Random-Tiling Quasicrystal in Three Dimensions

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A three-dimensional random-tiling icosahedral quasicrystal is studied by a Monte Carlo simulation. The hypothesis of long-range positional order in the system is confirmed through analysis of the finite-size scaling behavior of phason fluctuations and Fourier peak intensities. By investigating the diffuse scattering we determine the phason stiffness constants. A finite-size scaling form for the Fourier intensity near an icosahedral reciprocal wave vector is proposed.

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Recently, a new series of stable icosahedral quasicrystal alloys (AlCuFe, AlCuRu, etc.) has been discovered and studied in scattering experiments.[1-4] They were shown to possess very sharp peaks comparable to those of a crystalline material and exhibit no detectable peak shifts from icosahedrally symmetric positions.[2,3] Curiously, in an x-ray-diffraction study of single grains of *i*-AlCuFe, Bancel reported a loss of scattering intensity at a number of quasicrystal peaks as the sample was cooled down from 700 to 600 °C in a reversible manner.[4] This interesting observation leads one to speculate that formation of a quasicrystal phase in these materials is not solely energetic in origin. A plausible interpretation of Bancel's finding was given by Henley and by Widom, who argued that the high-temperature phase is a random-tiling quasicrystal stabilized by entropy. At lower temperatures the energy of the system, which plays a greater role, decreases the icosahedral order and eventually drives the system into a crystalline state.[5]

The random-tiling model was proposed earlier by Elser[6] and by Henley[7] as a geometrical structure of equilibrium quasicrystals. In this scenario, a quasicrystal is viewed as a space-filling tiling where rigid tiles of two or more distinct shapes are assembled in the *absence* of matching rules, and thus differ from an ideal quasiperiodic structure such as the Penrose tiling (PT). As a physical model, it emphasizes the role of configurational entropy, derived from different possibilities for packing the tiles, in stabilizing a quasicrystal of maximal symmetry,[7,8] rather than invoking the perhaps more delicate and demanding energy balance (e.g., matching rules) to force a quasiperiodic ground state.[9] Despite the large degree of local disorder in such a system, transfer-matrix[9] and Monte Carlo simulation[10] studies have confirmed the hypothesis of quasi-long-range positional order in the analogous two-dimensional (2D) random rhombus tilings. In this respect random tilings differ from the nonequilibrium icosahedral glass model,[11,12] for which only scattering peaks of nonvanishing width are expected.

In this Letter a set of finite-size scaling forms based on a linear phason elasticity theory of three-dimensional (3D) quasicrystals[13] is proposed. By numerically verifying them in a Monte Carlo simulation of a random-tiling icosahedral quasicrystal we confirm the hypothesis of *Bragg* diffraction peaks in such a system.[7] A phason Debye-Waller factor is determined. Furthermore, we present detailed studies of diffuse scattering in the random-tiling model, from which two phasons stiffness constants $K_1 \simeq 96$ and $K_2 \simeq 59$ are determined. Our data are in good agreement with a theory of diffuse scattering for icosahedral quasicrystals proposed by Jarić and Nelson.[14] A comparison of the Fourier intensity along a twofold axis in the random tiling and ideal 3D PT (approximate) of 10 336 tiles is shown in Fig. 1.

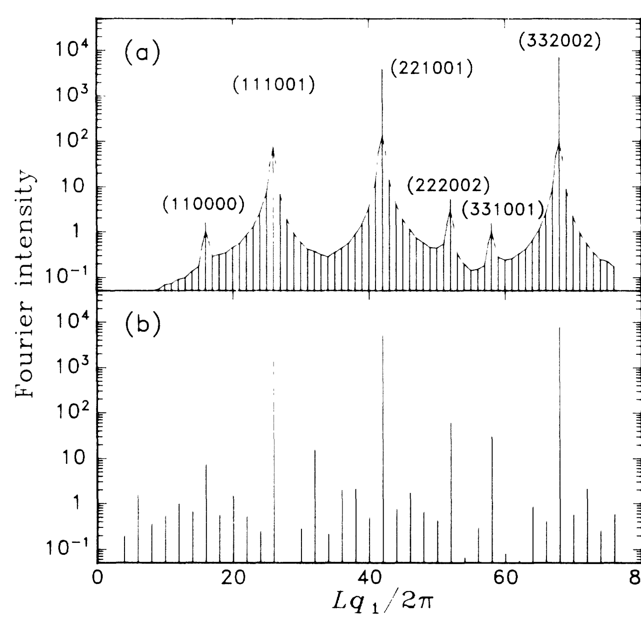

FIG. 1. Fourier intensity of (a) random and (b) (approximant) zero-temperature ideal 3D Penrose tiling of 10 336 tiles, measured at integer values of $Lq_1/2\pi$ from 1 to 76 along a twofold axis. A diffuse line shape conforming to (8) is sketched in (a). Peaks are indexed as in Ref. 18 throughout the paper.

