism by the abstract tile patch shown on the right of Figure 3. In both cases, the decoration of the A layers is the one shown in Figure 2c. As well as the two colored tiles, the two octagonal patches represent essentially identical infinite prisms. They only differ by being translated by half a lattice period in z-direction with respect to the other.

Since the arrowed octagon patches cover the whole Amman-Beenker tiling, there is a unique arrowing of the tiling consistent with the arrowing of our octagon patch. Moreover, once we have decided on the coloring of the first octagon patch, the coloring of all the other octagon patches is determined, since all octagons in the pattern are connected through overlaps. In these overlaps, the coloring must agree. A larger region of the colored and arrowed Ammann-Beenker tiling is shown in Figure 4. From this Figure, it should also be clear that every square in the tiling belongs to one or two octagons, while every rhombus belongs to two or three octagons. This observation may help to elucidate the local chemical structure in actual octagonal quasicrytals.

III. SPACE GROUP SYMMETRY

In this section we analyze the space group symmetry of the octagonal quasicrystal structure. Since our abstract tiles with their coloring and arrows have exactly the same symmetry as their decoration with atoms, this is best done considering the abstract tiling.

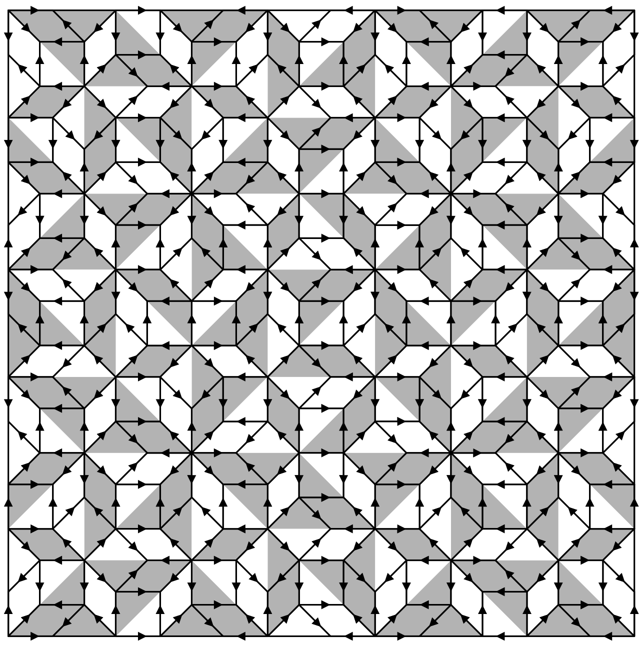

FIG. 4. Colored and arrowed Ammann-Beenker tiling.

For quasicrystalline tilings, the role of the lattice of translation symmetries is played by the *translation module*.[17] The translation module is an important concept, because it determines the Fourier module or reciprocal "lattice", which is experimentally observable. The translation module can be determined as follows. For any finite patch of tiles, one determines the set of all its translates (which must agree in every respect, also in coloring and arrowing). The set of distance vectors between pairs of such translates generates a free $\mathbb{Z}$-module, called the translation module of that patch. The translation module of the whole tiling is then the intersection of the translation modules of all its finite patches. Note that when a patch is enlarged, its translation module can only shrink, not increase. Fortunately, for *quasiperiodic* tilings like the Ammann-Beenker tiling, the translation modules do not shrink when a patch size is increased. It is therefore enough to consider the translation modules of single tiles. For the uncolored (but possibly arrowed) Ammann-Beenker tiling, it is well known that the translation module is the module generated by all its tile edges. For the colored tiling, this is no longer so. A closer look at Figure 4 shows that tiles of the same shape, orientation, arrowing *and coloring* are always separated by a path involving an *even* number of tile edges. On the other hand, tiles of different color but like orientation are separated by an odd number of tile edges. Only the "even" translations preserve the color, whereas the "odd" translations change the color. The same holds true for any kind of finite patch: if a translation maps one patch to another patch in the tiling, this other patch has the same color if the translation is even, and the other color if the translation is odd.

We should remember now that tiles which differ only in color actually represent the same prism, but translated by half a lattice period in z-direction. Therefore, the odd translations simply have to be combined with a translation in z-direction by half a lattice period, to make them elements of the translation module of the 3D quasicrystal structure. Color-preserving even translations, on the other hand, can be purely horizontal, or can be combined with lattice translations in z-direction. The translation module of the 3D quasicrystal therefore is a *centered octagonal* module.[18]

This finding is well in line with the experimental diffraction patterns.[8,9] Recall that the translation module is generated by a set of vectors which project on the eight tile edges, but which have also a z-component corresponding to half a lattice period, because these basis translations are odd. The translation module within a plane spanned by the z-axis and a tile edge therefore consists of two kinds of layers, even ones and odd ones, where different positions are occupied. On the other hand, in a plane spanned by the z-axis and a vector between two tile edges, there is only one kind of layer, because the odd layers are missing alltogether. In such a plane, there are only even translations.

