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Symmetry, Stability, and Diffraction Properties of Icosahedral Crystals

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SYMMETRY, STABILITY, AND DIFFRACTION PROPERTIES OF ICOSAHEDRAL CRYSTALS.

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ABSTRACT

In a remarkable experiment on an Mn-Al alloy Shechtman et al. observed a diffraction spectrum with icosahedral symmetry. This is inconsistent with discrete translational invariance since the symmetry includes a five-fold axis. In this paper it will be shown that the crystallography and diffraction pattern can be described by a six-dimensional space group. The crystal structure in 3d is obtained as a cut along a 3d hyperplane in a regular 6d crystal. Displacements of the 6d crystal along 6 orthogonal directions define 6 continuous symmetries for the icosahedral crystal, three of which are phase symmetries describing internal rearrangements of the atoms.

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1. INTRODUCTION

The symmetry of three-dimensional crystals on a regular discrete lattice can be described in terms of space groups composed of a Bravais lattice of translational symmetries and a point group of rotation and reflection symmetries. Only 2, 3, 4, and 6 -fold rotation symmetries are allowed. However, in a recent electron diffraction experiment on a rapidly quenched alloy of manganese and aluminum Shechtman et al. [1] observed a spectrum including a 5-fold rotation axis and overall symmetry identical to that of a regular icosahedron (Fig. 1). The diffraction spots do not form a regular periodic lattice, but the spectrum has a scaling structure: if the pattern is blown up by a factor G (the golden mean) the position, but not the intensities, remain invariant. The diffraction spots were rather sharp, indicating long range order of some sort. How can this be possible in wiev of the considerations above?

A similar picture emerges for incommensurate modulated systems which also display a nonperiodic spectrum reflecting the lack of discrete translational symmetry. However, in this case the diffraction spots occur at positions which can be formed as linear combinations of the reciprical lattice vectors a_i of a basic lattice and the modulation vectors g_i of the incommensurate structure [2]. In the icosahedral structure one can not isolate a set of basic vectors, and there is in fact only one length scale. Nevertheless it turns out that one can apply ideas originating from the study of incommensurate systems to describe symmetries and physical properties of icosahedral crystals.

In this paper it will be shown that the usual three-dimensional space group should be replaced by a six-dimensional space group formed by a six-dimensional discrete lattice of translations and a point group which is isomorphous with the icosahedral group. The actual physical density is the density along a three-dimensional hyperplane in this 6d crystal. All the symmetry operations in 6d space represent actual symmetry operations in 3d. The diffraction pattern should be thought of as the diffraction pattern of the 6d crystal. The five-fold symmetry found by Shechtman reflects the existance of a five-fold axis in the 6d point group. The crystallographer's task is to find the basis associated with the primitive unit cell, which is in fact a quite formidable problem! Just as the basis in regular 3d crystals usually consists of an arrangement of point-like objects (atoms), the basis for an icosahedral arrangement of atoms consists of an arrangement of 3d hypersurfaces imbedded in 6d space. These hypersurfaces intersect the 3d real world space at the positions of the atoms. The only requirement for the hypersurfaces is that they obey the 6d point group symmetries, and this leaves us with an enormous amount of flexibility. If the surfaces are chosen to be hyperplane segments the resulting structure becomes a space-filling non-periodic arrangement of tiles. such tilings have been described by several authors [3]-[5]. It is important to stress that the tilings or "quasicrystalline" arrangements only represent a limiting case of a much more general class of structures. There seems to be no a priori reason to believe that the actual structure found by Shechtman et al. is related to the tiling limit. In addition to the 6d case we shall first discuss, for pedagogical reasons, the much simpler case of a one-dimensional incommensurate system and a two dimensional system with a 5-fold axis. The latter system has essentially the same symmetry as a plane-filling system of tiles invented by the mathematician R. Penrose [6].

The icosahedral structures have 6 continuous symmetries corresponding to displacements of the underlying 6d crystal in 6 orthogonal directions, compared with 3 continuous displacement symmetries for 3d crystals. The remaining continuous symmetries describe internal rearrangements of the atoms, very similar to the phase symmetries in incommensurate systems. For a more complete account of the work presented here see the original references [7] and [8].

2. 6d CRYSTALLOGRAPHY OF ICOSAHEDRAL CRYSTALS AND PENROSE STRUCTURES.

