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Symmetry, stability, and elastic properties of icosahedral incommensurate crystals

Per Bak
Department of Physics, Brookhaven National Laboratory, Upton, New York 11973

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The symmetry and stability of icosahedral incommensurate structures and generalized two-dimensional Penrose pentagonal structures are studied. The crystallographic properties of Penrose lattices are described by five-dimensional (5D) super space groups, and the icosahedral structures are described by 6D space groups, with or without improper translations. The density in real space is given as the density along a three-dimensional plane in this 6D space. The fivefold symmetry of the diffraction spectrum of Mn-Al alloys, which is inconsistent with three-dimensional translational invariance, reflects a fivefold rotation axis of the 6D space group. The six continuous degrees of freedom associated with the 6D space represent the usual three orthogonal rigid displacements of the crystal, plus three phase shifts associated with internal rearrangements, leading to three acoustic-phonon modes and three phason modes. There are two independent elastic constants, which is fewer than in any regular crystal, representing one-dimensional and five-dimensional irreducible strains, respectively. If the phase degrees of freedom are included, there are five generalized elastic constants. The stability of icosahedral structures and "lyotropic" Penrose structures can be understood from a phenomenological Landau theory. The ideal icosahedral crystal has perfect positional order, which is stable with respect to thermal fluctuations at low temperatures. The melting transition is first order.

I. INTRODUCTION

In an exciting experiment on a manganese-aluminum alloy, Shechtman *et al.* observed a diffraction spectrum with fivefold symmetry, inconsistent with the usual lattice translations for periodic crystals.[1] The apparent point-group symmetry is icosahedral. The diffraction spots do not form a regular periodic pattern, and they cannot be indexed to any Bravais lattice.

How can this be possible? The diffraction spectrum mostly resembles the spectrum of structurally or compositionally incommensurate crystals,[2] where the diffraction spots can also not be indexed in the usual way by three Miller indices *hkl*. In incommensurate crystals the spectrum is generally characterized by linear combinations of two sets of vectors $\mathbf{q}$ and $\mathbf{g}$, where $\mathbf{q}$ represents a basic lattice and $\mathbf{g}$ represents the modulation vector, so more than three indices are usually needed to specify all reflections. The most obvious difference is that the spectrum of the icosahedral crystals does not separate into that of a basic three-dimensional (3D) lattice plus that of the additional modulation, so a characterization of the crystal symmetry can not possibly start with that of a real lattice.

The purpose of this paper is twofold, namely first to develop a systematic description of the symmetry of crystals with icosahedral diffraction patterns, and next to present a phenomenological theory of the stability of such structures. The crystallographic description is purely mathematical and does not rely on any specific picture of the underlying physical mechanisms. It should be viewed as an extension of the usual characterization of crystals in terms of space groups.

Usually, a space-group-symmetry operation consists of a three-dimensional translation $\boldsymbol{\tau}$ combined with a three-dimensional rotation or reflection R. The three basis vectors $\boldsymbol{\tau}_1$, $\boldsymbol{\tau}_2$, and $\boldsymbol{\tau}_3$ define a Bravais lattice, and the rotational operations R define the so-called point group. The existence of a Bravais lattice reduces the number of possible point groups. For instance, the point group cannot include fivefold rotations as found in the Mn-Al spectrum.[1] It will be shown that the symmetry of icosahedral structures can also be described by space-group operations consisting of translations combined with rotations. The translations, however, are in six-dimensional space, and the point group describes generalized six-dimensional rotations and reflections. All 6D space-group operations describe actual symmetry operations in the real 3D crystal. The diffraction spots can be labeled by six Miller indices $(n_1,\ldots,n_6)$, and the pattern is spanned by six linearly independent reciprocal-lattice vectors $\mathbf{q}_1,\ldots,\mathbf{q}_6$. The actual atomic or electronic densities can be thought of as superpositions of six density waves with wave vectors $\mathbf{q}_i$, and higher harmonics. Only one length scale is involved since $|q_1|=|q_2|=\cdots=|q_6|$. In this sense the structure is different from the usual incommensurate structures which involve at least two independent lengths. The 6D space group may or may not include "improper" translations corresponding to half-integer fractions of the basic lattice vectors, in analogy with the situation for simple-cubic (sc) and body-centered-cubic (bcc) structures. Comparison with experiments indicates that the actual 6D space group of the Mn-Al alloy is the sc (or rather "si") version with no improper translations.

Once the crystal symmetries are known, the resulting space groups provide a framework in which to discuss various physical properties which depend on the symmetry, such as elastic properties, lattice vibrations, and electronic structure. For instance, all translations in 6D space leave the energy invariant, and this defines six continuous symmetries in the real 3D systems. Three of these symmetries can be identified as rigid displacements of the crystals (as for regular 3D crystals). The three remaining symmetries describe internal rearrangements of the crystal. Those symmetries are very similar to the phase translations in incommensurate systems. The two types of continuous symmetries transform as two different representations of the six-dimensional point group. Since there are six continuous symmetries there exist six hydrodynamic acoustic vibrational modes which could be gapless as their wave vectors approach zero. Three of these modes are the usual acoustic phonon modes, and the remaining three modes can be described as phasons. There is some mixing between the modes. In principle, all these modes can be observed in an inelastic neutron-diffraction experiment, but the phason modes might well be overdamped or pinned either by impurities or by strong incommensurate coupling.

The elastic properties of the icosahedral crystals are particularly simple. There are only two independent elastic constants, in contrast to normal crystals, which have at least three independent constants. If the elastic strains of the phase displacements are included, there is a total of five generalized elastic constants which enter the dynamical matrix for the phonon and phason excitations.

