Formation of phason defects during "geometric" roughening of the surface of a growing quasicrystal

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(Submitted 16 September 1992)
Pis'ma Zh. Eksp. Teor. Fiz. **56**, No. 8, 395–399 (25 October 1992)

The layer-by-layer growth of an icosahedral quasicrystal from the melt is analyzed in a study of the stability of the growing face. At certain degrees of supercooling, seeds of a periodic crystal (with the approximant structure), whose height differs from the thickness of a completed quasicrystal layer, can arise on this growing face. The result may be a "geometric" roughening of the surface, accompanied by the appearance of a phason disorder, as has been observed in diffraction experiments.

The atomic structure of many quasicrystalline alloys[1] is characterized by phason defects, associated with local disruptions of the rules for the stacking of the rhombohedra which are the elementary building blocks.[2] Such defects lead to a characteristic shift of the diffraction peaks from their ideal positions or to a broadening of these peaks,[3] which depends on the orthogonal component of the corresponding wave vectors.[4] Some data indicate that the existence and extent of this disorder are related to characteristics of the method by which the sample is prepared, e.g., the growth rate.[5] It is thus natural to suggest that similar defects might form during the growth of quasicrystals. In this letter we propose and analyze a possible mechanism for the appearance of phason defects on the surface of a growing quasicrystal.

Some unusual features occur in the growth of quasicrystals because of their quasiperiodic atomic structure. It turns out that the formation of a perfect quasicrystal requires infinite–radius correlations on the growing surface; i.e., there must be a deviation from a local nature, and this deviation must be nonremovable.[6] A nonlocal growth of quasicrystals has the result that these entities grow much more slowly than their crystalline analogs.[7] A lower growth rate can be seen clearly in (for example) the growth forms of decagonal phases which are greatly stretched out in the "periodic" direction.[8,9]

Another unusual aspect of the formation of quasicrystal is the thermodynamic smoothness of the quasicrystal–melt interface at any temperature.[10,11] This smoothness is consistent with the polyhedral faceting of grains which has been seen in several experiments.[12,13] The surface smoothness promotes a layer-by-layer growth of the quasicrystals at a sufficiently small degree of supercooling, according to analytic[14] and numerical[15] calculations. In layer-by-layer growth, ordinary crystals grow by virtue of a fluctuation-related formation of 2D seeds on the smooth boundary and the subsequent growth of these seeds to the point that they fill the given layer. The thickness of this layer is equal to the lattice constant.[16] For quasicrystals, in contrast, the height of these seeds and thus the thickness of the layer which is occupied are not fixed; they can take on values from a dense discrete set of "interplanar distances."[14]

In the growth of ordinary crystals, one observes a roughening transition of the growing surface.[17] This transition occurs because the mean square size of the fluctuations in the position of the crystal–melt interface diverges. If this occurs at a zero degree of supercooling, one says that the interface has a thermodynamic roughness corresponding to a vanishing of the free energy of the elementary step. Since the surface of a quasicrystal is smooth at all temperatures, a thermodynamic roughening transition cannot occur on it. There can, on the other hand, be a dynamic roughening, which occurs because the energy of the critical seed is on the order of the thermal fluctuations. In this case the supercooling dependence of the growth rates switches from exponential to linear; this switch has been seen in numerical simulations.[15] At the microscopic level, there is accordingly a massive appearance of critical seeds on the unfilled previous layer; i.e., the rate at which the 2D seeds are nucleated is higher than the rate of their lateral growth.

The kinetics of the layer-by-layer growth of an icosahedral quasicrystal from the melt has been studied previously in a microscopic model[18] based on an orthogonal projection from a 6D space for a description of the atomic structure.[19] Along that approach, the attachment of an elementary rhombohedron from the melt to the quasicrystal is treated as the microscopic growth event. The faces are pictured as macroscopically planar surfaces which pass through the vertices of these rhombohedra and which are normal to the wave vectors of the maxima on the diffraction pattern. It has been shown that the bulk supercooling $\Delta\mu$ in the expression for the energy of a critical seed must be replaced by an "effective" supercooling $\Delta\mu_{\text{eff}}(h)=\Delta\mu-\Delta\sigma(h)/h$, which is determined by the behavior of the difference between the surface energies σ of the base and "roof" of a seed as a function of the seed height, h. This difference arises because of the translational invariance of the atomic structure of the quasicrystal.

A steady-state sequential layer-by-layer growth was studied. In other words, it was assumed (as in the continuum approximation[14]) that seeds can form only on a complete layer. In this case the average height of the 2D seeds corresponds to the highest nucleation probability $\omega\propto\exp(-Ah\Delta\mu_{\text{eff}}^{-1})$ and leads to the highest growth rate at the given degree of supercooling $\Delta\mu$. It was shown that the seed heights which correspond to these conditions are equal to the translation vectors of cubic crystalline approximants $\{h_m\}$:

$$h_{m+1}=\tau h_m=h_m+h_{m-1};\quad h_0=2a_R(3-\tau)^{-1/2};\quad \Delta\sigma(h_m)\propto\tau^{-2m}, \tag{1}$$

where $\tau=(\sqrt{5}+1)/2$ is the golden section, and a_R is an edge of the elementary rhombohedron. As the degree of bulk supercooling decreases, the height of the seeds diverges as $h\propto(\Delta\mu)^{-1/3}$.

