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ENTROPICALLY STABILIZED QUASICRYSTALS

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ABSTRACT

Microscopic models of quasicrystals suggest that equilibrium quasicrystal phases are likely to be characterized by a large entropy associated with low energy phason excitations. This entropy can stabilize the quasicrystal phase against competing crystal phases at moderate temperatures. Phason elastic constants which increase with temperature provide a clear signature of entropic stabiization, as does instability of the quasicrystal phase at low temperatures. Recent experiments on the icosahedral phase of $Al_{65}Cu_{23}Fe_{12}$ dramatically support this theory.

1. INTRODUCTION

Theory and experiment appear to be converging towards an understanding of the nature and mechanism of ordering in thermodynamically stable quasicrystalline alloys. It is evident that energetic considerations in certain materials encourage the formation of structures with short range icosahedral order.[1] The puzzle has been to explain the propagation of this order over macroscopic distances when crystal phases are available with similar local order.[2] The answer appears to lie in a near degeneracy of the crystalline and quasicrystalline phases.

In the absence of strong energetic preference for a crystalline structure, the difference in entropy between phases may become important in selecting the equilibrium phase. It turns out that entropy favors quasicrystalline order.[3-6] The idea is that the same

local structures which repeat periodically to form a crystal structure may be combined in many other ways with similar binding energy. The system naturally seeks to maximize entropy by forming a structure with the highest symmetry allowed by the local ordering. In alloys with a preference for local icosahedral symmetry, this means global icosahedral symmetry. Quasiperiodic translational order may also be induced by entropy because the entropy density is maximized by structures with zero phason strain.

Theoretical predictions of this model of entropic stabilization include two effects which are observed experimentally. At low temperatures when energy can dominate the free energy there may be a phase transition, most likely to a nearby crystal phase. At higher temperatures, within the icosahedral phase, the phason elastic constants should increase with temperature.

This paper begins with a description of a theoretical model of quasicrystalline order in two dimensions. The model is a binary alloy of Lennard-Jones atoms which has been shown, through computer simulation,[4,7,8] to possess a quasicrystal phase in thermodynamic equilibrium. We illustrate the near degeneracy of this model and two others, and suggest that near degeneracy may be quite widespread in quasicrystalline materials.

Next we describe the mechanism by which entropy favors quasicrystalline order. Numerical studies by transfer matrix methods[3,6] on a random tiling model indicate that entropy is an analytic function of phason strain (roughly speaking, "phason strain" means deviation from quasiperiodicity) with a maximum at zero. The curvature of entropy density as a function of phason strain determines the phason elastic constant. Monte Carlo simulations[5] demonstrate the applicability of the random tiling model to the original atomic system, and show that the phason elastic constant is proportional to temperature as is expected from its entropic origin.

We then turn to general considerations of elasticity to compute Debye-Waller factors and scattering intensity. Assuming elastic constants for phonons to be independent of temeprature, but elastic constants for phasons to be proportional to temperature, we find a low temperature elastic instability caused by coupling of phonons and

phasons. As a result, the low temperature phase is not quasicrystalline,[8] and in the quasicrystal phase intensities of certain diffraction peaks actually increase with temperature - remarkable facts which have been observed experimentally.[9]

2. COMPUTER SIMULATION

Because of the difficulties of determining structure from diffraction experiments, and the complexity of interactions between metal atoms in three dimensional space, it may be useful to construct artificial models which capture the essence of quasicrystal structure while dispensing with unnecessary complications. Given such a model one may try to extract general properties of the quasicrystal state which are model independent. Since the ultimate goal is to learn about real materials, care must be taken in distinguishing between universal properties and peculiarities of the model. The ultimate test of the theory, of course, comes in comparing predictions with experiment.