In addition to the three-dimensional icosahedral case, a slightly simpler two-dimensional crystal will be discussed. The two-dimensional structure is formed by superposition of five density waves with wave vectors $\mathbf{q}_1, \ldots, \mathbf{q}_5$ forming a regular pentagon. The resulting crystal has a fivefold rotational symmetry, but no discrete translational invariance. We call this crystal a generalized "Penrose" structure after Penrose,[3] who constructed explicit space-filling "tilings" with the same symmetry. The Penrose structures are characterized by a five-dimensional space group, and the mysterious fivefold local symmetry of the Penrose lattices reflects the existence of a fivefold rotational axis in 5D space. To my knowledge, the underlying 5D space-group symmetry of the Penrose lattices has not been revealed before. Although no physical systems with Penrose symmetry have been discovered so far, such structures could, in principle, exist in the form of layers of atoms or molecules absorbed on isotropic substrates or as three-dimensional rodlike liquid crystals. The icosahedral crystals cannot in general be formed by tilings so they are not "quasicrystals" in the sense defined by Levine and Steinhardt.[10]

A discussion of the stability of icosahedral structures must involve some elements of the underlying physics in contrast to the purely mathematical crystallographic description. Ideally, one would like to explain the structure from first-principles calculations taking into account the actual electronic properties of the constituent atoms. Such a calculation of crystal stability is hardly possible for regular metal crystals and is thus well beyond the state of the art for incommensurate crystals today. Hence, any understanding of the stability must be phenomenological. Landau's theory of phase transitions[4] constitutes a useful framework in which to discuss the stability of ordered structures which can arise by condensation of a liquid phase with full translational and rotational symmetry. The analysis follows the philosophy of Alexander and McTague,[5] who used the Landau theory to discuss stability of bcc crystal phases and, in fact, predicted the existence of icosahedral crystals. Landau theory allows for the existence and complete stability of systems with Penrose symmetry, and icosahedral crystals. The icosahedral ordering is described as a multi-$\mathbf{q}$ structure formed by superposition of compositional density waves. Depending on the actual phenomenological expansion coefficients entering the theory the resulting structure could be either a 15-$\mathbf{q}$ structure corresponding to a 6D space group with improper translations (6D bci structure), or a 6-$\mathbf{q}$ structure corresponding to a 6D space group with integer translations only. Nelson[6] has pointed out that the experiments on Mn-Al alloys are indicative of the latter situation rather than the 15-$\mathbf{q}$ structure suggested in a short version of the present paper.[7] In any case, it is predicted that the melting transition of icosahedral structures is first order and thus involves a latent heat.

The paper is organized as follows. First, in Sec. II the stability of icosahedral and Penrose structures is discussed in terms of Landau theory. While the relevance of Landau theory with respect to the nature of the melting transition can be argued, the theory at least allows us to define the symmetry of the systems that we are dealing with. Section III contains the general crystallographic description of icosahedral structures. This section also includes the discussion of the elastic properties and hydrodynamic modes of icosahedral structures and Penrose lattices. The reader who is interested in the crystallographic description may proceed to Sec. III, which contains the most important results of this paper.

II. STABILITY OF ICOSAHEDRAL STRUCTURES AND PENROSE LATTICES

Consider a two- or three-dimensional liquid with full translational and rotational symmetry. Which are the possible ordered structures that the liquid may condense into at low temperatures? According to the theory of Landau and Lifshitz,[4] the condensed phase is described by a symmetry-breaking order parameter which transforms as an irreducible representation of the symmetry group of the liquid phase. Because of the translational symmetry, the irreducible representations are labeled by the wave vector $\mathbf{q}$, and the density of the ordered, low-temperature phase can be written

$$\rho(\mathbf{r})=\rho_0+\sum_{\mathbf{q}}\rho_{\mathbf{q}}\exp(i\mathbf{q}\cdot\mathbf{r})+\text{c.c.} \quad (2.1)$$

The complex constants $\rho_{\mathbf{q}}$, labeled by the wave vector $\mathbf{q}$, are the order parameters of the phase transition. To determine which structures may actually become stable, the free-energy density of the system is expanded in terms of the possible order parameters $\rho_{\mathbf{q}}$. Because of the rotational symmetry, the free energy depends only on the magnitude $|q|$ and not on the direction. The expansion of the free energy in terms of order parameters corresponding to wave vectors of a single length takes the form (with $\rho_i \equiv \rho_{q_i}$)

$$F=\sum_{|q_i|=q}\left[r_q\rho_i\rho_{-i}+u_q(\rho_i\rho_{-i})^2+w\rho_i\rho_{-i}\rho_j\rho_{-j}+v_3\rho_i\rho_j\rho_k\delta(\mathbf{q}_i+\mathbf{q}_j+\mathbf{q}_k)\right.$$
$$\left.+v_5\rho_i\rho_j\rho_k\rho_l\rho_m\delta(\mathbf{q}_i+\cdots+\mathbf{q}_m)+\text{c.c.}+\cdots\right], \tag{2.2}$$

where we have explicitly included higher-order terms with wave vectors adding up to zero. Depending on the coefficients shown in (2.2) (and coefficients not shown) a variety of structures may become stable.[8] To map out precisely which structures are stable for what combination of coefficients would be a formidable task and of little interest, since the coefficients are phenomenological anyhow and cannot be calculated from microscopic theory. For instance, a single density wave $\rho=A\exp(i\mathbf{q}\cdot\mathbf{r})$ describes a smectic liquid crystal [see Fig. 1(a)]. The translational invariance is broken in one direction only. A structure composed by superposition of three waves with wave vectors forming an equilateral triangle [Fig. 1(b)] can take advantage of the third-order term v_3. The role of this term is to lock the three waves together. In two dimensions, the resulting "triple-$\mathbf{q}$" structure represents a two-dimensional triangular (or honeycomb) crystal absorbed on a smooth substrate.[9] In three dimensions it represents a lyotropic rodlike structure where the translational symmetry is broken in two directions but with liquid translational symmetry in the third direction.

However, it has been pointed out by Alexander and McTague[5] that the free energy can often be lowered further by combining six vectors forming a tetrahedron, or six pairs of vectors $\pm\mathbf{q}_i$ forming an octahedron. The latter structure represents a three-dimensional body-centered-cubic structure. In order to prepare for the subsequent discussion on the more complicated icosahedral case, we now review the bcc case in some detail. The density can be written

$$\rho_{\text{bcc}}(\mathbf{r})=\sum_{\text{octahedron}}\frac{\rho}{\sqrt{6}}\cos(\mathbf{q}_i\cdot\mathbf{r}+\theta_i)+\cdots, \tag{2.3}$$

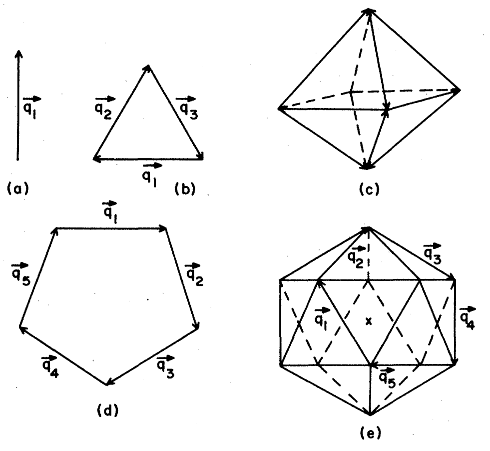

FIG. 1. Wave-vector combinations representing (a) smectic structure, (b) rodlike triangular structures or triangular atomic monolayers, (c) bcc structures, (d) 2D Penrose structures or 3D rodlike lyotropic structures, and (e) icosahedral incommensurate structures.