During layer-by-layer growth of a quasicrystal, seeds of various heights unavoidably arise. The reason is that once a layer of height h_m has been filled, the critical energy for the nucleation of the next layer is determined by a surface-energy difference $\Delta\sigma$ which is now reckoned from the new position of the boundary (Fig. 1). A shift of the boundary to the position h_{m+1}, which corresponds to a decrease in σ, is then favorable. The seed of the next layer therefore has a different height. A Monte Carlo simulation of the growth, in which an equivalent quasiperiodic pining potential $v(h)$ was used as σ, has shown[20] that a wide discrete spectrum of seed heights occurs during

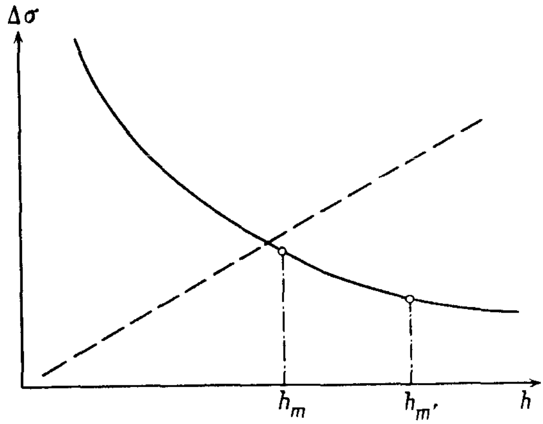

FIG. 1. Selection of the height of the nucleating region during the growth of a quasicrystal. The slope of the straight line is equal to $h \times \Delta\mu$. The only nucleating regions which can grow without bound are the those which correspond to the condition $\Delta\sigma < \Delta\mu h$.

the growth. The average height behaves in accordance with the results of analytic calculations.[14,18] The growth is limited by the formation of seeds of the maximum height; i.e., the growing surface surmounts layers of lower height comparatively rapidly, while it is delayed at sites with low values of σ, at which only seeds of the maximum height can arise and then propagate without restriction over the face.[20] As a result, there are characteristic features in the supercooling dependence of the growth rate.

How does the picture of layer-by-layer growth of a quasicrystal change if we allow the possibility of nucleation on an incomplete layer? Numerical calculations have shown that the probabilities for the appearance of seeds corresponding to the various h_m in the height spectrum differ by several orders of magnitude. Accordingly, even if seeds of all heights, except the greatest, arise at a rate far higher than the layer growth rate (which is proportional to h), a true roughening transition will not occur. The reason is that transverse fluctuations of the position of the quasicrystal–melt interface are limited to the distance between successive positions which require the nucleation of layers on maximum height. In addition, the large differences in the probabilities for the nucleation of quasicrystal layers of different thicknesses prevents a disruption of the smoothness of the growing face by the simultaneous appearance (in the same layer) of seeds of various heights. Consequently, a dynamic roughening transition of the standard type on the smooth surface of a growing quasicrystal[15] requires a bulk supercooling such that the critical energy for the formation of a nucleating region of maximum height is on the order of the thermal fluctuations.

However, a fundamentally different mechanism for the roughening of a growing surface can operate. This other mechanism stems from the possibility of a congruent nucleation of crystalline phases with the cubic-approximant structure. Crystals of this sort form through a periodic stacking of the same elementary rhombohedra which make up a quasicrystal.[8] The height of the seed of such a crystal is the same as the lattice constant of this crystal, h_m. During nucleation on a complete layer of the quasicrystal of the same thickness, no change in the atomic structure of the surface occurs, because of the condition $\Delta\sigma = 0$. The place of $\Delta\mu_{\text{eff}}$ in the nucleation energy is taken by the bulk supercooling of the melt with respect to the crystal, $\Delta\mu_{AP}$, which differs from $\Delta\mu$ by the difference between the specific free energies of the quasicrystal and the approximant. Upon a change in the bulk supercooling, the nucleation energies for a quasicrystal and an approximant with equal periods behave differently, so the type of structure (quasicrystal or crystal) which is forming may change at a certain critical supercooling,[18] found from the condition

$$\Delta\mu_{\text{eff}}(h_m)=\Delta\mu-\frac{\Delta\sigma(h_m)}{h_m}\simeq\Delta\mu_{AP}(h_{m'})=\Delta\mu-\Delta\epsilon_{m'}. \tag{2}$$