It seems reasonable that the existence of icosahedral long range order in metals should be related to the tendency of many metals towards short range icosahedral order. Many amorphous and crystalline alloys are known to possess icosahedral clusters.[1,10] In fact icosahedral order would be favored over FCC or HCP order for atoms interacting through central forces, except for the impossibility[1] of packing icosahedra in R^3. With these observations in mind Widom, Strandburg and Swendsen[4] constructed a model binary alloy (also developed independently by Lancon, Billard and Chaudhari[11]) in two dimensions which would incorporate a preference for five-fold or ten-fold order. The fundamental property of the model is that atoms like to bond with the opposite species, and optimal bond lengths are set to allow packing of 5 large around a small or 10 small around a large. It turns out that several other structures (figure 1) can form also satisfying the optimal nearest neighbor bond lengths. The Lennard-Jones potential was chosen for the interactions.

Monte Carlo simulation reveals that quasicrystalline solid structures (see figure 2a) occur in equilibrium over a range of temperatures. At high temperatures the quasicrystal melts into a liquid. The very low

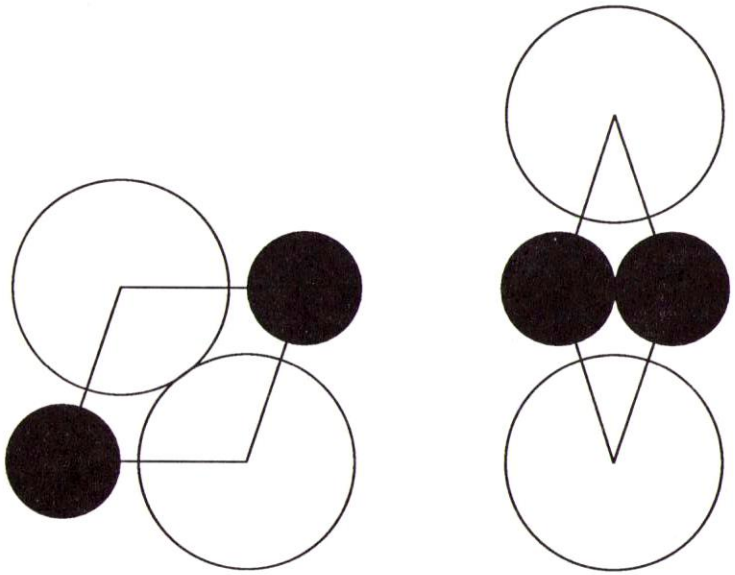

Figure 3. Fat (72°) and thin (36°) rhombi decorated with large and small atoms.

relatively ordered structures may be produced.[7] It appears that rotation of one large and two small atoms play a significant role in achieving order. This is precisely a continuous realization of the "flip".

The atomic rearrangements resulting from flips are short wavelength phasons. Simulations of this model thus suggest that allowing phasons to fluctuate is important in reaching equilibrium, and that the most perfect quasicrystalline order will occur in materials in which such rearrangements take place on short or moderate time scales. The time scale presumably varies dramatically with temperature (say, like e^{Δ/k_BT} where Δ is an activation energy for rotation or vacancy formation) leading to the likelihood that quasicrystal forming materials fall out of equilibrium before reaching their low temperature ground states.

Because the energy change of the flips is so small, atomic rearrangements may provide a significant source of entropy. In fact the entropy per atoms, S, in a related, random tiling model is about

$0.2\ k_B$, dominating any energetic contribution to the free energy down to temperatures about $\Delta E/S \approx 0.05$ or 1/4 of the melting temperature. Above this temperature, but below melting, the equilibrium phase will be determined by the maximization of entropy within the confines of tiling structures. It will be shown in the next section that this entropy favors quasicrystallinity, thereby explaining the occurrence of an equilibrium quasicrystal phase in this model.

But first we must address the question raised at the beginning of this section. What lessons can we take from this simple model and apply to real materials? The importance of relaxing phason strain to reach equilibrium is surely quite general, but is a fairly trivial observation. Perhaps more significant is the observation that phason strain can be relaxed, in contrast to earlier speculations.[12] There is no sign of phason pinning[13] in this model over a wide temperature range.

The most significant finding is probably the importance of entropy in stabilizing the quasicrystal phase.[4] Initial theoretical models of quasicrystals[14] involved special "matching rules" which force a particular nonperiodic structure, and charge energy for any local violation of these rules such as a phason excitation. The perfect quasicrystal is the ground state of such a system. Although there is little doubt (but a finite amount, see Anderson[15]) that atomic systems which force such rules can exist in principal, no specific atomic system has ever been shown to obey such rules. The entropic mechanism for quasicrystal stabilization is thus a more natural explanation than invoking quasiperiodic ground states.