where the sum includes one term from each pair of vectors and the ellipsis represents higher harmonics. The octahedron has four pairs of triangular faces, each of which gives a contribution to the free energy, so one expects, in general, the bcc structure to have lower free energy than the rodlike lyotropic structure. Other terms in the expansion may change this picture. Not all six pairs of vectors $\mathbf{q}_i\sim(1,1,0)$ are linearly independent; they can all be formed by linear combinations of the three vectors (1,0,0), so ρ_{bcc} can be reduced to a 3-$\mathbf{q}$ structure, with higher harmonics. Inserting (2.3) into (2.2) the third-order term takes the form

$$F_3=-\sum_{4\text{ triangles}}\frac{v_3}{6\sqrt{6}}\rho^3\cos(\theta_i+\theta_j+\theta_k). \tag{2.4}$$

The free energy can be minimized by choosing $\theta_i+\theta_j+\theta_k=2\pi p$, p being an integer. Only three of the four constraints are linearly independent, so there are only three degrees of freedom leaving the free-energy density invariant. They represent rigid translations of the crystal in three orthogonal directions. If we denote the three translations ϕ_1, ϕ_2, and ϕ_3, the relations between the ϕ's and the θ's are $\theta_1=\phi_1+\phi_2$, $\theta_2=-\phi_2+\phi_3$, $\theta_3=-\phi_1-\phi_3$, etc. It will be seen that F_3 is independent of the ϕ's. The structure (2.3) is invariant under the translations $\theta_i\rightarrow\theta_i+2\pi p_i$, p_i an integer. These translations define a Bravais lattice in the 6D θ space, so the symmetry of the bcc crystal can be described by a 6D space group, consisting of the 6D translations combined with certain permutation operations of θ_i defining the point group. Alternatively, of course, the translational symmetry can be expressed in the ϕ space. However, the 3D space group now includes improper translations $\phi_i\rightarrow\phi_i+\Delta\phi_i$ with $\Delta\phi_i\neq2\pi p_i$; for instance, $\phi_1\rightarrow\phi_1+\pi$, $\phi_2\rightarrow\phi_2+\pi$, $\phi_3\rightarrow\phi_3+\pi$ leaves the structure invariant as it indeed should for a bcc crystal.

The fifth-order term favors a two-dimensional structure composed of five density waves with wave vectors forming a regular pentagon [Fig. 1(d)]. Writing $\rho_i=(1/2\sqrt{5})\rho\exp(i\theta_i)$, $i=1,\ldots,5$, the density becomes

$$\rho(\mathbf{r})=\sum_{i=1}^{5}\frac{\rho}{\sqrt{5}}\cos(\mathbf{q}_i\cdot\mathbf{r}+\theta_i), \tag{2.5}$$

and the fifth-order term of the free energy takes the form

$$F_5=\frac{v_5}{25\sqrt{5}}\rho^5\cos(\theta_1+\theta_2+\theta_3+\theta_4+\theta_5). \tag{2.6}$$

The operation $\theta_i\rightarrow\theta_i+2\pi p_i$ leaves ρ invariant. However, in contrast to the situation for the triangular 2D case and the three-dimensional bcc case these operations cannot be represented by ($d=2$)-dimensional translations. This is related to the fact that the five vectors $\mathbf{q}_i$ can not be formed as linear combinations of two vectors spanning a regular reciprocal lattice. Four of the vectors are linearly independent. In general, higher-order terms such as

$$\rho' \cos[(\mathbf{q}_i+\mathbf{q}_{i+1})\cdot\mathbf{r}],\quad \rho''\cos[(\mathbf{q}_i+\mathbf{q}_{i+2})\cdot\mathbf{r}]$$

will be generated by higher-order terms in the Landau expansion. The resulting $\rho(\mathbf{r})$ (for $\theta_i=0$) has fivefold symmetry, but does not form a regular space-filling Bravais lattice. We shall denote such structures generalized Penrose structures[3] after Penrose, who first constructed explicit tilings with fivefold symmetry. The structure formed by associating a δ-function atom with the vertices of the Penrose tiles corresponds to a particular choice of higher harmonics. The general structures can not be formed as tilings. For $\theta_i=0$ the structure has actually tenfold symmetry since $\theta_i \rightarrow \theta_i+\pi$ leaves it invariant. Figure 2 is an attempt to visualize the symmetry of the structure (2.5). The straight lines represent maxima of the individual density waves, so at the center $\mathbf{r}=0$ the density is maximized since all the waves have maxima at this point. For $\theta_i=\pi/2$,

$$\rho(\mathbf{r})=\sum_i \frac{\rho}{\sqrt{5}}\sin(\mathbf{q}_i\cdot\mathbf{r}) ,$$

the structure has fivefold symmetry, as do the original Penrose tilings.[3] In principle, such structures may condense from two-dimensional liquids absorbed on substrates, but none has been observed so far. Note that the lattice has perfect long-range order, since the order parameter $\rho_i=(\rho/\sqrt{5})\exp(i\theta_i)$ is uniform throughout the sample. There is long-range order in the most rigorous meaning of the term, so there is no reason to think of the structure as being glasslike, or in any way intermediate between liquids and crystals, or as having "bond orientational order" (BOO) only. There is both positional and orientational ordering and the diffraction spectrum consists of δ-function Bragg peaks.

