

## Icosahedral Crystals: Where Are the Atoms?

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The positions of atoms in icosahedral crystals are shown to correspond to arrangements of three-dimensional hypersurfaces in six-dimensional periodic lattices. The six-dimensional space-group symmetry allows for crystals which cannot be formed by space-filling decorated tilings (quasicrystals). Structures with continuously varying "unit cells" are possible. The connection between tilings, projections, cuts, and density-wave descriptions is pointed out.

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Most textbooks in condensed-matter physics state, without a proof, that crystalline ordering is associated with regular three-dimensional translationally invariant Bravais lattices; as a consequence of this assumption, fivefold rotation symmetries are not permitted in conventional crystallography. The exciting electron-diffraction experiment by Shechtman *et al.*<sup>1</sup> on an alloy of manganese and aluminum showing a diffraction pattern with icosahedral symmetry (including fivefold axes) therefore ignited an unprecedented controversy in the world of crystallographers.<sup>2</sup> Soon after the Shechtman experiment, Poon, Drehman, and Lawless<sup>3</sup> discovered an alloy of palladium, uranium, and silicon also showing icosahedral symmetry. Has nature indeed invented a more elaborate way of arranging atoms in space with long-range ordering as indicated by the sharpness of the diffraction spots? From a mathematical point of view there are no obstacles to the concept of icosahedral crystals, since it has been shown that there exist space-filling arrangements of a small number of different building blocks (Penrose tiles)<sup>4,5</sup> with icosahedral diffraction patterns. But are these tilings indeed related to the underlying structures which produce the diffraction patterns observed in experiments?

In previous articles<sup>6</sup> it was shown, by the use of a general density-wave formulation, that the most general icosahedral structures can be represented by cuts in regular discrete lattices in six dimensions, with symmetry described by a regular six-dimensional space group. The symmetry elements of the 6D point group are twofold, threefold, and fivefold planes, which are all consistent with six-dimensional discrete translational invariance. The wave vectors of the diffraction spots should be thought of as projections of wave vectors  $Q$  forming a regular periodic 6D reciprocal lattice. Also, it has been shown by several authors<sup>7-9</sup> that the Penrose-tiling structure can be formed by projection of all lattice points within a slice or tube in 6D space onto a 3D plane. The resulting tiling produces a very specific diffraction pattern where the intensity depends only on the component of the wave vector  $Q$  perpendicular to the plane. The existence of Penrose tiles has

led many researchers to believe that icosahedral crystals are necessarily of this type, and there has been a great activity trying to fit experimental data to models where each tile is decorated with a basis of atoms.<sup>10,11</sup> In these models the tiling lattice is thus treated as a Bravais lattice in analogy with the structure of the conventional periodic crystals. However, it has not been demonstrated that the tiling models provide a reasonable fit to the intensities and this has caused suspicion that the icosahedral crystals may be, after all, merely conventional crystals with very large unit cells,<sup>2</sup> although I am not aware of any conventional crystal structure which produces a diffraction pattern with the slightest resemblance with experiment.

The object of this Letter is to give a description of the most general crystal lattices with icosahedral symmetry (the simple icosahedral structures defined in Ref. 6), and to demonstrate the connection between the seemingly unrelated physical and mathematical models which have been used to describe icosahedral structures: the density-wave formalism<sup>6,7,12</sup> (Landau theory), the tiling constructions,<sup>4,5</sup> and the projection method.<sup>7-9</sup> It turns out that icosahedral crystal structures correspond to arrangements of 3D hypersurfaces, or hypersurface segments, in 6D space, in analogy with regular crystals which are defined by arrangements of 1D points in 3D space. A variety of interesting topologies are possible, with interesting consequences for the diffraction spectrum and other physical properties such as the excitation spectrum. It will be seen that *the general icosahedral crystal structures cannot be thought of as tiling structures ("quasicrystals")*. Unfortunately (from a practical point of view) there are many continuous degrees of freedom for arranging the atoms in ways which are compatible with the space-group symmetry. Each surface is specified by three functions of three variables. To determine the actual structure the crystallographer must, in principle, go through the painful process of determining the positions of the hypersurfaces by doing a complete 6D crystal analysis of the diffraction spectrum, and different icosahedral crystals may have widely different atomic arrangements. The quasicrystal structure defined by the projection method

is simply a special limit, with no extra symmetry, and so attempts to fit experimental data to decorated tiling structures are bound to fail.