Intellectual satisfaction is insufficient grounds for accepting the model. We must show that other models share a near degeneracy associated with phason excitations, and that the model makes predictions which are uniquely in agreement with experiment. Comparison with experiment is discussed in the final section of this paper. Now we briefly discuss other models.

Another 2-D binary alloy, similar in spirit to that shown in figure 1 is the 12-fold quasicrystal system of Leung, Henley and Chester.[16] This system achieves 12-fold symmetry by combining the 3-fold symmetry of equilateral triangles with the 4-fold symmetry of

squares (figure 4). The locally preferred structures (squares and equilateral triangles) can tile the plane to infinity. Again, there

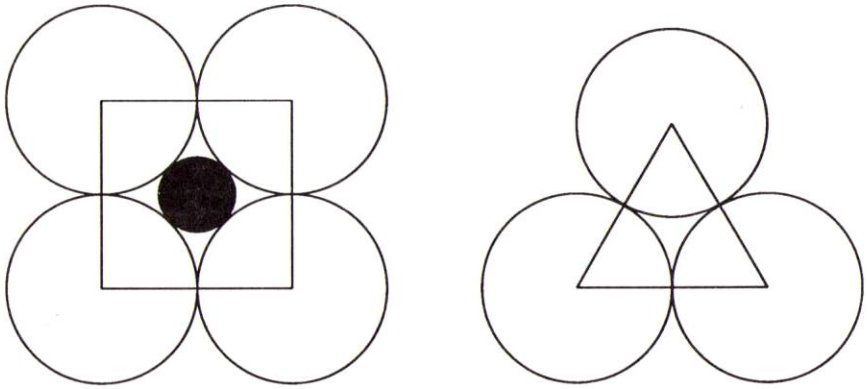

Figure 4. Large and small atoms form squares and equilateral triangles.

is a finite entropy[17] associated with the tiling and the entropy is thought to be responsible for stability of the quasicrystal phase.[16]

Unfortunately there is no 3-D atomic model which has been shown to have a quasicrystal phase. There are many proposals for decorating rhombahedra[18] and other shapes[19] with atoms in manners that can then be used to tile space with quasicrystalline order. What is lacking is a prescription for the atomic interactions which lead to stable quasicrystalline structures. None of the models of which this author is aware impose Penrose-like matching rules. Figure 5 shows a typical model. Clearly the tiles can be put together in many ways at essentially identical energy providing the dominant interactions are with nearest neighbors and angle independent.

In summary, modeling quasicrystals on a microscopic level with plausible atomic interactions suggests that quasicrystals can occur as stable phases over a finite temperature range. The stability appears

to be related to a near degeneracy associated with phason fluctuations which create an entropy not present in competing crystal phases.

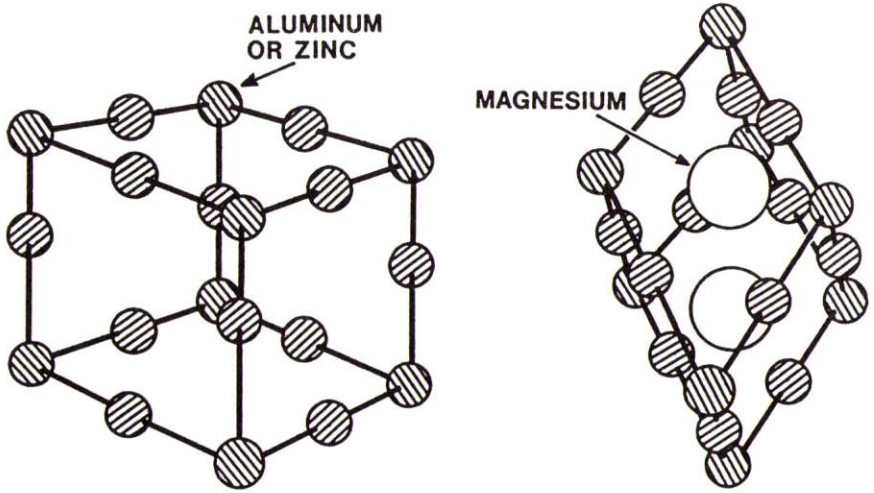

Figure 5. Decoration of prolate (a) and oblate (b) rhombahedra with three types of atoms (vertex, edge and diagonal).