In three dimensions the fifth-order term in combination with the third-order term favors more complicated structures composed of waves with wave vectors forming regular icosahedra or dodecahedra [Fig. 1(e)]. The stability and symmetry of these structures is the subject of the present paper. An icosahedron has twenty regular triangular faces, twelve corners, and thirty edges [Fig. 1(e)]. The 15 pairs of edge vectors $\pm\mathbf{q}_i$ define a structure

$$\rho_{\mathrm{ic}}(\mathbf{r})=\sum_i \frac{\rho}{\sqrt{15}}\cos(\mathbf{q}_i\cdot\mathbf{r}_i+\theta_i) , \tag{2.7}$$

and the phase-locking third- and fifth-order terms become

$$F_3=\frac{\rho^3 v_3}{15\sqrt{15}}\sum_{10\ \text{triangles}}\cos(\theta_i+\theta_j+\theta_k) ,$$
$$F_5=\frac{\rho^5 v_5}{225\sqrt{15}}\sum_{6\ \text{pentagons}}\cos(\theta_i+\theta_j+\theta_k+\theta_l+\theta_m) . \tag{2.8}$$

The latter terms arise because it is possible to combine sets of five vectors to form regular planar pentagons, for instance, the vectors $\mathbf{q}_1,\ldots,\mathbf{q}_5$ in Fig. 1(e). Assuming no conflict between the signs of v_3 and v_5, both F_3 and F_5 are minimized by $\theta_i=0$, or $\theta_i=\pi$, and the resulting free energy becomes

$$(F_3+F_5)_{\min}=-\frac{2\rho^3 v_3}{75\sqrt{15}}-\frac{2\rho^5 v_5}{3\sqrt{15}} , \tag{2.9}$$

which, for small enough v_3/v_5, can become favorable compared with both the energy of the bcc structure,

$$F_3^{\mathrm{bcc}}=-\frac{2\rho^3 v_3}{3\sqrt{6}} ,$$

and the energy of the Penrose structure, which in three dimensions is a rodlike lyotropic structure. Of course, it is possible to add up five of the icosahedral vectors to zero without forming a regular pentagon. Three of the five vectors may form a triangle and the two remaining vectors may be simply $\pm\mathbf{q}_i$, where $\mathbf{q}_i$ is any icosahedral edge vector. Such terms (which will have a different coefficient) may further favor the icosahedral structure.

The minimization of (2.8) leads to nine linearly independent constraints of the phases θ_i, so there are six degrees of freedom leaving the free-energy invariant (compared with three for the bcc structure and four for the Penrose structures). This is related to the fact that each edge vector $\mathbf{q}_i$ can be formed as a sum of two vectors τ_α and τ_β along the directions of the two corners which are connected with the particular edge vector, $\mathbf{q}_i=\tau_\alpha+\tau_\beta$, and the density waves $\rho_i(\mathbf{r})$ can be written as density waves with wave vectors in the six corner directions,

$$\rho_i(\mathbf{r})=\frac{\rho}{\sqrt{15}}\exp[i(\mathbf{q}_i\cdot\mathbf{r}+\theta_i)]$$
$$=\frac{\rho}{\sqrt{15}}\exp\{i[(\tau_\alpha+\tau_\beta)\cdot\mathbf{r}+\phi_\alpha+\phi_\beta]\} . \tag{2.10}$$

The 15 phases θ_i can be related to the six ϕ's: $\theta_1=\phi_1+\phi_2$, etc., in perfect analogy with the situation discussed above for the bcc crystals. The structure (2.7) is invariant under the translations $\theta_i\rightarrow 2\pi p_i$, p_i an integer, and also under the translations $\phi_\alpha\rightarrow\phi_\alpha+2\pi p_\alpha$. The free energy is independent of the phases ϕ_α.

In the Landau expansion, higher-order terms like $\rho_{q_1+q_2}\rho_{-q_1}\rho_{-q_2}$ induce higher harmonics of the density

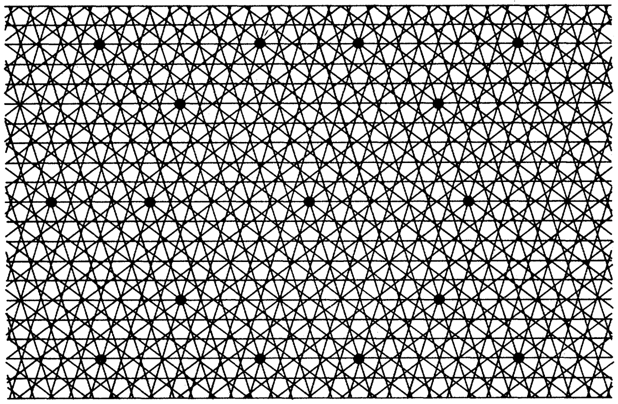

FIG. 2. Generalized Penrose structure represented by a superposition of five waves with wave vectors forming a regular pentagon. The straight lines indicate the maxima of the individual waves. The dots indicate positions with high density which could represent actual atoms.

waves, with wave vectors $\mathbf{q}=n_1\mathbf{q}_1+n_2\mathbf{q}_2$, etc. These harmonics do not change the symmetry of the original structures. The symmetries can always be discussed in terms of the phases of the basic waves since the phases of the higher harmonics are coupled to the basic phases through the higher-order terms. To model the actual atomic or electronic density which is observed in an electron or x-ray experiment the higher-order terms are essential. The relative intensity of higher-order diffraction spots depend on the actual content of higher harmonics and cannot be predicted from the symmetry considerations above. A full-scale electronic calculation must be performed, and this is beyond not only the scope of this paper, but also well beyond what is possible today. One would not expect the intensity pattern of the spectrum to be self-similar, as suggested by Steinhardt and Levine from their study of an artificial model with icosahedral symmetry.[10] There is also no reason to expect the structure factor to decompose into the product of three one-dimensional factors as suggested by the same authors. There is no reason either that the structure should be composed of identical "building blocks" since this occurs only for very selective choices of harmonics. The appropriate "building blocks" are, in fact, the density waves.

The diffraction spectrum of Mn-Al alloys measured by Shechtman *et al.*[1] has precisely the icosahedral symmetry of the structure (2.7). The spots in the threefold and fivefold planes can all be indexed in terms of the 15 vectors $\mathbf{q}_i$ (Fig. 3). For instance, considering the fivefold plane spanned by the vectors $\mathbf{q}_1,\ldots,\mathbf{q}_5$ defined in Fig. 1(e), the point A can be written as $\mathbf{q}=\mathbf{q}_1$, the point B as $\mathbf{q}_1+\mathbf{q}_2$, and the point C as $\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_4$. Note that the length of the vector C is related to the length of the basic vectors by the golden-mean ratio $G=(\sqrt{5}-1)/2$. The golden mean thus enters in a purely geometrical way and there is only one basic length $|q|$ involved.

However, there is a problem in understanding the spectrum in the twofold plane. In fact, as was pointed out by D. Nelson,[6] there appear to be spots at the positions τ_α of the corner vectors. It seems more natural to choose the corner vectors as the basic vectors. The two structures give the same spots in the threefold and sixfold planes since these planes do not include corner vectors τ_α. Hence the structure can be written simply

$$\rho'_{\text{ic}}(\mathbf{r})=\sum_{\alpha=1}^{6}\frac{\rho'}{2\sqrt{6}}\exp[i(\tau_\alpha\cdot\mathbf{r}+\phi_\alpha)]\ . \qquad (2.11)$$

In the next section we shall see that the 15-$\mathbf{q}$ icosahedral edge structure and the 6-$\mathbf{q}$ icosahedral corner structure are related to each other in the same way as the sc and bcc structures are related in three dimensions.