The most general structure with icosahedral symmetry can be written as a density<sup>6</sup>

$$\rho(\mathbf{r}) = \sum_i A \cos(\mathbf{q}_i \cdot \mathbf{r}) + \sum_{\{n\}} B_{\{n\}} \cos(\sum n_i \mathbf{q}_i \cdot \mathbf{r} + \psi_{\{n\}}), \quad (1)$$

where  $\mathbf{q}_i$ ,  $i = 1, 2, \dots, 6$ , are six vectors pointing toward vertices of a regular icosahedron as shown in Fig. 1. The second summation is over all sets of integers  $\{n\} = (n_1, n_2, n_3, n_4, n_5, n_6)$ . The icosahedral symmetry implies that coefficients  $B_{\{n\}}$  for which the vectors  $\sum n_i \mathbf{q}_i$  are related to each other by one of the 120 icosahedral symmetry operations are identical. For instance,  $B_{(100\ 000)} = B_{(000\ \bar{1}00)}$ . The expression (1) defines a function  $\rho_0$  of six variables:

$$\rho(\mathbf{r}) = \rho_0(\theta_1, \theta_2, \theta_3, \theta_4, \theta_5, \theta_6), \quad (2a)$$

where the density in the real  $r$  space is obtained by setting

$$\theta_i = \mathbf{q}_i \cdot \mathbf{r}. \quad (2b)$$

The function  $\rho_0$  is periodic in all its arguments with period  $2\pi$ ; hence it represents a six-dimensional crystal. The six-dimensional function  $\rho_0$  contains precisely the same information as the three-dimensional function  $\rho$ : In six dimensions the crystal gives diffraction peaks at  $Q = (n_1, n_2, n_3, n_4, n_5, n_6)$ , which have precisely the same intensity as the diffraction peaks of the real 3D crystal at  $\sum n_i \mathbf{q}_i$ . The permutations of  $\pm \mathbf{q}_i$  which leave the icosahedron invariant define permutations of  $\pm \theta_i$  which leave (2a) invariant. These 120 operations form the point group of the 6D crystal. The point group has fivefold, threefold, and twofold planes. For instance, there is a threefold plane  $m_3$  spanned by the vectors (111 000) and (000 111), a fivefold plane  $m_5$

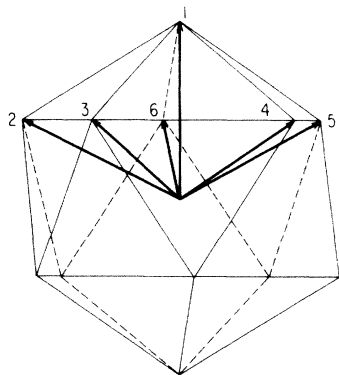


FIG. 1. Fundamental wave vectors  $q_i$  characterizing the simple icosahedral structure.

spanned by (1000 000) and (011 111), and a twofold plane  $m_2$  spanned by (110 000) and (001 001). Equation (2b) states that the actual density in 3D space is the density along the 3D plane  $P$  in 6D space which is traced out as  $\mathbf{r}$  traverses real space. This plane forms an invariant subspace since all symmetry operations in 6D space correspond to rotations of  $\mathbf{r}$ . The various possible icosahedral structures correspond to the various ways of choosing the periodic function (2a) or, equivalently, the basis to associate with the 6D unit cell. This basis has to obey the icosahedral symmetry. The real Bravais lattice of the structure is thus six dimensional.

Until now I have not made any assumptions about the objects which form the basis. I now want to describe structures which can be formed by arrangements of atoms in 3D space. This necessarily implies that the basis must consist of one or more 3D hypersurface segments, where the intersection points between the hypersurfaces and the 3D real-world plane define the positions of the atoms. *There is a one-to-one relation between the possible ways to arrange hypersurfaces on a 6D lattice and the possible ways to arrange atoms in 3D icosahedral crystals.* The size and density of the atoms can be represented by the association of a width to the hypersurface along  $P$ . Figure 2 illustrates various periodic arrangements of hypersurfaces (the figure could also illustrate how a one-dimensional incommensurate structure can be constructed from a two-dimensional regular structure).

