# Phenomenological Theory of Icosahedral Incommensurate ("Quasiperiodic") Order in Mn-Al Alloys

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The crystal structure with icosahedral point-group symmetry and long-range orientational order observed by Shechtman *et al.* in Mn-Al alloys can be explained as a multiple-**q** density-wave structure with only one length scale. Its existence and stability can be understood from a simple Landau theory. The diffraction spots can be indexed by six- (or more-) dimensional space-group symmetries. Icosahedral incommensurate structures constitute natural extensions of smectic, rodlike, and cubic crystal structures.

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In an exciting experiment on Al-Mn alloys, Shechtman *et al.*[1] have observed a phase with long-range orientational order and icosahedral point-group symmetry which is inconsistent with lattice translation invariance. In this paper it will be shown that the existence of such structures can be understood in a simple and natural way from a Landau-Ginzburg theory. The icosahedral order arises as a natural extension of smectic, rodlike, and cubic crystal order, in the sense that all these structures are described by the same order parameter, namely, a mass-density (or compositional-density) wave. The icosahedral structure is a multi-**q** structure[2] formed by superposition of fifteen density waves with wave vectors along the edgtes of an icosahedron. The melting transition is predicted to be first order in agreement with experiment. The diffraction spots are given by linear combinations of these vectors and can be indexed to a higher-dimensional space group, as is the case for other incommensurate ("quasiperiodic") structures. Penrose lattices[3] can be represented in a similar way as "quintuple-**q**" structures. The phonon spectrum has three acoustic phonon modes and three acoustic phason modes representing a total of six continuous symmetries.

We start from a high-temperature disordered isotropic liquid phase; possible Landau order parameters are mass-density waves $\rho_{q_i}$ labeled by the wave vector **q**. Because of the rotational symmetry, the free energy depends only on the magnitude $|\mathbf{q}|$ and not on the direction. The expansion of the free energy in terms of these order parameters takes the form

$$F = r\rho_i\rho_{-i} + u(\rho_i\rho_{-i})^2 + \ldots + v_3\rho_1\rho_2\rho_3\delta(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3) + \text{c.c.}$$
$$+ v_5\rho_1\rho_2\rho_3\rho_4\rho_5\delta(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3+\mathbf{q}_4+\mathbf{q}_5) + \text{c.c.} + \ldots, \quad (1)$$

where I have explicitly included higher-order terms with wave vectors adding up to 0. Several different ordered structures can be formed by this order parameter. For instance, a single $\rho_i$ represents a smectic ordering,

$$\rho(r) = \rho_i \exp(i\mathbf{q}_i\cdot\mathbf{r}) + \text{c.c.}$$

The third-order term favors multi-**q** structures with wave vectors forming equilateral triangles [Fig. 1(b)]. A "triple-**q**" structure, with higher harmonics, represents a two-dimensional (2D) hexagonal phase or a three-dimensional (3D) rodlike phase. However, it was pointed out by Alexander and McTague[4] that the free energy can often be lowered further by combining density waves with eight vectors forming an octahedron (Fig. 1) or six vectors forming a tetrahedron, representing the reciprocal lattices of bcc and fcc structures, respectively.

In two dimensions, the fifth-order term favors a structure formed by superimposing five density waves with vectors forming an equilateral pentagon (Fig. 1). If we write the order parameter as $\rho_i = A\exp(i\theta_i)$, the

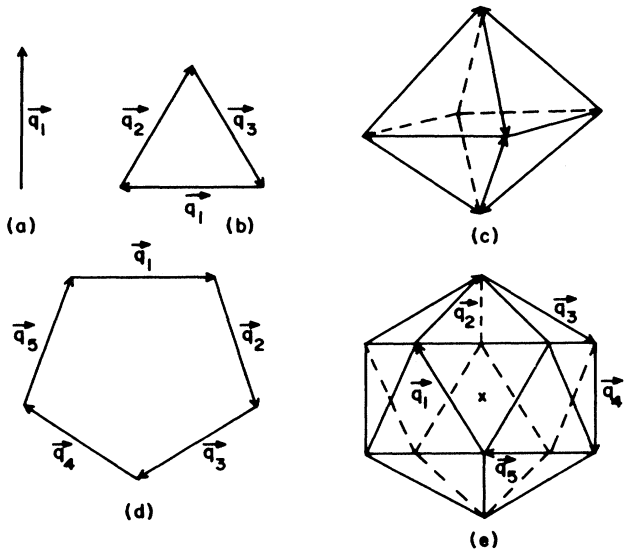


FIG. 1. Wave-vector combinations representing (a) smectic structures, (b) rodlike structures, (c) bcc structures, (d) 2D Penrose structure or 3D rodlike lyotropic structure, and (e) icosahedral incommensurate structure.