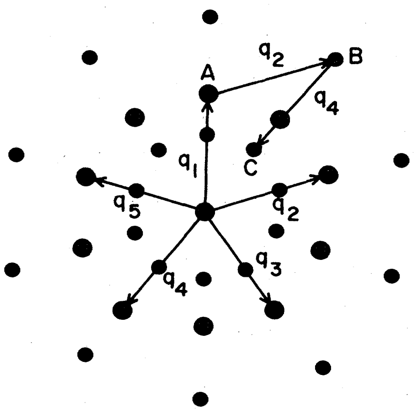

FIG. 3. Diffraction pattern of the Penrose structure, or in the fivefold plane of the icosahedral structures. The spots can be indexed by five "Miller indices" $(n_1,\ldots,n_5)$. The point A is (10000), point B (11000), and point C (11010).

How can the stability of the corner structure be understood from the Landau expansion? It is not possible to combine a subset of the six τ vectors to form closed polygons since they are linearly independent. However, it is possible first to combine the vectors pairwise to form the 15 edge vectors $\mathbf{q}_i=\tau_{\alpha_i}+\tau_{\beta_i}$, and then combine sets of three or five $\mathbf{q}$ vectors to form triangles and pentagons as before. Hence, defining order parameters ρ_α describing complex amplitudes of the six waves, the third-order term takes the form

$$F_3=-v_3(\rho_{\alpha_1}\rho_{\beta_1})(\rho_{\alpha_2}\rho_{\beta_2})(\rho_{\alpha_3}\rho_{\beta_3})\delta(q_1+q_2+q_3)+\text{c.c.}\ , \qquad (2.12)$$
$$F_5=-v_5(\rho_{\alpha_1}\rho_{\beta_1})\cdots(\rho_{\alpha_5}\rho_{\beta_5})\delta(q_1+\cdots+q_5)+\text{c.c.}\ .$$

The third-order terms in (2.2) become sixth-order terms when expressed in terms of the corner vectors, and the fifth-order terms become tenth-order terms in ρ_α. Apart from this, the discussion on the relative stability of the various structures remains the same. It may seem artificial that terms of high orders such as six and ten play a role in stabilizing the structure. However, these are the lowest-order terms in the primary order parameter which lock the directions and the phases of the waves onto each other. The importance of including the higher harmonics was pointed out first by Kalugin *et al.*[11]

The discussion in this section is purely phenomenological, and cannot be used to predict the existence of icosahedral structures in any given material. However, the Landau theory allowed us to show that the icosahedral structures may, in principle, be stable, and that they appear as a natural extension of liquid-crystal structures and regular solids, such as sc or bcc crystals. The "ideal" icosahedral structure has perfect long-range order (although the icosahedral symmetry is only local) and there is no intrinsic reason to consider them glasslike. In fact, we shall see that they are stable with respect to thermally induced excitations at low temperatures. The melting transition of icosahedral structures is first order since the order parameter is the same as for regular crystals, and the Landau expansion includes third-order terms. Most important, the Landau theory provides a language in which to define and describe the symmetries involved. In the next section a crystallographic description of the icosahedral structures in terms of the symmetries as defined by the Landau theory will be given. Of course, a crystallographic description is purely mathematical and not "theory dependent," i.e., it remains valid whether or not the Landau theory actually describes the melting and solidification transitions of icosahedral crystals.

III. SYMMETRY OF GENERALIZED PENROSE STRUCTURES AND ICOSAHEDRAL INCOMMENSURATE CRYSTALS

How does one describe the symmetry of Penrose structures and icosahedral incommensurate structures such as the one found in Mn-Al alloys by Shechtman *et al.*[1]? Usually, the symmetry of crystals in two or three dimensions are described by the so-called space groups whose operations $\{\tau \mid R\}$ consist of lattice translations τ combined with generalized rotations and reflections R. The group of rotations and reflections R, which leave at least one point of the lattice invariant, is called the point group. The lattice translations can be written

$$\tau = n_1\tau_1 + n_2\tau_2 + n_3\tau_3 ,$$

where n_1, n_2, and n_3 are integers and τ_i are linearly independent basis vectors.

The formulation of Penrose structures and icosahedral structures in terms of density waves (which arises naturally from the Landau expansion) is particularly suitable for discussing the symmetry operations which leave the crystal invariant.

Consider first the generalized Penrose structures

$$\rho(\mathbf{r}) = \sum_{i=1}^{5} \frac{\rho}{\sqrt{5}} \cos(\mathbf{q}_i \cdot \mathbf{r} + \theta_i) + \cdots , \tag{3.1}$$

where $\mathbf{q}_i$ are five vectors forming a regular pentagon and the ellipsis denotes higher harmonics. In general, the density $\rho(\mathbf{r})$ in the ground state, including all possible higher harmonics, can be written

$$\rho(\mathbf{r}) = \rho_0(\mathbf{q}_1 \cdot \mathbf{r}, \mathbf{q}_2 \cdot \mathbf{r}, \mathbf{q}_3 \cdot \mathbf{r}, \mathbf{q}_4 \cdot \mathbf{r}, \mathbf{q}_5 \cdot \mathbf{r}) , \tag{3.2}$$

where $\rho_0(\theta_1,\theta_2,\theta_3,\theta_4,\theta_5)$ equals

$$\rho_0(\theta_1 + 2\pi p_1, \theta_2 + 2\pi p_2, \theta_3 + 2\pi p_3 , \theta_4 + 2\pi p_4, \theta_5 + 2\pi p_5) ,$$

where p_i are integers. Hence the two-dimensional density $\rho(\mathbf{r})$ is invariant under discrete translations in the 5D space spanned by $\theta_1, \ldots, \theta_5$. The actual 2D structure is the density along the 2D plane in 5D space defined by (3.2). Any symmetry operation in the 5D space represents, obviously, a symmetry operation in the real 2D structure. The symmetry operations (3.2) define a five-dimensional Bravais lattice, so the Penrose structures in two dimensions have a hidden five-dimensional supersymmetry. The density $\rho(\mathbf{r})$ may have further symmetries represented by permutations of the arguments of ρ_0 constituting point-group rotational and superreflection symmetry in 5D space. The point-group symmetries depend upon the values of the θ's in the ground state. Consider first the state with $\theta_i = \pi/2$:

$$\rho_0(\mathbf{q}_i \cdot \mathbf{r}) = \sum_{i=1}^{5} \frac{\rho}{\sqrt{5}} \sin(\mathbf{q}_i \cdot \mathbf{r}) . \tag{3.3}$$