Here $\Delta\epsilon_{m'}$ is the difference between the free energies of the quasicrystal and the approximant with a period $h_{m'}$. If the values h_m and $h_{m'}$ corresponding to condition (2) appear in the spectrum of seed heights during the growth of the quasicrystal at the given $\Delta\mu$, seeds of a quasicrystal, of height h_m, and of a crystal, of height $h_{m'}$, may arise simultaneously on a complete layer of thickness $h_{m'}$. After the next atomic layer is completed, some of it may consist of a quasicrystalline structure, while the rest is a crystal. Regions in which there is disruption of the regular quasiperiodic stacking of elementary rhombohedra thus arise; i.e., phason deformations appear in the growing quasicrystal. These regions, which become disconnected from each other, subsequently grow at different rates, thereby giving rise to a roughness of the growing surface. This type of surface roughening might be called "geometric" since it is generated by a change in the nucleation geometry.

It has been observed[18] that, as h_m increases, the relation between the supercoolings $\Delta\mu_{\text{eff}}$ and $\Delta\mu_{AP}$ changes in the quasicrystal direction if it is assumed that the quasicrystal is stabilized as a perfect stacking, while it changes in the crystal direction in the approximation of a random stacking. In the model of a perfect quasicrystal, condition (2) can thus be satisfied for arbitrary heights in the spectrum, with the condition $\Delta\mu_{\text{eff}}(h_{\max})>\Delta\mu_{AP}(h_{\max})$ also holds for the maximum height. In this case, a quasicrystal forms globally, since it is the formation of layers of thickness $h_{\max}$ which determines the quasicrystal growth kinetics. Accordingly, in each of the unconnected regions of the growing boundary, there must necessarily be quasicrystal fragments, which may be separated by crystalline phase. This mechanism of geometric roughening thus leads to the appearance of nonuniform phason deformations in the growing quasicrystal in this case.

In the random-stacking model, condition (2) unavoidably leads to the relation $\Delta\mu_{\text{eff}}(h_{\max})<\delta\mu_{AP}$ for the maximum height $h_{\max}$. The growth kinetics is thus controlled by the formation of the crystalline layers. In this case the growth should result in the formation of a periodic structure with nonuniform phason deformations, consisting of a combination of crystalline fragments with various periods.

The geometric mechanism proposed here for the roughening of the surface of a growing quasicrystal, in a model in which this quasicrystal stabilizes as a perfect stacking, can thus lead to the appearance of the nonuniform phason deformations which are observed in diffraction experiments.

I wish to thank A. V. Artem'ev, V. E. Dmitrienko, and A. A. Chernov for useful discussions of questions touched on in this paper.

[1] D. Shechtman *et al.*, Phys. Rev. Lett. **53**, 1951 (1984).
[2] C. L. Henley, Commun. Cond. Matt. Phys. **13**, 59 (1987).
[3] P. M. Horn, *et al.*, Phys. Rev. Lett. **57**, 1444 (1986).
[4] J. D. Budai, *et al.*, Phys. Rev. Lett. **58**, 2304 (1987).
[5] H. S. Chen *et al.*, Phys. Rev. B **38**, 1654 (1988).
[6] M. V. Jaric and M. Ronchetti, Phys. Rev. Lett. **62**, 1209 (1989).
[7] C. Dong *et al.*, J. Mater. Res. **6**, 2637 (1991).
[8] K. H. Kuo, J. Non-Cryst. Solids **117/118**, 756 (1990).
[9] A. Yamamoto *et al.*, Phys. Rev. Lett. **65**, 1603 (1990).
[10] A. Garg and D. Levine, Phys. Rev. Lett. **59**, 1683 (1987).
[11] R. Lipowsky and C. L. Henley, Phys. Rev. Lett. **60**, 2394 (1988).
[12] B. Dubost *et al.*, Nature **324**, 48 (1986).
[13] A. P. Tsai, A. Inoue, and T. Masumoto, Jpn. J. Appl. Phys. **26**, L1505 (1987).
[14] J. Toner, Phys. Rev. B **43**, 915 (1991).
[15] J. A. Jaszczak, W. F. Saam, and B. Yang, Phys. Rev. B **41**, 6864 (1990).
[16] A. A. Chernov, *Modern Crystallography III*, Springer-Verlag, New York (1984).
[17] P. Nozieres and F. Gallet, J. Phys. (Paris) **48**, 353 (1987).
[18] M. A. Fradkin and A. A. Chernov, Pis'ma Zh. Eksp. Teor. Fiz. **55**, 170 (1992) [JETP Lett. **55**, 162 (1992)].
[19] P. A. Kalugin, A. Yu. Kitaev, and L. S. Levitov, Pis'ma Zh. Eksp. Teor. Fiz. **41**, 119 (1985) [JETP Lett. **41**, 145 (1985)].
[20] A. V. Artem'ev and M. A. Fradkin, Pis'ma Zh. Eksp. Teor. Fiz. **55**, 340 (1992) [JETP Lett. **55**, 343 (1992)].

Translated by D. Parsons