Consider a space-filling tiling by prolate and oblate rhombohedra, each formed by a triplet of icosahedral vertex vectors of unit length $\hat{\mathbf{e}}_\alpha^{\parallel}$ (the same set of tiles occur in the 3D PT). The position of an arbitrary vertex in such a tiling is given by $\mathbf{r}=\sum_{\alpha=1}^{6} n_\alpha \hat{\mathbf{e}}_\alpha^{\parallel}$, and the integers n_α specify a 6D hypercubic lattice point $\mathbf{R}=\{n_\alpha\}$. The phason variable $\mathbf{h}(\mathbf{r})=\sum_{\alpha=1}^{6} n_\alpha \hat{\mathbf{e}}_\alpha^{\perp}$ gives coordinates of $\mathbf{R}$ in a 3D "perpendicular space" complementary to the space of the tiling. Hence $\hat{\mathbf{e}}_\alpha^{\perp}$ is a complementary set of icosahedral vertex vectors of unit length.[15]

Using the phason variable $\mathbf{h}(\mathbf{r})$, the structure factor at a wave vector $\mathbf{q}=\mathbf{Q}^{\parallel}+\mathbf{k}$ can be expressed as

$$S_N(\mathbf{q})\equiv\sum_{\mathbf{r}}\exp(i\mathbf{q}\cdot\mathbf{r})=\sum_{\mathbf{r}}\exp[-i\mathbf{Q}^{\perp}\cdot\mathbf{h}(\mathbf{r})+i\mathbf{k}\cdot\mathbf{r}]\,, \quad (1)$$

where $\mathbf{Q}^{\parallel}=\pi\sum m_\alpha \hat{\mathbf{e}}_\alpha^{\parallel}$ and $\mathbf{Q}^{\perp}=\pi\sum m_\alpha \hat{\mathbf{e}}_\alpha^{\perp}$ are complementary components of a 6D reciprocal-lattice vector, with m_α being integers. The sum in (1) is over all N vertices of the tiling. The *Fourier intensity*

$$I_N(\mathbf{q})\equiv\langle|S_N(\mathbf{q})|^2/N\rangle \quad (2)$$

has Bragg peaks at $\mathbf{q}=\mathbf{Q}^{\parallel}$ as $N\to\infty$ if the mean-square width of phason fluctuation

$$w_N^2\equiv\left\langle\frac{1}{N}\sum_{\mathbf{r}}\left[\mathbf{h}(\mathbf{r})-\frac{1}{N}\sum_{\mathbf{r}'}\mathbf{h}(\mathbf{r}')\right]^2\right\rangle \quad (3)$$

and higher-order moments remain properly bounded in the thermodynamic limit. Angular brackets in (2) and (3) denote proper ensemble average over phason fluctuations.

For a 3D icosahedral quasicrystal, an elastic phason free energy can be written in terms of

$$\mathbf{h}(\mathbf{p})=\int e^{-i\mathbf{p}\cdot\mathbf{r}}\mathbf{h}(\mathbf{r})d^2r\,,$$

i.e.,

$$F/k_BT=\tfrac{1}{2}\int\mathbf{h}(-\mathbf{p})\mathbf{C}(\mathbf{p})\mathbf{h}(\mathbf{p})(2\pi)^{-3}d^3p\,, \quad (4)$$

where in the component form

$$C_{ij}(\mathbf{p})=K_1|\mathbf{p}|^2\delta_{ij}-K_2[(\tfrac{1}{3}|\mathbf{p}|^2+2p_i^2+\tau^{-1}p_{i+1}^2-\tau p_{i-1}^2)\delta_{ij}-2p_ip_j]\,, \quad (5)$$

and K_1 and K_2 are two phason stiffness constants associated with two independent quadratic invariants of the icosahedral symmetry group, respectively.[13,14] Here $\tau=(\sqrt{5}+1)/2$, δ_{ij} is the Kronecker symbol, and indices in (5) are understood modulo 3. Assuming phason fluctuations are governed by (4), the ensemble averages (2) and (3) can be carried out in Fourier space. For an *infinite* 3D system (3) takes a finite value w_∞^2, while the result for (2) is given in Ref. 14,