In this case there is an additional permutation symmetry,

$$\rho_0(\theta_1,\theta_2,\theta_3,\theta_4,\theta_5) = \rho_0(\theta_2,\theta_3,\theta_4,\theta_5,\theta_1) .$$

This symmetry operation is a fivefold rotation axis in the 5D θ space. Hence, while a fivefold axis is inconsistent with three-dimensional translational symmetry, it is certainly consistent with the five-dimensional translational symmetry. The peculiar local fivefold symmetry of the Penrose lattices thus reflects the existence of a fivefold rotation axis in the underlying 5D space. In addition to the fivefold axis c_5, the 5D point group includes superspace reflections

$$\theta_1 \leftrightarrow \theta_1, \quad \theta_2 \leftrightarrow \theta_5, \quad \theta_3 \leftrightarrow \theta_4 . \tag{3.4}$$

The operation (3.4) is a reflection in the 3D hyperplane $\theta_2 = \theta_5, \theta_3 = \theta_4$.

To summarize, the symmetry of (3.2) can be described by a 5D space group composed of a 5D Bravais lattice of translations combined with a point group of generalized rotations. The character table of the point group P can easily be written using standard group theory (see Table I). The point group has ten elements in four classes.

If, instead of $\theta_i = \pi/2$ the ground state is given by $\theta_i = 0$ (or $\theta_i = \pi$), the point group would also include 5D inversion symmetry $\theta_i \leftrightarrow -\theta_i$, and the resulting group $P \times I$ consists of 20 elements, namely the original ten elements plus the same elements combined with the inversion. The group P is isomorphous with the group C_{5v}. Figure 2 shows the structure corresponding to $\theta_i = 0$, where the crystal actually has local tenfold symmetry.

In addition to the discrete symmetries which leave the structure invariant there are continuous operations which leave the energy invariant. These operations correspond to rigid translations of regular crystals in two or three dimensions. Not all translations in 5D space leave the energy invariant since the energy depends on $\sum_i \theta_i$. Let us consider the representation Δ of the group consisting of displacements $\delta\theta_i$ of the five phases. Clearly, Δ is a 5D representation since the five translations transform among themselves when subjected to the symmetry operations. The representation Δ can be decomposed into irreducible representations of P:

$$\Delta = \Gamma_1 + \Gamma_2 + \Gamma_{2'} . \tag{3.5}$$

The combination

$$\delta\theta_1 + \delta\theta_2 + \delta\theta_3 + \delta\theta_4 + \delta\theta_5$$

transforms as the identity representation Γ_1. This dis-

TABLE I. Character table of point group P obtained using standard group theory. E is the identity operation, G is the golden mean, and the Γ's denote four irreducible representations. The representations Δ, $\Gamma_2 \times \Gamma_{2'}$, and $\Gamma_2 \times \Gamma_2$ are explained in the text.

P	E	$2C_5$	$2C_5^2$	$5m$
Γ_1	1	1	1	1
Γ_1'	1	1	1	-1
Γ_2	2	G	$-1-G$	0
Γ_2'	2	$-1-G$	G	0
Δ	5	0	0	1
$\Gamma_2 \times \Gamma_2$	4	G^2	$(1+G)^2$	0
$\Gamma_2 \times \Gamma_{2'}$	4	-1	-1	0

placement does not leave the energy invariant. The two combinations

$$u_x=\sum_i(\mathbf{q}_i\cdot\hat{\mathbf{e}}_x)\delta\theta_i\ ,$$
$$u_y=\sum_i(\mathbf{q}_i\cdot\hat{\mathbf{e}}_y)\delta\theta_i\ , \tag{3.6}$$

where $\hat{\mathbf{e}}_x$ and $\hat{\mathbf{e}}_y$ are unit vectors in two orthogonal directions, transform as Γ_2. Here, u_x and u_y describe uniform translations in the x and y directions, respectively, and, of course, they leave the energy invariant. The combinations

$$\alpha_x=\sum_i\cos[2\gamma(\mathbf{q}_i,\mathbf{e}_x)]\delta\theta_i\ ,$$
$$\alpha_y=\sum_i\cos[2\gamma(\mathbf{q}_i,\mathbf{e}_y)]\delta\theta_i\ , \tag{3.7}$$

where $\gamma(\mathbf{q}_i,\mathbf{e}_\alpha)$ is the angle between the vectors $\mathbf{q}_i$ and $\mathbf{e}_\alpha$, transform as $\Gamma_{2'}$. The displacements α_x and α_y describe certain internal rearrangements of the 5-$\mathbf{q}$ structure which leave the energy invariant. The continuous symmetries associated with α_x and α_y are very similar to the phase-translation symmetries in incommensurate systems.[12] The α displacements are fundamentally different from the optical degrees of freedom in multiatom crystals which have a potential energy associated with them.

Thus, there are four continuous symmetries, namely two rigid-translation symmetries and two phase-displacement symmetries. This is related to the fact that four of the five vectors are linearly independent, whereas the fifth vector is the sum of the four others. Hence, one could, in principle, describe all symmetries in terms of four of the five phases and reduce the dimension of the space group by one. However, this would obscure the fivefold symmetry. A similar situation occurs in conventional crystallographics. A crystal with hexagonal symmetry is usually described in terms of three basis vectors in the basal plane plus a vector in the axial direction. The use of a redundant vector in the basal plane makes the threefold symmetry explicit.

Diffraction spots occur at angles corresponding to wave vectors

$$n_1\mathbf{q}_1+n_2\mathbf{q}_2+n_3\mathbf{q}_3+n_4\mathbf{q}_4+n_5\mathbf{q}_5\ ,$$

and they are thus given by a set of five Miller indices $(n_1n_2n_3n_4n_5)$. Again because of the redundancy there is not a one-to-one correspondence between the Miller index and the diffraction spot. Figure 3 shows the positions of the spots (10000), (11000), and (11010). The latter spot could alternatively be labeled as $(00\bar{1}0\bar{1})$.