fifth-order terms becomes

$$F_5 = v_5 A^5 \cos(\theta_1+\theta_2+\theta_3+\theta_4+\theta_5), \quad (2)$$

which can be made negative for suitable choices of $\theta_1, \ldots, \theta_5$. The resulting structure,

$$\rho(r) = \sum_{i=1}^{5} A \cos(\mathbf{q}_i \cdot \mathbf{r} + \theta_i) + \text{higher harmonics},$$

has precisely the symmetry of Penrose lattices.[3] However, in analogy with the Alexander-McTague arguments one can often, in three dimensions, do better by choosing fifteen pairs of vectors forming the edges of a dodecahedron, or a regular icosahedron. In the latter case [Fig. 1(e)] one can take advantage of *both* the third-order term and the fifth-order term since ten pairs of triangles and six pairs of pentagons can be formed by the vectors. With the choice $A_i = \rho/(15)^{1/2}$ the third- and fifth-order terms become

$$F_3+F_5 = -\frac{\rho^5 v_5}{225(15)^{1/2}} \sum_{6\ \text{pentagons}} \cos(\theta_i+\theta_j+\theta_k+\theta_l+\theta_m) - \frac{\rho^3 v_3}{15(15)^{1/2}} \sum_{10\ \text{triangles}} \cos(\theta_i+\theta_j+\theta_k). \quad (3)$$

With the assumption of no conflict between the signs of $v_3$ and $v_5$, minimization of the free energy gives rise to nine constraints of the fifteen phases, and the resulting energy becomes

$$F_3+F_5 = -2\rho^5 v_5/75(15)^{1/2} - 2\rho^3 v_3/3(15)^{1/2},$$

which, for small enough $v_3/v_5$, can become favorable compared with the energy of the bcc structure with $A_i = \rho/(6)^{1/2}$:

$$F_3^{\text{bcc}} = -2\rho^3 v_3/3(6)^{1/2}.$$

The resulting structure $\rho(r) = \sum_{i=1}^{15} A \cos(\mathbf{q}_i \cdot \mathbf{r})$ has precisely the symmetry of the diffraction spectrum observed by Shechtman *et al.* This is my suggested explanation for the fivefold symmetry. All the spots can be indexed by the proper linear combination of the fifteen basic reciprocal-lattice vectors. Of course, not all these vectors are linearly independent, but to preserve the symmetry it is useful to use an overcomplete set, in a way perfectly analogous to the indexing of hexagonal structures where four indices are commonly used. For instance, considering the diffraction spectrum in a plane containing one of the pentagons spanned by $\mathbf{q}_1, \ldots, \mathbf{q}_5$ (or the Penrose lattices), the point $A$ in Fig. 2 can be indexed as (10000), the point $B$ as (11000), and the point $C$ as (11010). Note that the length of the vector $C$ is related to the basic vectors by the golden-mean ration $(\sqrt{5}-1)/2$. The golden mean thus enters in a simple geometrical way *unrelated* to the choice of building blocks used to form the structure. There is only one length scale involved.

The experimental observation of the diffraction pattern is consistent with the idea of a three-dimensional incommensurate structure. The high-order diffraction spots represent higher harmonics of the basic density waves, needed to form the actual electronic density. The intensities depend on an effective structure factor, and there is no reason that the intensity pattern of the spectrum be self-similar, and there is no reason that the structure factor decompose into a product of one-dimensional structure factors as in a model proposed by Levine and Steinhardt.[5] In fact, it is observed experimentally that the intensities of the spot decay rapidly with the order of the spots, showing a relatively small content of higher harmonics. As with all other 3D incommensurate structures, there are diffraction spots arbitrarily close to any given point in reciprocal space.

What are the acoustic $q \to 0$ phonon modes of the icosahedral structure? Consider first the Penrose lattice. The fifth-order term fixes the sum of five phases, and so there are four continuous symmetries left. Two of these represent phonon modes, and the two remaining modes are phason modes describing continuous internal rearrangements. In the icosahedral case there are nine linearly independent constraints on the fifteen phases, leading to six acoustic modes. The continuous translational symmetries, $\theta_i \to \theta_i + \mathbf{q}_i \cdot \boldsymbol{\delta}$, define three normal acoustic phonon modes, and the remaining three modes are phason modes. The phason modes might in principle be gapless, but could be overdamped or pinned, in which case a gap will appear. The phason modes can be characterized and measured as described by Axe and Bak[6] for mercury chain compounds, etc.

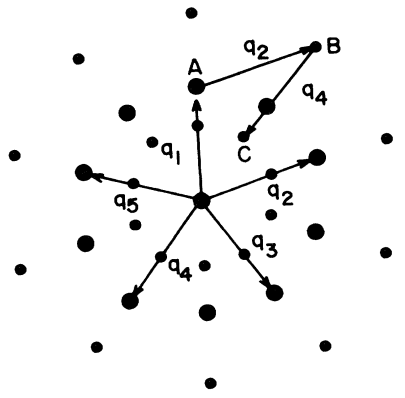


FIG. 2. Diffraction spectrum in fivefold plane of icosahedral structure, or of the Penrose structure. The spots can be indexed by five "Miller indices" $(n_1, \ldots, n_5)$. The point $A$ is (10000), the point $B$ (11000), the point $C$ (11010).