$$I(\mathbf{q})\simeq(2\pi)^3\rho\sum_{\mathbf{Q}}\tilde{g}(\mathbf{Q}^{\perp})[\delta(\mathbf{q}-\mathbf{Q}^{\parallel})+\tfrac{1}{2}\mathbf{Q}^{\perp}\mathbf{C}^{-1}(\mathbf{q}-\mathbf{Q}^{\parallel})\mathbf{Q}^{\perp}]\,, \quad (6)$$

where ρ is the number density of tiles and $\tilde{g}(\mathbf{Q}^{\perp})\equiv g(\mathbf{Q}^{\parallel})$ is the normalized Fourier intensity at a peak $\mathbf{Q}^{\parallel}$.

For a finite system of N tiles and linear size L under periodic boundary conditions, there is a lower cutoff at $|\mathbf{p}|=2\pi/L$ for the Fourier-space integration. This leads to a $1/L$ correction to the mean-square width

$$w_N^2\simeq w_\infty^2-a/L\,, \quad (7)$$

where a is a constant related to K_1 and K_2.[16] A finite-size scaling form of (6) can also be derived:

$$I_N(\mathbf{Q}^{\parallel}+\mathbf{k})\simeq(2\pi)^3Ng(\mathbf{Q}^{\parallel})\times[\Phi(L\mathbf{k})+\tfrac{1}{2}L^{-1}\mathbf{Q}^{\perp}\mathbf{M}(L\mathbf{k})\mathbf{Q}^{\perp}]\,, \quad (8)$$

where we have assumed that all but one term in the sum over $\mathbf{Q}$ are negligible at sufficiently small $\mathbf{k}=\mathbf{q}-\mathbf{Q}^{\parallel}$.[17] Comparing (6) with (8), we see that the δ-function term is replaced by

$$L^3\Phi(L\mathbf{k})\equiv(2\pi)^{-3}(k_1k_2k_3)^{-1}\times\sin(Lk_1)\sin(Lk_2)\sin(Lk_3)\,,$$

which grows to a Bragg peak as $L\to\infty$. The matrix $\mathbf{C}^{-1}(\mathbf{k})$ in the diffuse part is replaced by a scaling form $L^2\mathbf{M}(L\mathbf{k})$ which satisfies $\lim_{L\to\infty}L^2\mathbf{M}(L\mathbf{p})=\mathbf{C}^{-1}(\mathbf{p})$. Thus $\mathbf{M}(\mathbf{p})\simeq\mathbf{C}^{-1}(\mathbf{p})$ for $|\mathbf{p}|\gg2\pi$, but it crosses over to a finite value at $\mathbf{p}=0$. In particular, (8) implies a $1/L$ correction to the peak intensity,

$$I_N(\mathbf{Q}^{\parallel})/N\simeq g(\mathbf{Q}^{\parallel})[1+4\pi^3L^{-1}\mathbf{Q}^{\perp}\mathbf{M}(0)\mathbf{Q}^{\perp}]\,. \quad (9)$$

The goal of our simulation is to verify the scaling forms (7)-(9).

We have simulated a series of cubic approximants to the icosahedral quasicrystal tiling under periodic boundary conditions. Each approximant is related to a rational number p/q close to the golden mean τ. Taking the edge length of rhombohedra to be 1, the total number of tiles (or equivalently, vertices) in a cubic box of linear size $L=2(p\tau+q)/\sqrt{\tau+2}$ is $N=4[2p^3+3(p+q)pq]$. The *best* approximants correspond to (p,q) being successive Fibonacci numbers, and have an average phason strain on the order of $N^{-2/3}$.

In the present simulation all tilings are assumed to have the same energy. The basic Monte Carlo move consists of flipping a rhombic dodecahedron formed by two prolate and two oblate rhombohedra. It is possible to show that (i) any tiling allowed by the boundary condition may be reached from a given one through the flips, and (ii) the detailed-balance condition may be fulfilled. In order to study the (Monte Carlo) dynamics of phason relaxation, averages are performed over a number of systems (300–500, except for $N=43\,784$) which evolve stochastically from a given initial configuration (an approximate 3D PT). The relaxation time (in unit of one trial per site) into the steady state is proportional to L^z, with $z\approx2$. Details of the simulation algorithm will be reported elsewhere.