The arrangement of hyperplanes must obey the icosahedral space-group symmetry defined above. If a surface is placed at a general position in the unit cell it must be accompanied by 119 others generated by application of the point-group operations  $R$  to the surface; this causes messy unphysical arrangements with overlapping atoms. To avoid this the surface must be placed at positions with special symmetry. The simplest structures correspond to hypersurfaces which are invariant under  $R$ . The simplest invariant hypersurface is a 3D hyperplane  $P'$  perpendicular to  $P$  [Fig. 2(a)]. Clearly the resulting crystal structure can be viewed as arising from a projection on  $P$  of 6D lattice points within a distance from  $P$  defined by the size of the hyperplane segment. The symmetry planes  $m_3$ ,  $m_5$ , and  $m_2$  defined above intersect both  $P$  and  $P'$  along symmetry axes. Figure 2 shows a fivefold plane intersecting  $P$  and  $P'$  along fivefold axes. In principle, the hyperplane may extend arbitrarily along  $P'$ . If the surface is chosen to be the projection of the 6D unit cube onto  $P'$  the hyperplane segment becomes a three-dimensional rhombic triacontahedron and the Penrose-tiling structure is recovered as shown by Duneau and Katz<sup>8</sup> and Elser.<sup>9</sup> A tiling structure also emerges if the segment is chosen to be a sphere.<sup>7</sup> We have thus demonstrated that the tiling structures arise

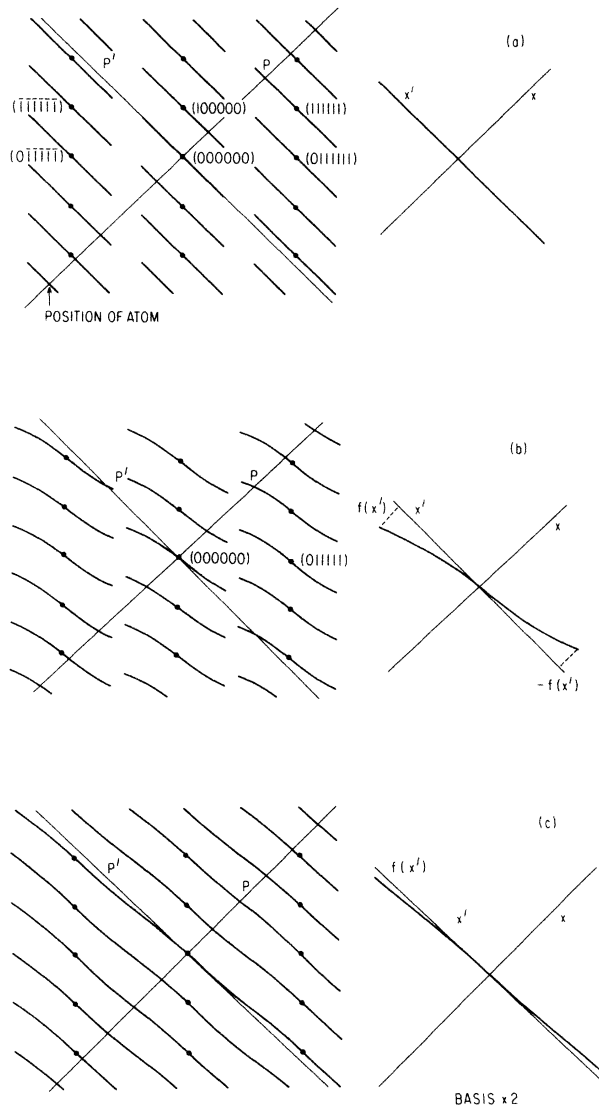


FIG. 2. Periodic arrangement of real-space 3D surfaces in 6D space. The figures show cuts along a fivefold plane. The plane  $P$  represents real space.  $P'$  is the invariant space orthogonal to  $P$ . (a) The 3D surfaces are planes along  $P'$ , (b) the surfaces are distorted planes, and (c) the surface segments form a multiply connected extended surface.

as special limits of much more general structures.

In general, the diffraction pattern can be derived simply as the Fourier transform of the content of the 6D unit cell, in analogy with regular 3D crystals. In the quasicrystal limit where the unit cell contains only a plane segment the intensities of Bragg peaks obviously depend only on the component of the corresponding 6D vector  $Q$  perpendicular to  $P$ . Unfortunately this simple result does not apply to the general case.