The Fourier module of such a translation module is spanned by a similar umbrella of generating vectors. This umbrella is rotated, however, by $22.5°$. Therefore, in Fourier space, the missing odd layers are in vertical planes containing the tile edges, whereas the vertical planes between the tile edges contain two different kinds of layers, odd ones and even ones, with different sets of Bragg positions. This is exactly what is found in electron diffraction patterns.[8,9]

The missing layers in planes spanned by a tile edge and the z-axis are therefore *not* due to a glide plane, but due to the centered Bravais lattice. However, this plane nevertheless *is* a glide plane, as can be seen in Figure 4. Neglecting the coloring, there are many local patches invariant under such a mirror. The colors, however, are exchanged by the mirror, so that a translation in z-direction must be added to make it a symmetry. On the other hand, local mirrors between the tile edges preserve the coloring and are therefore true mirror planes, not glide planes. From this it follows that the eightfold rotation from the 2D Ammann-Beenker tiling becomes an 8_4-screw axis, so that the space group is $I8_4/mcm$. The glide planes cannot cause any further extinctions, because all Bragg peaks that are candidates for extinction are already extinct due to the lattice centering condition.

IV. COVERING CLUSTER DESCRIPTION

In the preceeding section, we have seen that the octagonal quasicrystal structure is covered by two types of infinite prisms with octagonal base. The only difference between the two prism types is that they are translated by half a lattice period in z-direction with respect to each other. Both kinds of prisms can be regarded as being covered by a *single* kind of cluster, C. This is achieved by dividing the two kinds of prisms at different hights into clusters. For the cluster C we choose a prism with octagonal base, consisting of five layers, $B'AB''AB'$. The top and bottom B' layers are then shared with the neighboring clusters. Since the quasicrystal is covered by infinite prisms, it is also completely covered by copies of the cluster C.

We shall now determine the class of structures that can be completely covered by the cluster C. By construction, the perfect octagonal quasicrystal structure is among these. If we insist that neighboring clusters in z-direction overlap by one layer, the clusters C can only form correct, infinite prisms. If, in turn, these infinite prisms are to cover the whole, infinite structure, they can do this only by overlapping to some extent with their neighbors in the xy-plane. In these overlaps, they will have to share the atoms with their neighbor clusters, and so the decoration with atoms will have to agree in the overlap. Because the abstract octagons shown in Figure 3 admit exactly the same overlaps as the atomic decoration, any structure that is completely covered by the cluster C can be represented by a two-dimensional tiling completely covered by these abstract, colored and arrowed octagons.

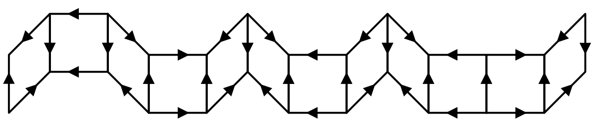

FIG. 5. The alternation condition requires that along any lane of tiles, the two types of rhombi must alternate. This is enforced by the arrowing of the tiles, which must match.

Any square-rhombus tiling that is completely covered by arrowed octagons necessarily satisfies the alternation condition.[19] The alternation condition, illustrated in Figure 5, is enforced by the matching of the arrows on the tile edges. The coloring does not impose any further constraint. By inspection of the possible local neighborhoods, it is easy to see that any tiling covered by arrowed

octagons can always consistently be colored in exactly two ways, which differ only by a trivial color switch.
In Ref. 6 it has been shown that among all tilings completely covered by the arrowed octagon (and thus satisfying the alternation condition), the octagonal Ammann-Beenker tiling is the unique tiling with the highest octagon density. And since there is so much overlap of octagons in the Ammann-Beenker tiling, is is hardly imaginable that there is a tiling not completely covered that has an even higher density. We can therefore conclude that the octagonal quasicrystal structure is the unique structure having the highest density of C clusters.

V. DISCUSSION AND CONCLUSION

In this paper we have shown that the octagonal quasicrystal structure determined in Ref. 11 is completely covered by a single kind of cluster, C. Moreover, this structure is even the one with the highest density of C clusters. Since C clusters are so abundant, they must be energetically preferred, and atoms inside such a cluster must have a favorable environment. Since every atom in the structure is contained in several such C clusters, every atom must therefore be in a favorable environment. The maximization of C clusters therefore seems to be the natural ordering principle that is reponsible for the formation of octagonal quasicrystals.
Our conclusions rely heavily on the results of Ref. 6, where a similar result for the two-dimensional Ammann-Beenker tiling was obtained. In that paper, it was suggested that the arrowed octagon might be replaced by a larger, undecorated patch, which has exactly the same asymmetry as the arrowed octagon, and therefore imposes the same overlapping constraints. In the present case this is not necessary, quite on the contrary. It is, in fact, the atomic decoration of the tiles, which provides us with exactly the right overlapping constraints that are needed to enforce the perfect octagonal structure through the maximization of C clusters.
The octagonal quasicrystal therefore appears almost like a textbook example that illustrates how the maximization of a single cluster can create quasiperiodic order. This order is created through constraints of overlap, which are the result of the particular atomic structure of the cluster. In this way, one can see how the global order of the structure follows from its local order.

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