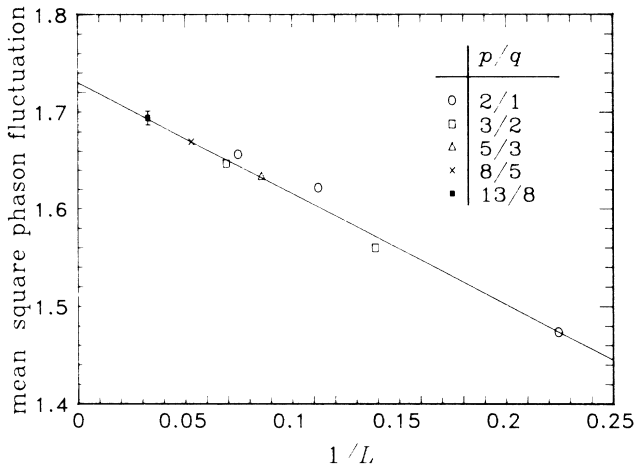

FIG. 2. Mean-square phason fluctuation vs inverse linear size. Error bars on the data are comparable to the size of the plotting symbols. The straight line is a guide to the eye.

Figure 2 shows the equilibrium phason-fluctuation data w_N^2 plotted against inverse size $1/L$. Apart from the $p/q=2/1$ series (open circles), where the effect of the average phason strain appears to be significant, all data lie approximately on a straight line, thus conforming (7). From the $1/L$ scaling we conclude that w_∞^2 for the infinite 3D random tiling in fact saturates to a finite value 1.73 ± 0.01 (as compared to 1.236... for an ideal 3D PT).

The scaled Fourier intensity $I_N(\mathbf{Q}^\parallel)/Ng(\mathbf{Q}^\parallel)$ for a set of best approximants at a number of peaks is depicted in Fig. 3. Points corresponding to the same peak are connected by a straight line. The $1/L$ scaling predicted by (9) seems to be in good agreement with our data. The slight decrease ($1/L$ correction) in intensity and the increase in phason fluctuations seen in Fig. 2 can be qualitatively understood as due to longer-wavelength phasons allowed in larger systems. For each peak, extrapolating the $1/L$ scale (9) to $L\to\infty$ yields a finite intensity $g(\mathbf{Q}^\parallel)$, supporting the existence of Bragg-diffraction peaks in the system. The numerically determined intensities for the infinite system are well represented by $\tilde{g}(\mathbf{Q}^\perp)\simeq\tilde{g}_P(\mathbf{Q}^\perp)\exp(-|\mathbf{Q}^\perp|^2/6)$ for $|\mathbf{Q}^\perp|\le3.4$. Here $\tilde{g}_p(\mathbf{Q}^\perp)$ is the normalized Fourier intensity of the ideal 3D PT.[18]

We now turn to the diffuse scattering in the 10336-tile system. The Fourier intensity shown in Fig. 1(a) is obtained from a scan along a twofold axis q_1 at integer multiples of $2\pi/L$.[19] We note that peaks with a visible diffuse profile have nearly identical diffuse line shape on the semilogarithmic scale, as is expected from (8). Figure 4 is a plot of the scaled diffuse intensity $LI_N(\mathbf{q})/4\pi^3Ng(\mathbf{Q}^\parallel)|\mathbf{Q}^\perp|^2$ along this axis, centered at three peaks, (111001), (221001), and (332002), together with the data for three other system sizes. Contribution from the Φ term in (8) has been removed. A reasonably good agreement between the simulation data and the scaling form (8) is achieved.

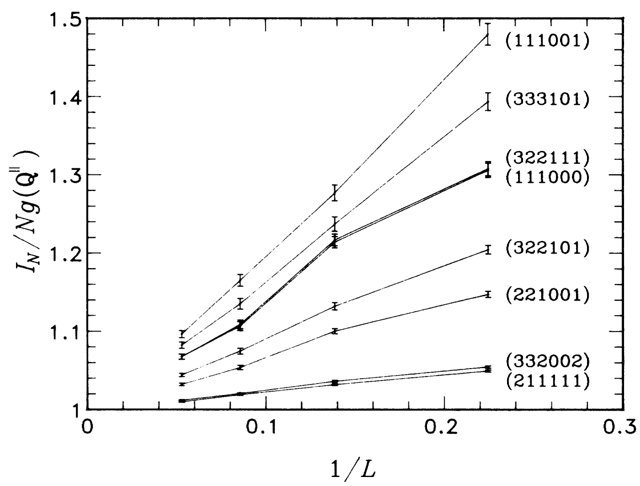

FIG. 3. Scaled peak intensity vs linear size.