In order to illustrate the concepts that will be introduced to explain the icosahedral crystals let us first consider a simple 1d incommensurate structure. The density of the most general 1d incommensurate crystal with two length scales or wave numbers q_1 and q_2 can be written

$$f(x) = \sum_{m,n} A_{m,n} \cos(m\, q_1 x + n\, q_2 x) = f_0(q_1 x, q_2 x), \qquad (1)$$

where m and n are integers. This equation defines a two-dimensional function $f_0(v_1, v_2)$ which is periodic in both its arguments with period 2 . Hence the function defines a two dimensional periodic structure or crystal. The density in the real 1d space is the density along the line $v_1 = q_1 x$, $v_2 = q_2 x$ (Fig.2). The slope of the line, q_2/q_1, represents the incommensurability of the structure which for instance could be the golden mean Θ. Because of the incommensurability the line gets infinitely close to all points belonging to the basis, so all the information in the 2d lattice is used to generate the 1d incommensurate structure. The amplitudes of the diffraction spots are simply the Fourier transforms of the 2d function f_0:

$$S(q) = 1/L \int_0^L dx\, f(x) \exp(iqx) = 1/L \int_0^L dx\, f_0(q_1 x, q_2 x) \exp(iqx) \qquad (2)$$

$$= \int_0^{2\pi} dv_1 \int_0^{2\pi} dv_2\, f_0(v_1, v_2) \exp(iqx) = \sum_{n,m} A_{n,m} \delta(m q_1 x + n q_2 x - q),$$

so the diffraction pattern of any one dimensional incommensurate structure can be thought of as the diffraction pattern of a regular periodic two-dimensional crystal. The various incommensurate structures differ simply in the basis associated with each unit cell in the 2d lattice. Choose first a basis consisting of a line of delta-functions crossing the unit cell diagonally (Fig. 2b), i.e. $f_0(v_1, v_2) = \delta(v_1 - v_2)$. The resulting structure is an uninteresting array of equidistant delta function atoms. If the straight line is modulated by a sine function, or some other periodic function (Fig. 2c) the resulting structure is an array of atoms with modulated displacement around equidistant positions.

An interesting case is the one where the basis is chosen to be a line segment of delta functions perpendicular to the real world line (Fig. 2d), $f_0(v_1, v_2) = \delta(q_2 v_1 - q_1 v_2)$. The resulting structure is a chain of atoms with interatomic distances which interchange in a regular pattern between two different values. The incommensurate structure can thus be formed by an arrangement of two different one-dimensional building blocks or "tiles". This is precisely the quasicrystal introduced by Levine and Steinhardt [4], which is merely a special limit of an incommensurate structure. Note that in the quasicrystal limit one can alternatively think of the incommensurate structure as a projection of 2d lattice points onto the line. In an experiment the actual function f_0 must be found by fitting to the intensities of the Bragg spots and the actual density can then be found by cutting the 2d space along the appropriate line defined by Eq. (1). The various cases discussed here do not exhaust the possibilities for 1d incommensurate structures. For some simple models the structures are highly nonanalytic pinned incommensurate configurations. Such structures would correspond to a "fractal" choice of basis.

Consider now a two-dimensional structure formed by superimposing density waves with wave vectors q_1.......q_5 forming a regular pentagon, and their higher harmonics:

$$f(\mathbf{r}) = \sum_n A \cos(q_n \cdot \mathbf{r}) + B \cos([q_n + q_{n+1}] \cdot \mathbf{r}) + C \cos([q_n + q_{n+2}] \cdot \mathbf{r}) + \ldots\ldots \qquad (3)$$

$$= f_0(q_1 \cdot \mathbf{r}, \ldots\ldots\ldots, q_5 \cdot \mathbf{r})$$

The structure has been built in a way which preserves the permutational symmetry of the wavevectors defined by the pentagon. Equation 3 defines a function $f_0(v_1, \ldots, v_5)$ of five variables, and the equation expresses that the actual physical density is found along a 2d plane in the 5d hyperspace. The function f_0 defines a 5d crystal lattice since it is invariant under translations 2 in all its arguments. In addition the function is invariant under certain permutation operations on its arguments. These operations form the point group of the five dimensional crystal. For instance, the five-fold rotation $v_i - v_{i+1}$ is a symmetry operation. It is this symmetry operation which is responsible for the peculiar fivefold symmetry of the Penrose structures. Thus, the symmetry group which describes the "generalised" Penrose structures is a 5d space group formed by a 5d Bravais lattice combined with a point group which is isomorphous with C_{5v}, the symmetry group of the pentagon.