The four continuous symmetries allow for the existence of four hydrodynamic long-wavelength modes, each breaking one of the four symmetries:

$$u_x(\mathbf{r})=u_{0x}\exp[i(\mathbf{q}\cdot\mathbf{r}-\omega t)]\ ,$$
$$u_x(\mathbf{r})=u_{0y}\exp[i(\mathbf{q}\cdot\mathbf{r}-\omega t)]\ ,$$
$$\alpha_x(\mathbf{r})=\alpha_{0x}\exp[i(\mathbf{q}\cdot\mathbf{r}-\omega t)]\ ,$$
$$\alpha_y(\mathbf{r})=\alpha_{0y}\exp[i(\mathbf{q}\cdot\mathbf{r}-\omega t)]\ . \tag{3.8}$$

The dispersion relations $\omega(\mathbf{q})$ and the normal modes which are generally linear combinations of the four modes can be found from the appropriate 4×4 dynamical matrix. To set up the dynamical matrix one must construct the elastic potential energy which is bilinear in the strains $u_{ij}=\partial_{u_i}/\partial_j$ and $\alpha_{ij}=\partial\alpha_i/\partial_j$. The strains u_{ij} transform as the representation $\Gamma_2\times\Gamma_2$ and the strains α_{ij} transform as $\Gamma_2\times\Gamma_{2'}$, since the vector ∂_x,∂_y transforms as Γ_2, and u_i and α_i transform as Γ_2 and $\Gamma_{2'}$, respectively. To find the number of second-order invariants, one decomposes these representations in irreducible representations of P:

$$\Gamma_2\times\Gamma_2=\Gamma_1+\Gamma_1'+\Gamma_{2'}\ ,$$
$$\Gamma_2\times\Gamma_{2'}=\Gamma_2+\Gamma_{2'}\ . \tag{3.9}$$

The Γ_1 strain is $u_{xx}+u_{yy}$ and the two-dimensional $\Gamma_{2'}$ strain is $(u_{xx}-u_{yy},\frac{1}{2}(u_{xy}+u_{yx}))$. The Γ_1' strain is $u_{xy}-u_{yx}$, which has no elastic energy associated with it since it is not symmetric. There are thus two elastic constants, namely the usual Lamé coefficients associated with the u strains. Similarly, there are two elastic constants associated with the Γ_2 and $\Gamma_{2'}$ representations, respectively, for the α strains. Finally, since both representations in (3.9) contain $\Gamma_{2'}$, there is a term which mixes the two strains. Hence, there are altogether five independent elastic coefficients, c_1^u, c_2^u, c_1^α, c_2^α, and $c^{u\alpha}$. If the dynamical matrix is constructed,[12] the term $c^{u\alpha}$ will mix the phonon modes with the phason modes, as is usually the case for incommensurate systems.

Now, let us extend these ideas to the icosahedral crystals. First, consider the situation with 15 density waves with wave vectors forming the edges of the icosahedron:

$$\rho(\mathbf{r})=\sum_{i=1}^{15}\frac{\rho}{\sqrt{15}}\cos(\mathbf{q}_i\cdot\mathbf{r}+\theta_i)\ . \tag{3.10}$$

Of course, $\rho(\mathbf{r})$ can be written in terms of the 15 arguments $\mathbf{q}_i\cdot\mathbf{r}$, and since it is periodic in each of the arguments the structure could be described by a 15D space group. However, not all vectors are linearly independent. All the edge vectors can be written as sums of two corner vectors $\tau_{i\alpha}$ and $\tau_{i\beta}$, so $\rho(\mathbf{r})$ can be written

$$\begin{aligned}\rho(\mathbf{r})&=\sum_{i=1}^{15}\frac{\rho}{\sqrt{15}}\cos[(\tau_{i\alpha}+\tau_{i\beta})\cdot\mathbf{r}+\theta_i]+\cdots\\&=\rho_0(\tau_1\cdot\mathbf{r},\tau_2\cdot\mathbf{r},\tau_3\cdot\mathbf{r},\tau_4\cdot\mathbf{r},\tau_5\cdot\mathbf{r},\tau_6\cdot\mathbf{r})\\&=\rho_0(\phi_1,\phi_2,\phi_3,\phi_4,\phi_5,\phi_6)\ .\end{aligned} \tag{3.11}$$

The function ρ_0 is invariant under the six-dimensional translation operations $\phi_i\rightarrow\phi_i+2\pi p_i$. These translations define a 6D Bravais lattice

$$(\phi_1,\ldots,\phi_6)=2\pi(n_1,\ldots,n_6)\ .$$

However, since the vectors τ_α occur only in pairs in (3.11), the density is also invariant under the improper translations

$$2\pi(\pm\tfrac{1}{2},\pm\tfrac{1}{2},\pm\tfrac{1}{2},\pm\tfrac{1}{2},\pm\tfrac{1}{2},\pm\tfrac{1}{2})\ .$$

The situation is very similar to that of a bcc crystal in three dimensions, where the density is invariant under the translation $2\pi(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The actual density is the density found along the 3D plane in 6D space defined by (3.11). Because of the translational invariance and the incommensurability of the τ vectors, *all* the information of the 6D lattice is relevant for the 3D structure: The 3D plane includes points of all possible coordinates within the 6D unit cell. Hence, there is a simple one-to-one connection between symmetry operations in 6D space and symmetry operations on the actual 3D crystal.

The space group of the icosahedral crystal consists of the proper and improper translations plus all permutations of $\phi_1, \ldots, \phi_6$ which leave $\rho(\mathbf{r})$ invariant. These operations can be understood as hyper-rotations and reflections in 6D space. In the case $\theta_i = 0$ in (3.10), which is favored by certain combinations of the v_3 and v_5 terms in the Landau expansion, the function $\rho(\mathbf{r})$ is symmetric in its arguments and the point group is, in fact, isomorphous with the icosahedral group although the actual operations cannot be identified with three-dimensional symmetry operations. The character table of the icosahedral permutation group is shown in Table II. The various classes have been labeled with their 3D analogues. The apparent fivefold symmetry of the diffraction spectrum along certain directions is associated with the fivefold rotation axis in 6D space.

The free energy is invariant under all possible translations, discrete or continuous, in 6D space. This is due to the fact that the ϕ's do not appear explicitly in the expression for the free energy when substituted for the θ's. The six translations $\delta\phi_i$ form a six-dimensional representation Δ of the group I, which can be decomposed into irreducible representations of I:

$$\Delta = \Gamma_3 + \Gamma_{3'} \, . \tag{3.12}$$

Hence there are three translational symmetries which transform as the irreducible vector representation Γ_3. These translations represent rigid translations of the crystal in three orthogonal directions. The three modes transforming as $\Gamma_{3'}$ represent some internal rearrangements of the density, or atoms, of the crystal which do not shift the center of gravity. The rigid displacements correspond to shifts of the 6D crystals along the 3D plane defined by (3.11). The remaining phase displacements correspond to displacements of the 6D crystal perpendicular to this plane.