Incommensurate structures (by definition) are not translationally invariant so that there is no reason that they obey 3D space-group symmetries. If one insists on applying space-group arguments, this can be done in an elegant way discovered by Janner and Janssen.[7] Consider again the "quintuple-**q**" Penrose structure. The phases $\theta_1, \ldots, \theta_5$ define a five-dimensional space. A discrete shift $\theta_i \rightarrow \theta_i + 2p\pi$ leaves the structure invariant, and so the system has a 5D Bravais lattice symmetry. The fivefold axis in 3D space corresponds to a fivefold axis along (11111) in 5D space which permutes the **q** vectors, or phases, $\theta_1 \rightarrow \theta_2 \rightarrow \theta_3 \rightarrow \theta_4 \rightarrow \theta_5 \rightarrow \theta_1$. In addition there are five three-dimensional reflection planes, $\theta_1 \leftrightarrow -\theta_1$, $\theta_2 \leftrightarrow -\theta_4$, $\theta_3 \leftrightarrow -\theta_5$, etc., and inversion symmetry. The 5D space group has "pentagonal" symmetry. The four phonon modes can be formed by two different two-dimensional representations of the 5D point group "$C_5m^3$." The most general electronic density with this symmetry can be written

$$\rho(\mathbf{q}_1\cdot\mathbf{r},\ \mathbf{q}_2\cdot\mathbf{r},\ \mathbf{q}_3\cdot\mathbf{r},\ \mathbf{q}_4\cdot\mathbf{r},\ \mathbf{q}_5\cdot\mathbf{r}),$$

where $\rho(\theta_1,\theta_2,\theta_3,\theta_4,\theta_5)$ is invariant under the space-group transformations defined above. In analogy with these considerations, the symmetries of the icosahedral structure can be represented by a fifteen-dimensional space group, if one so desires. Since there are only six independent vectors, represented by the vertices of the icosahedron, the space group can be reduced to six dimensions, the spot can be indexed by six Miller indices, and the phonons and phasons have the symmetry of two three-dimensional irreducible representations.[8]

The melting transition is first order because the order parameter and the Landau expansion are precisely the same as for normal 3D melting,[9] with third-order invariants. In fact, fluctuations would cause the transition to be first order in any case because of the rotational symmetry.[10]

Superficially, it seems that the construction above can be generalized to produce crystalline structure with arbitrary rotational symmetry and only one length scale. This is not the case, however. This is related to the fact that there is only a *finite* number of regular polyhedra, which have already been exhausted here. A seventh-order term can produce only a rodlike structure, or a uniaxial structure with two length scales, since it is not possible to combine regular heptagons to form a "cubic" structure, and so the story ends here.

Then, are we dealing with a fundamentally new "state of matter" as speculated by Levine and Steinhardt[5]? I am afraid not! The structure should be classified simply as an incommensurate structure with one length scale.[11] For simplicity, consider the two-dimensional "quintuple-**q**" case, and define arbitrarily two of the vectors to define a basic lattice. Because of the different directions of the three remaining vectors, they cannot be measured in terms of rational fractions of the first two vectors, and they are thus incommensurate. Thus, in higher than one dimension, it is perfectly possible to have incommensurate vectors with the same length. To reduce confusion one might use the term "incommensurate" to describe all spatially incommensurable structures and leave the term quasiperiodic to describe systems with temporally incommensurable periods.

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

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

[3]See, for instance, M. Gardner, Sci. Am. **236**, No. 1, 110 (1977).

[4]S. Alexander and J. P. McTague, Phys. Lett. **41**, 102 (1978).

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

[6]J. D. Axe and P. Bak, Phys. Rev. B **26**, 4963 (1982).

[7]A. Janner and T. Janssen, Phys. Rev. B **15**, 643 (1977).

[8]D. Nelson (private communication) has pointed out to me that a structure formed by six corner vectors gives a better fit to the diffraction pattern in the twofold plane. The resulting 6D space group differs from the 6D space group discussed here only in not containing "improper" translations in 6D space. In a way the two structures correspond to sc and bcc structures, respectively. The Landau theory for the two structures is essentially the same. The full symmetries will be described in detail in a forthcoming publication.

[9]P. Bak, in *Modern Theory of Crystal Growth,* edited by A. A. Chernov and H. Müller Krumbhaar (Springer-Verlag, Berlin, 1982), p. 23.

[10]S. A. Brazovsky, Zh. Eksp. Teor. Fiz. **68**, 42 (1975) [Sov. Phys. JETP **41**, 85 (1975)].

[11]For another example of a physical system described by a five-dimensional space group, see the analysis by P. Bak and T. Janssen, Phys. Rev. B **17**, 436 (1978), on the low-temperature phase of TTF-TCNQ. In that case, the five wave vectors have three different lengths.