Finally, let us proceed to the icosahedral crystals which should by now be quite easy to understand. Consider a 3d density function $f(\underline{r})$ which is formed as a superposition of waves with wave vectors given as the six pairs of vectors pointing to the vertices of a regular icosahedron. Again, we shall allow all possible higher harmonics as long as they do not lower the icosahedral permutation symmetry of the basic vectors:

$$f(\underline{r}) = \sum_n A\cos(q_n \cdot \underline{r}) + \text{higher harmonics} \qquad (4)$$

$$= f_0(q_1 \cdot \underline{r}, \ldots\ldots, q_6 \cdot \underline{r}) .$$

The function $f_0(v_1, \ldots\ldots, v_6)$, defined in six-dimensional space, has the symmetry of a 6d bravais lattice since it is invariant under translations of 2 of all its arguments. As the vector $\underline{r}$ traverses 3d space, a 3d plane is traced out in 6d space. The 3d plane is spanned by the vectors $(q_{1x}, \ldots, q_{6x})$, $(q_{1y}, \ldots, q_{6y})$, $(q_{1z}, \ldots, q_{6z})$. Hence, the real 3d quasicrystal is to be found along a 3d hyperplane in 6d space. The point group consists of the permutation operations among v_i which leaves the function f_0 invariant. This point group is obviously by construction isomorphous with the icosahedral group which has 120 elements. One of these elements is a 5-fold axis, $v_1 \to v_1$, $v_2 \to v_3 \to v_4 \to v_5 \to v_6 \to v_2$. It is this 5-fold axis which is responsible for the surprising 5-fold symmetry observed by Shechtman et al.!

A structure analysis could in principle be done as follows. First, the function f_0 could (again in principle) be determined by analysing the diffraction pattern. The spots at positions q $= n_1q_1 + \ldots + n_6q_6$ *should simply be thought of as the* (n_1 ..... n_6) spots of a six dimensional crystal! Once the basis to associate with each unit cell in 6d space has been determined the real structure can be found simply by cutting the 6d crystal along the hyperplane. Note that since the vectors q_i are incommensurate with the basic vectors of the 6d lattice the density along the 3d plane samples the whole 6d unit cell, so all information in the 6d lattice is relevant for the 3d icosahedral crystal.

The choice of basis must be compatible with the point group symmetry defined above. So far we have ignored the fact that the crystal should be formed by an arrangement of Mn and Al atoms. So where are the atoms? An arrangement of delta-function atoms in 3d space must correspond to a periodic arrangement of 3d hypersurface segments in 6d space which intersect the 3d real-world hyperplane at the positions of the atoms. This is completely analogous to the 1d incommensurate case discussed above where the positions of atoms are given as the intersection points between 1d curves and the 1d real space line. If the positions of the 3d Al and Mn hypersurfaces are not chosen carefully the resulting arrangement of atoms becomes unphysical. For instance, the surfaces can not intersect each other since this would lead to overlapping atoms. If the surface is not placed at a symmetry position the point group symmetry requires 120 surfaces in the unit cell, many of which would in general intersect. However, it is possible to choose a surface which is invariant under all 120 point group operations.

The surface does not have to be a hyper<u>plane</u>, but to be specific let us assume for the moment that it is. A "natural" arrangement with Mn atoms surrounded icosahedrally with 12 Al atoms arises if the Mn surface is a hyperplane perpendicular to the 3d plane through the point (000000) and the Al positions correspond to 6 Al surfaces through the 6 symmetric points (1/2 00000). Thus,the basis of the 6d unit cell consists of one Mn 3d hyperplane and 6 Al hyperplanes. This limit corresponds to an arrangement of identical three dimensional tiles, so this would again be the quasicrystal limit. Note that the positions of atoms are given as projections of all 6d lattice points within a certain distance from the 3d plane onto this plane. It has thus been demonstrated that the projection methods introduced by others [3]-[6], [9] can be recovered as special, and probably rather unrealistic, limits. More general structures can be constructed by modulating the positions of the hypersurfaces in analogy with the construction for 1d incommensurate systems depicted in Fig. 2c. The general icosahedral crystal is related to the tiling structures in a way which is quite analogous to the way incommensurate structures are related to regular periodic structures.