Corresponding to the six continuous symmetries there are six hydrodynamic modes, u_x, u_y, u_z and $\alpha_x, \alpha_y, \alpha_z$. The elastic energy can be constructed by forming the second-order invariants in the symmetrized strains u_{ij}, α_{ij}. Since $\delta_x, \delta_y, \delta_z$ transform as the representation Γ_3, u_{ij} transform as $\Gamma_3 \times \Gamma_3$ and α_{ij} transform as $\Gamma_3 \times \Gamma_{3'}$. One finds

$$\begin{aligned} \Gamma_3 \times \Gamma_3 &= \Gamma_1 + \Gamma_3 + \Gamma_5 \, , \\ \Gamma_3 \times \Gamma_{3'} &= \Gamma_4 + \Gamma_5 \, . \end{aligned} \tag{3.13}$$

It is left as an exercise to the especially dedicated reader to actually work out the combinations of strains transforming as the various representations. Since there is no elastic energy related to the Γ_3 strain (which is a rotation), there are two elastic constants c_1 and c_2 in the u variables, corresponding to the irreducible strains Γ_1 and Γ_5. Hence, the number of elastic constants for icosahedral structures is smaller than for any regular crystal, where there are at least three independent elastic constants. There are also two elastic constants associated with the α degrees of freedom corresponding to the irreducible strains Γ_4 and Γ_5 and there is a term mixing the u strains and the phase strain since both $\Gamma_3 \times \Gamma_3$ and $\Gamma_3 \times \Gamma_{3'}$ contain the Γ_5 representation. Hence, if the dynamical matrix of dimensions 6×6 is computed, there will be terms mixing the phonon and phason modes. For an analogous situation in incommensurate crystals, see the analysis by Axe and Bak.[12] In the mercury chain system $Hg_{3-\delta}AsF_6$ five well-defined gapless modes have actually been observed in accordance with theory.[13] In principle, the number of propagating modes might be reduced to three, because of various pinning mechanisms[2] and effective viscosities associated with the sliding[14] of waves. A strong coupling between the density waves is one such mechanism.

The stability of icosahedral structures with respect to thermal fluctuations can be discussed as for regular crystals.[4] The fact that there are six modes $\omega_\alpha \sim v_\alpha q$ with velocities v_α does not change the usual result, namely that in three dimensions the mean-square displacements $\langle u(\mathbf{r})^2 \rangle$, $\langle \alpha(\mathbf{r})^2 \rangle$, etc., remain finite at low temperature, so long-range order persists. The intensities of the Bragg peaks are reduced by the usual Debye-Waller factor $\exp[-a\langle u(\mathbf{r})^2 \rangle]$. In two dimensions, thermal fluctuations destroy long-range order, and the mean-square displacements diverge for the Penrose lattice. The correlation functions $\langle u(\mathbf{r})u(0) \rangle$ decay with a power proportional to the temperature, and the Bragg peaks acquire a width.

In principle, the phason modes (or internal rearrangement modes) may be overdamped and not propagating, or they may have a gap because of impurities, etc. Also, the phase translations could be intrinsically pinned in analogy with the pinned phasons in incommensurate systems.[2] Symmetry considerations are certainly insufficient to deal with these questions. The phasons might be observable in an inelastic neutron scattering experiment. The fact that the symmetry of icosahedral structures can be represented by 6D crystal symmetries, and the existence of three phason branches was discovered independently by Kalugin *et al.*[11]

The diffraction spectrum can either be described by the

TABLE II. Character table of the icosahedral point group.

I	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$
Γ_1	1	1	1	1	1
Γ_3	3	$1+G$	$-G$	0	-1
$\Gamma_{3'}$	3	$-G$	$1+G$	0	-1
Γ_4	4	-1	-1	1	0
Γ_5	5	0	0	-1	0
Δ	6	1	1	0	-1

fifteen Miller indices corresponding to the appropriate linear combination of the 15 edge vectors, or more efficiently by the six corner vectors. However, since the τ vectors appear only in pairs there will not be spots at all positions $(n_1 n_2 n_3 n_4 n_5 n_6)$. For instance, the (100000) spots will be absent and the (110000) spots present. Inspection of the diffraction pattern measured by Shechtman *et al.* indicates that the (100000) spots are, in fact, present in the twofold plane.[6] This indicates that the actual structure of the Mn-Al alloys is the simpler 6-$\mathbf{q}$ corner structure

$$\rho(\mathbf{r})=\sum_{i=1}^{6}\frac{\rho}{\sqrt{6}}\cos(\tau_i\cdot\mathbf{r}+\phi_i)+\cdots .$$

For the corner structure the translational group contains no improper translation, and the space group is the 6D "sc" icosahedral group and not the 6D "bcc" structure formed by the edge vectors. It may be useful to denote these structures "si" and "bci" structures, respectively.

In conclusion, we have seen that the symmetry of icosahedral structures can be represented by 6D space groups, with or without improper translations, and their stability can be understood from a simple phenomenological Landau theory. The icosahedral structures form natural extensions of liquid crystals and regular crystals with 3D translational symmetry.

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

[4] L. D. Landau and I. E. Lifshitz, *Statistical Physics*, 2nd ed. (Pergamon, New York, 1968), Chap. XIV.

[5] S. Alexander and J. P. McTague, Phys. Rev. Lett. **41**, 702 (1978).

[6] D. R. Nelson (private communication); D. R. Nelson and S. Sachdev, Phys. Rev. B **32**, 689 (1985).

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

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

[9] P. Bak and D. Mukamel, Phys. Rev. B **19**, 1604 (1979); P. Bak, D. Mukamel, J. Villain, and K. Wentowska, Phys. Rev. B **19**, 1610 (1979).

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

[11] P. Kalugin, A. Kitayev, and L. Levitov, Pis'ma Zh. Eksp. Teor. Fiz. **41**, 119 (1985) [JETP Lett. **41**, 145 (1985)].

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

[13] I. U. Heilman, J. D. Axe, J. M. Hastings, G. Shirane, A. J. Heeger, and A. G. MacDiarmid, Phys. Rev. B **20**, 751 (1979).

[14] H. Brand and P. Bak, Phys. Rev. A **27**, 1062 (1983).