Measured diffuse intensity data around four major peaks with a displacement wave vector $\mathbf{k}$ are listed in the top of Table I. Error bars on the data are about 10% of their value. Assuming the asymptotic form $\mathbf{M}=\mathbf{C}^{-1}$ holds already at these spots, we can check (8) and determine the phason stiffness constants. For $\mathbf{k}$ considered here $\mathbf{C}(\mathbf{k})$ is a diagonal matrix. A two-parameter linear least-squares fit is performed using the three data points associated with the peak (221001). This yields $K_1\simeq96$ and $K_2\simeq59$. The bottom of Table I lists a set of computed diffuse intensities using (8) and the above determined values of stiffness constants and peak intensities. We see an agreement of better than 10% for most spots. The two lines in Fig. 4 are computed in the same way.

In conclusion, we have presented a detailed study of phason fluctuations and Fourier intensities in a 3D random-tiling icosahedral quasicrystal. By verifying the

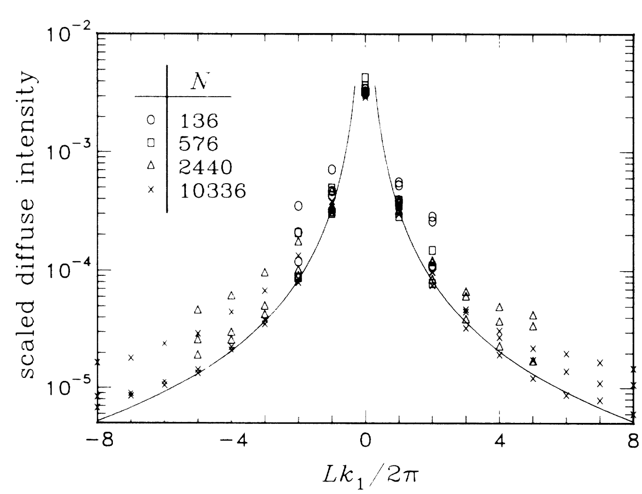

FIG. 4. A scaling plot of diffuse profile along a twofold axis centered at three peaks, (111001), (221001), and (332002). The lines are computed using fitted phason stiffness constants.

TABLE I. Measured ($N=10336$) and computed diffuse scattering data.

$L\mathbf{k}/2\pi$	(221001)	(211111)	(111000)	(322111)
		Measured		
(100)	13.8	14.3	5.5	6.6
(010)	26.2	7.4	10.8	10.0
(00$\bar{1}$)	6.15	6.7	17.9	20.4
		Computed		
(100)	13.8	14.9	5.2	6.3
(010)	26.5	7.6	11.3	9.3
(00$\bar{1}$)	6.14	7.6	17.4	17.4

$1/L$ scaling forms we confirmed the hypothesis of long-range positional order in the system. The diffuse scattering data were found to be in good agreement with a theory of Jarić and Nelson for icosahedral quasicrystals, and allowed us to determine the phason stiffness constants. A finite-size scaling form for the Fourier intensity near an icosahedral reciprocal-lattice vector is proposed.

In a more realistic model for experimental quasicrystals, one needs to consider the local energetics of atomic clusters (which the rigid tiles are supposed to represent) in breaking the perfect degeneracy of all tilings assumed here. In the case when such energetics lead to a quasiperiodic ground state, one expects an increase in quasicrystal peak intensity and a decrease in diffuse scattering as the temperature is lowered. Interestingly, it has been argued that the linear phason elasticity theory, Eq. (4), may not apply to a tiling model with a matching-rule energy at zero and sufficiently low temperatures.[20,21] Thus the low-temperature phase of such a model may exhibit a different dynamical behavior and diffuse scattering pattern than the random-tiling model discussed in this paper.

A perhaps more interesting case is when the local energetics of tiles actually favors a crystalline state. One then expects a first-order transition between a quasicrystal and a crystal phase similar to the facetting transition of a solid surface. It would be interesting to study such a transition in light of recent experiments on the *i*-AlCuFe system.

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[15]Our $\hat{\mathbf{e}}_\alpha^{\parallel}$ and $\hat{\mathbf{e}}_\alpha^{\perp}$ differ from those of Ref. 14 by a factor of $\sqrt{2}$.

[16]In general, one may expect a to depend on the average phason strain which is necessarily present in a finite system under periodic boundary conditions. This dependence is responsible for the nonmonotonic behavior seen in Fig. 2.

[17]Despite a dense set of scattering peaks for a quasicrystal of infinite size, the intensity of the spots sufficiently close to a given peak may be much weaker than the diffuse intensity in a given finite system, as seen in Fig. 1.

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