3. ENTROPICALLY INDUCED ORDER

It seems paradoxical at first that entropy, a measure of a systems randomness, could be responsible for creating long range order. There is precedent: many antiferromagnetic spin systems select their ground state on the basis of entropy. Crystallization in hard disk or hard sphere systems at high pressure is another, especially appropriate example. Entropy in hard sphere systems is maximized when each atom has the maximum amount of room to vibrate. The atomic volumes are largest, in an average sense, when the atoms take on a crystalline structure. Much the same effect occurs in quasicrystals. Phason fluctuations provide a source of entropy.[4] Yet the entropy available is largest when the average phason strain vanishes over large distances.[3,6]

Elser and Henley first proposed entropy as a mechanism for achieving quasicrystalline order. They began with the assumption that

entropy is an annalytic function of phason strain (not a trivial assumption - in matching rule systems energy is nonanalytic in phason strain). Then by noting that quasicrystals possess great symmetry they proposed that the first nonconstant in the taylor expansion of entropy density as a function of phason strain should be quadratic, with negative curvature.

$$\sigma(\underset{\sim}{E}) = \sigma_0 - \frac{1}{2}K|\vec{\nabla}\vec{v}|^2 + \ldots \qquad (1)$$

where $\vec{v}$ is the phason variable and $\vec{\nabla}\vec{v}$ is the phason strain.

This formula is similar to the dependence of energy on phonon strain ($\vec{\nabla}\vec{u}$). On the basis of (1) one concludes[3] there will be fluctuations in the phason variable $\vec{v}$ analogous to vibrations in the phason variable $\vec{u}$. Two-point $\vec{v}$ correlation functions will be bounded in three dimensions, but grow logarithmically in two dimensions. That is, true long range order will be present in three dimensions, but only quasi-long range order in two dimensions. The diffraction pattern will have Bragg (delta function) peaks in three dimensions but only power law peaks in two dimensions.

Equation (1) must be verified in order to demonstrate the ability of entropy to favor quasicrystalline order. For atomic systems in the continuum with long range interactions, the only way to understand the precise behavior of the system is through computer simulation. Unfortunately, entropy is extremely difficult to obtain through computer simulation. Computer simulation can obtain K if equation (1) is assumed valid by measuring $\vec{v}$ fluctuations.[5]

Widom, Deng and Henley[6] made simple approximations to the model then evaluated the entropy through a transfer matrix calculation. The first step in the approximation is to truncate the potential at nearest neighbors. This allows the interactions to be restricted to atomic layers. Then each bond is set to its optimal length. This has the effect of discretizing the set of atomic configurations. Within the approximations one finds the system has an exact degeneracy within the set of allowed configurations. Each allowed configuration is precisely a tiling of the plane by 36° and 72' rhombi. Thus we call the approximation a "random tiling approximation". The binary alloy

allows not the most general set of tilings, but rather a subset capable of being decorated with 2 species of atoms. Hence our model is a binary random tiling.[7]

For details of the calculation the reader is referred to reference 6. Here we just note that equation (1) is confirmed for the binary random tiling model and values obtained for σ_0 and K. Agreement of the value of K with that obtained by computer simulation[5] lends credence to the approximation. Of course, at low temperatures the approximation of truncating the interactions becomes quite bad. We expect a phase transition out of the quasicrystal phase into low temperature coexisting crystal phases, behavior which cannot be found in a pure random tiling model.

This expectation is based on the prejudice[15] that ground states of simple atomic systems in the continuum are spatially periodic. Of course, there is no proof of this assertion, and quasicrystals provide an opportunity to reexamine the problem. However I now show that entropically stabilized quasicrystals have a low temperature elastic instability, caused by coupling of phonons and phasons, thus the ground state is surely <u>not</u> a quasicrystal. Furthermore, I suggest that this instability actually occurs in real, stable, quasicrystalline materials.