In addition to the operations which leave the structure invariant there are also continuous operations which leave the energy invariant, in analogy with rigid displacements of a regular 3d crystal. A rigid shift of the underlying 6d crystal in any direction must correspond to a continuous symmetry since the 3d plane traverses the unit cell ergodically. It is easy to see that a shift of the 6d crystal parallel to the 3d real space hyperplane corresponds to a rigid displacement of the icosahedral crystal. Displacements of the 6d crystal perpendicular to the plane define the three remaining symmetries which in general describe certain internal rearrangements or "phase shifts" of the atoms. The density along the broken lines in Fig. 2 represents the result of a phase displacement perpendicular to the real-space line in the case of a 1d incommensurate structure. In some cases (Fig. 1c) the atoms are displaced continuously while in other cases (Fig. 2d) the actual displacements of the atoms are discontinuous despite the fact that the phase shift is a continuous symmetry. The two cases are usually denoted unpinned and pinned incommensurate structures, respectively [2].

Once the continuous symmetries have been defined one can construct the elastic energy associated with strains in these hydrodynamic coordinates. A little group theory reveals that for the Penrose structures there are in general two elastic constants for the displacement strains, two elastic constants for the phase strains, and one elastic constant mixing the strains, so altogether there are 5 elastic constants. The situation is precisely the same for the icosahedral crystals [8].

So far we have discussed only the crystallographic properties of icosahedral crystals, and totally ignored the question as to what makes such structures stable. In order to really answer this question one must in principle perform an enormous electronic structure calculation, involving a determination of the total energy, and compare with all other possible structures. Such calculations are just on the borderline of the state-of-the-art for simple regular lattices, and it seems prohibitively difficult in a situation where one does not have a periodic lattice. Any discussion on the stability of icosahedral structures must necessarily be quite phenomenological at present. A Landau theory [7-8] reveals that the icosahedral structures may indeed in principle be stable compared with all other structures, in particular compared with bcc cubic crystals. The density wave description used here to describe the crystallographic properties of icosahedral crystals arises in a natural way from the Landau theory.

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REFERENCES

[1] D. Shechtman, I. Blech, D. Gratias, and J. W. Cahn, Phys. Rev. Lett. 53 (1984) 1951.

[2] P. Bak, Rep. Prog. Phys. 45 (1981) 587.

[3] P. Kramer and R. Neri, Acta Cryst. A40 (1984) 580.

[4] D. Levine and P. Steinhardt, Phys. Rev. Lett. 53 (1984) 2477.

[5] V. Elser, preprint.

[6] For a popular article on Penrose tilings see M. Gardner, Sci. Am. 236 ,january issue (1977) 110

[7] P. Bak, Phys. Rev. Lett. 54 (1985) 1517

[8] P. Bak, Phys. Rev. B, in press

[9] P. Kalugin, A. Kiteyev, and L. Levitov, ZhETF 41 (1985) 119

FIGURE CAPTIONS

Fig. 1 Diffraction pattern of $Mn_{0.14}Al_{0.86}$ as measured by Shechtman et al. [1] along a five-fold axis (Schematic). Note the lack of translational invariance.

Fig. 2 One-dimensional incommensurate structure as a 2d periodic crystal. The physical density along the x-direction is the density along a line through (0,0) with slope q_2/q_1. The various incommensurate structures differ only with respect to the basis associated with each lattice point. a) General case. The cases b)-d) are discussed in the text. The broken line represents the density associated with a phase translation.