The general structures cannot be formed as projections, even in the simple case of one invariant surface. Symmetry does not restrict the invariant hypersurface to be a plane. It is possible to distort the plane without destroying the invariant properties. Consider a general point  $(\mathbf{x}', 0)$  on the plane segment along  $P'$ , where the second coordinate indicates the component along  $P$ . A distorted plane is given by points  $(\mathbf{x}', f(\mathbf{x}'))$  [see Fig. 2(b)]. The application of any point-group operation  $R$  to this point yields the point  $(R(\mathbf{x}'), Rf(\mathbf{x}'))$ . The surface is invariant as long as  $R(f(\mathbf{x}')) = f(R(\mathbf{x}'))$  for all  $\mathbf{x}'$ . The distorted surface can be generated by rotating the surface within an irreducible section of the plane segment along  $P'$ . The distortion  $f(\mathbf{x}')$  is restricted only if  $\mathbf{x}'$  is along one of the  $n$ -fold rotation axes in  $P'$  where  $R(\mathbf{x}') = \mathbf{x}'$ , since then the distortion must be along the corresponding  $n$ -fold axis in  $P$  to assure invariance. Figure 2(b) shows the intersection of the hypersurface arrangement with a fivefold plane. The surface must be symmetric around the center because of the twofold plane perpendicular to the plane. In order to specify the position  $f(\mathbf{x}')$  or just one plane one must determine three functions  $f$  of three variables  $\mathbf{x}'$ . And in a realistic model there must be several surfaces that correspond to the different constituents of the alloy. Clearly the intensities of the Bragg spots obtained by Fourier transformation of the arrangement of hypersurfaces do not depend on  $Q$  in a simple way.

For small distortions  $f$  the resulting crystal structure can be viewed as a modulation of the Penrose tiles, and  $Q$  spots with a large perpendicular component will be weak. The case shown in Fig. 2(b) is essentially a tiling model with atomic relaxations. For larger distortions *new classes of structures appear*, for instance because it is possible to connect surfaces which correspond to different cells without violating the symmetry. Figure 2(c) shows a cut along a fivefold plane of such a surface. Note that the distance between two successive atoms is modulated around an average distance, as for incommensurate crystals, in contrast to Fig. 2(a) where two distinct lengths are involved. A detailed analysis reveals that it is not possible to connect the surfaces to form extended surfaces with the topology of 3D planes. In general the resulting surfaces are *multiply connected*. (For a lower dimensional analog think, for instance, of the multiply connected Fermi surface in a cubic material like copper; the cubic symmetry forbids extended planes. The analogy should not be taken too far: One might suspect that saddle points would cause two lattice points to come arbitrarily close together. In 6D it is possible to have connected surfaces with rather small variations of the distances.) A variety of interesting topologies are possible. The connectedness implies that the crystal structure can be formed by stacking a continuous dis-

tribution of unit cells; these icosahedral crystals can be thought of physically as caused by the frustration due to the inability of the "natural" unit cell to fill space: As a compromise the unit cell adjusts to the local environment by distorting. Nevertheless, the long-range order is strictly preserved. The tiling or quasicrystal picture loses its meaning completely! The connected topology has interesting consequences for the continuous phase degrees of freedom associated with a shift of  $P$  along  $P'$ : Some atoms are shifted continuously whereas in the tiling limit the phase shifts describe rearrangement of tiles.<sup>6</sup>

So where are the atoms in a particular icosahedral crystal? Unfortunately, the conclusion of this paper is that there is no "quick fix" to solve the crystal structure since the icosahedral symmetry is sufficiently low to allow for complicated continuous possibilities of arranging the atoms. No simple mathematic model can possibly describe the structure. One might speculate that in the Mn alloy there is an Mn hypersurface through (000000) and six Al surfaces through ( $\frac{1}{2}$ 00000), but this is merely a guess. Even if this were the case it would be a monumental job to determine the surfaces. The stoichiometry is not of much help: The extensions of the hypersurfaces and therefore the concentrations can vary continuously. If one really wants to know where the atoms are there is no way out: One has to perform a complete six-dimensional crystal analysis to determine the positions of the hypersurfaces within the unit cell. Only then

can one determine the arrangement in real space by cutting the 6D space along the plane defined by Eq. (2b)!

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