4. ELASTICITY AND DEBYE-WALLER FACTORS

One may write down the general form of elastic free energy without reference to particular models. The idea is to assume the free energy is analytic in both phonon and phason strain, then write down the most general formula consistent with the symmetry of the quasicrystal. In the harmonic approximation, one keeps only terms of second order in strain. Such expansions can be found in the literature[13,20,21] and take the general form

$$F_{elastic} = F_{phonon} + F_{phason} + F_{coupling} \ . \qquad (2)$$

The precise forms of the terms in equation 2 depend on symmetry and spatial dimensionality. First consider C_{5v} symmetry in two dimensions. The free energy density is[13]

$$f_{el} = \frac{1}{2}\lambda(\vec{\nabla}\cdot\vec{u})^2 + \mu u_{ij}u_{ij}, + \frac{1}{2}C_1\nabla_i v_j \nabla_i v_j$$

$$+C_2[\nabla_x v_x \nabla_y v_y - \nabla_x v_y \nabla_y v_x] \quad . \tag{3}$$

$$+C_3[u_{xx}-u_{yy})(\nabla_x v_x + \nabla_y v_y) + 2u_{xy}(\nabla_x v_y - \nabla_y v_x)] \quad .$$

Thermodynamic stability requires f_{el} be positive definite. To determine the conditions for stability we write equation (3) in matrix form

$$f = \frac{1}{2}\vec{w}^T \overleftrightarrow{M} \vec{w} \ , \tag{4}$$

where

$$\vec{w} = \begin{bmatrix} u_{xx} \\ u_{yy} \\ u_{xy} \\ \nabla_x v_x \\ \nabla_x v_y \\ \nabla_y v_x \\ \nabla_y v_y \end{bmatrix} \tag{5}$$

and

$$\overleftrightarrow{M} = \begin{bmatrix} \lambda+2\mu & \lambda & 0 & C_3 & 0 & 0 & C_3 \\ \lambda & \lambda+2\mu & 0 & -C_3 & 0 & 0 & -C_3 \\ 0 & 0 & 4\mu & 0 & 2C_3 & -2C_3 & 0 \\ C_3 & -C_3 & 0 & C_1 & 0 & 0 & C_2 \\ 0 & 0 & 2C_3 & 0 & C_1 & -C_2 & 0 \\ 0 & 0 & -2C_3 & 0 & -C_2 & C_1 & 0 \\ C_3 & -C_3 & 0 & C_2 & 0 & 0 & C_1 \end{bmatrix} \tag{6}$$

$\overleftrightarrow{M}$ is positive definite provided

$$\lambda+\mu > 0, \quad C_1 > C_2, \quad \mu(C_1+C_2) > 2C_3^2 \quad . \tag{7}$$

Now consider the temperature dependencies of the elastic constants. The Lamé constants λ and μ are, of course, temperature independent. Assuming the quasiperiodic order is stabilized by entropy suggests $K_1 \equiv C_1 + C_2$ should be proportional to temperature,

$$K_1 \equiv KT \quad , \tag{8}$$

since entropy enters free energy multiplied by temperature, F = E - TS. Little is known about the behavior of C_3. Let us assume it is nonzero at all temperatures. The third inequality in (7) reveals the quasicrystal is unstable to a simultaneous phonon and phason strain at a temperature

$$T_1 = 2C_3^2/\mu K \quad . \tag{9}$$

The quasicrystal phase is the high temperature phase.