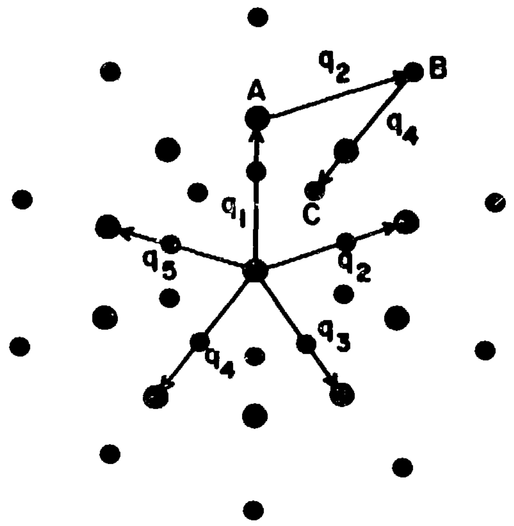

Fig. 1

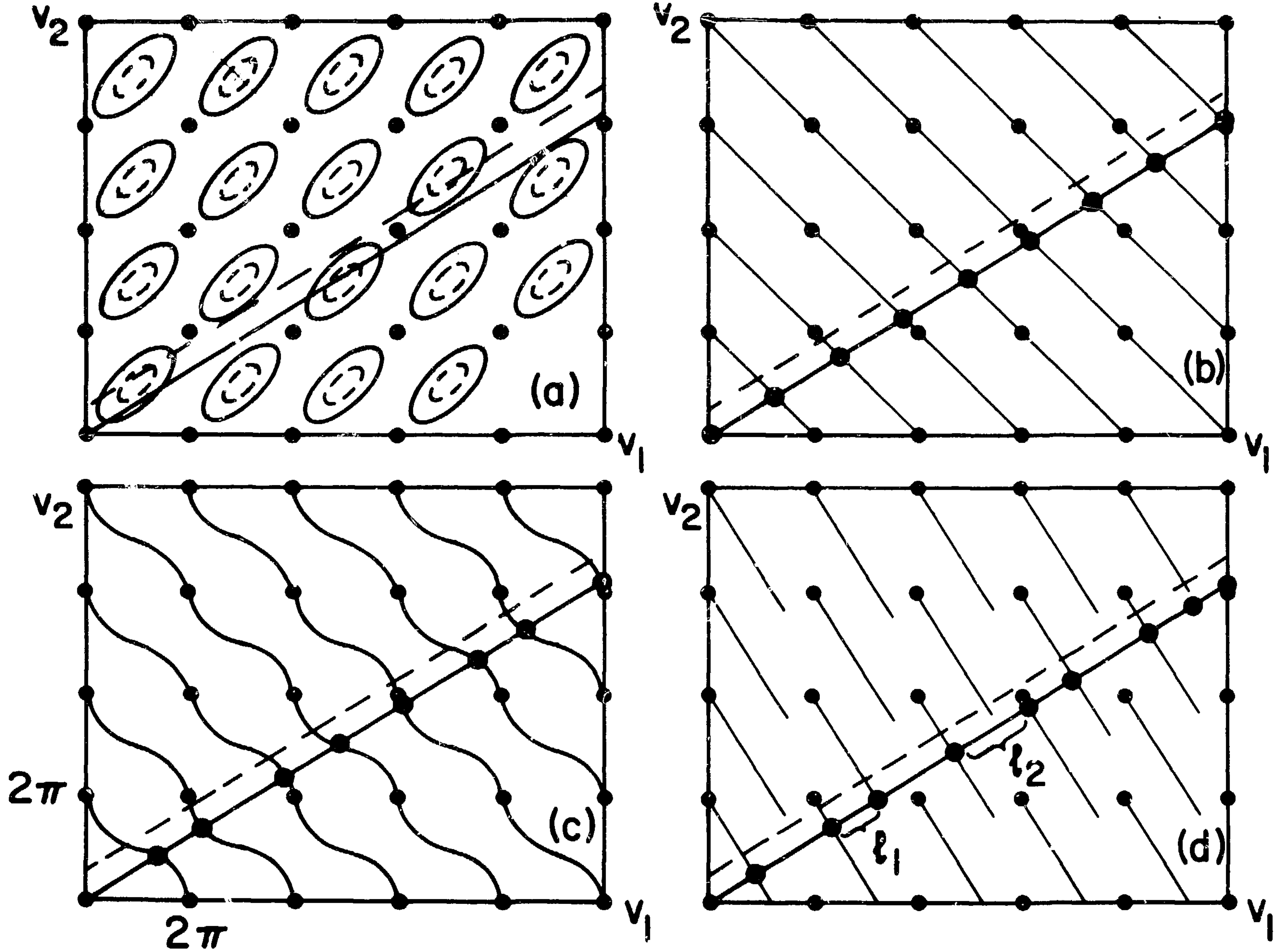

Fig. 2