It is also of interest to consider the intensities of diffraction peaks as functions of temperature. In two dimensions the peaks are power-law peaks rather than delta functions. That is, the intensities for a peak with wave vector $\vec{G}$ grow with size R as

$$I_{\vec{G}} \sim R^{4-\eta_{\vec{G}}} \ . \tag{10}$$

The coefficient $\eta_{\vec{G}}$ is defined by

$$\eta_{\vec{G}} \log R = \langle[(\vec{G}_\parallel,\vec{G}_\perp)\cdot(\vec{u},\vec{v})]^2\rangle = \frac{G_\parallel^2}{2}\langle|\vec{u}|^2\rangle + \frac{G_\perp^2}{2}\langle|\vec{v}|^2\rangle \ . \tag{11}$$

Thus η measures the phonon and phason fluctuations. To calculate the fluctuations we rewrite (3) in matrix notation and Fourier transform

$$F = \frac{1}{2}\int\frac{d^2\vec{q}}{(2\pi)^2}\vec{w}^T(-\vec{q})\ \overleftrightarrow{C}(\vec{q})\ \vec{w}(\vec{q}) \tag{12}$$

where

$$\vec{w} = \begin{bmatrix} u_x \\ u_y \\ v_x \\ v_y \end{bmatrix} \tag{13}$$

and

note the inequality $T_1 < T_2$ where T_2 is the temperature of the first order phase transition out of the quasicrystal phase.

In summary, the dependence of phason elastic constant on temperature predicted by the mechanism of entropic stabilization leads to a temperature T_o below which peak intensities vanish. For $T > T_o$ peaks with large $G_\perp$ should increase monotonically in intensity from zero as long as the harmonic approximation remains valid. Peaks with large $G_\parallel$ should first increase, then decrease as ordinary phonon Debye-Waller behavior is regained. The behavior for $T_o < T < T_1$ cannot be observed in equilibrium because of an elastic instability at T_1. The elastic instability itself should be preempted by a first order phase transition at $T_2 > T_1$.

Key predictions of this theory appear to be observed experimentally[9] in studies of the Debye-Waller factor of the icosahedral phase in $Al_{65}Cu_{23}Fe_{12}$. In particular, peaks with large $G_\perp$ show a rapid increase in intensity with temperature followed by a levelling off at high temperatures. There is no obvious anomaly in peaks with large $G_\parallel$. I conjecture that this behavior is due to the effects of diverging fluctuations at T_o.

5. Conclusion

This paper reviews key ideas of the theory of entropically stabilized quasicrystals. Several points have been made: (1) realistic microscopic models of quasicrystalline order achieve thermodynamic stability as a result of entropy associated with phason excitations; (2) The ground state of such a system will most likely consist of crystalline structures; (3) The phason elastic constant should depend roughly linearly on temperature; (4) The temperature dependence of phason elastic constants leads to a low temperature elastic instability driven by phonon-phason coupling; (5) Several experiments on AlCuFe alloys support key elements of this theory.

Let us turn now to summarize the results of experiments. What is most clearly shown by experiment is that the quasicrystal phase is a high temperature phase. There is some indication that the dominant low temperature phase is a complex Rhombahedral crystal structure, most likely an approximant to the quasicrystal.[8] It will be of great

interest to study disorder within the crystal structure. For sufficiently close approximants to the quasicrystal phase there should be vestiges of phason excitations corresponding to disorder within the unit cells.

The dramatic dependence of scattering peak intensity on temperature[9] offers a challenge for theorists to explain. This paper presents one possible explanation based on an elastic instability. Experimental tests of this proposal should be possible by searching for soft modes. Traditional elasticity measurements may suffice, but it must be remembered that it is the phason modes which most dramatically display the instability. Inspecting the formulae for diffuse scattering derived by Jaric and Nelson,[20] it seems that study of diffuse scattering lineshapes offers a means of rather directly measuring eigenvalues of the hydrodynamic matrix $\overleftrightarrow{C}(\vec{q})$. Given the eigenvalues one can determine whether the peak intensity variations result from the elastic instability described here. Prior knowledge of λ and μ from, say, sound speed experiments would help in extracting phason elastic constants and coupling from the eigenvalues. Given values of the elastic constants one can check for linear behavior of phason elastic constants within the icosahedral phase.

In conclusion, the mechanism for stability of the quasicrystal phase appears to be primarily entropic. Evidence for this comes both from theoretical models and experiment. The entropic stabilization theory makes both quantitative and qualitative predictions some of which have been experimentally confirmed and others which can be tested.

Acknowledgment

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