Elastic instability and spontaneous disorder of icosahedral quasicrystals

M. A. Fradkin
I. P. Bardin Central Scientific-Research Institute of Ferrous Metallurgy

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Topological disorder in icosahedral quasicrystals is analyzed from the standpoint that this disorder results from a phase transition consisting of an elastic instability with respect to "phonon" displacements. "Phason" strain is either a conjugate order parameter or an analog of an external field in a corresponding Ginzburg-Landau expansion, depending on the particular conditions of the problem. The model proposed here satisfactorily reproduces the results of diffraction experiments on stable quasicrystals.

Icosahedral quasicrystals[1] have a spontaneous disorder which is manifested as shifts of diffraction peaks from their positions in an ideal Penrose network or a broadening of these peaks.[2] The extent of this disorder is related to the particular procedure used to produce the sample, e.g., the growth rate.[3] This effect is generally interpreted as a consequence of "phason" displacements of the atoms of the quasicrystal, since several experiments on rapidly quenched samples have revealed that the width of the peaks depends on the orthogonal component of their wave vectors.[4]

A different pattern is observed in some recently discovered stable Al–Cu–Fe (Ref. 5) and Al–Cu–Ru (Ref. 6) quasicrystals. The diffraction peaks of samples produced by slow cooling or annealing coincide with the ideal positions, while their width depends either on both the phason and phonon components of the wave vector[7] or on the phonon component alone.[8] The broadening of the peaks is far smaller than in rapidly quenched samples. Bancel[9] has observed a distortion of a quasicrystal of an Al–Cu–Fe alloy below 670 ° C as the result of an instability with respect to atomic displacements.

Jarić and Mohanty[10] have predicted such an instability. They used a method involving an atomic-density functional to calculate the elastic constants of icosahedral quasicrystals. The corresponding diffuse scattering was analyzed in Ref. 11, and the symmetry of the phason displacements was analyzed in Ref. 12. The phason instability, however, is incapable of explaining the dependence of the peak width on the longitudinal wave vector in the Al–Cu–Ru alloy.[8]

In the present letter we propose an alternative approach, along which the shift and broadening of the diffraction peaks are interpreted as resulting from an instability of the quasicrystal with respect to phonon strain. According to this interpretation, the phason shifts arise from the presence of a mixed term in the expansion of the elastic energy of an icosahedral quasicrystal. This mixed term couples the phonon strain components with the phason components.[13] Below T_c, the instability temperature, a spontaneous strain arises in the quasicrystal and leads to a shift of the reflections (in a single-domain sample) or to a splitting of the reflections (in a polydomain sample).

On the diffraction pattern, these changes are seen as a shift and broadening of the peaks.

An instability with respect to phonon shifts was studied on the basis of Landau's theory of continuous phase transitions in Ref. 14. Analysis of a corresponding phase diagram revealed that a spontaneous strain lowers the symmetry from icosahedral to pentagonal or triangular, depending on the relation between the third- and fourth-order elastic constants, through a first-order phase transition.

The phason displacements result from atomic displacements over distances on the order of interatomic distances, so an activation barrier must be surmounted. The component of the elastic energy due to these displacements is therefore determined by the kinetics of the phason relaxation in the region in which we are interested.[15] For convenience we can introduce an effective temperature at which the phasons "freeze," T_f; above this temperature the corresponding degrees of freedom are equilibrium degrees of freedom, while below it they are frozen.[11]

Let us look at the Ginzburg-Landau expansion for this problem. Since the structure of the spontaneous strain below the transition point is fixed by the lowering of the symmetry, the magnitude of the phonon strain, $\eta_{\parallel}$, can be used as a single-component order parameter. The phason terms in this expansion will have different meanings, depending on the relation between T_f and T_c. While the phasons can relax in the critical region, the magnitude of the symmetrized phason strain $\eta_{\perp}$ is a conjugate (or secondary) order parameter:

$$\Delta F = \frac{\alpha}{2}(T - T_c)\eta_{\parallel}^2 + \frac{\beta}{3}\eta_{\parallel}^3 + \frac{\gamma}{4}\eta_{\parallel}^4 + C_{\perp}\eta_{\perp}^2 + C_{int}\eta_{\perp}\eta_{\parallel}. \tag{1}$$

The phonon part of the expansion describes a first-order transition at the temperature

$$T_* = T_c + \frac{2\beta^2}{9\alpha\gamma}. \tag{2}$$

The equilibrium value of $\eta_{\perp}$ is found by minimizing expression (1):

$$\frac{\partial \Delta F}{\partial \eta_{\perp}} = 2C_{\perp}\eta_{\perp} + C_{int}\eta_{\parallel} = 0. \tag{3}$$

The result is

$$\eta_{\perp} = -\frac{C_{int}}{2C_{\perp}}\eta_{\parallel}. \tag{4}$$

Substituting this expression into (1), we find a renormalized one-component expansion,

$$\Delta F = \frac{\alpha'}{2}(T - T_c')\eta_{\parallel}^2 + \frac{\beta}{3}\eta_{\parallel}^3 + \frac{\gamma}{4}\eta_{\parallel}^4, \tag{5}$$

where the new values of the stiffness and the critical temperature are given by

$$\alpha' = \alpha - 2\frac{\partial}{\partial T}|_{T=T_c'}\left(\frac{C_{int}^2}{2C_\perp}\right); \quad T_c' = T_c + \frac{C_{int}^2}{2\alpha C_\perp}. \tag{6}$$

If the correction to T_c is small, the analysis of the phonon instability in Ref. 14 remains valid. There is no change in the positions of the regions on the phase diagram which correspond to a lowering of the symmetry to the various maximal subgroups of the icosahedral group.

In quasicrystals in which this situation prevails, the broadening of the diffraction peaks should be proportional to simultaneously the longitudinal and transverse components of the corresponding wave vector. The relation between the proportionality factors does not change with the temperature, by virtue of (4), until the phason freezing point T_f is reached (Fig. 1). This picture apparently applies to the Al–Cu–Fe quasicrystal,[7] in which a lowering of the symmetry to D_{3h} has been observed.[9] That lowering of the symmetry is consistent with a nonzero mixed term in the expansion of the elastic energy. Note that since the phonon-instability phase transition is of first order, it is seen as a finite jump in $\eta_\parallel$ and may not be accompanied by any significant softening of the corresponding modes.[16]

If the phason freezing temperature T_f lies above the point of the phonon instability, T_c, the frozen spontaneous phason strain $\eta_\perp^f(\vec{r})$ is an analog of an external field.

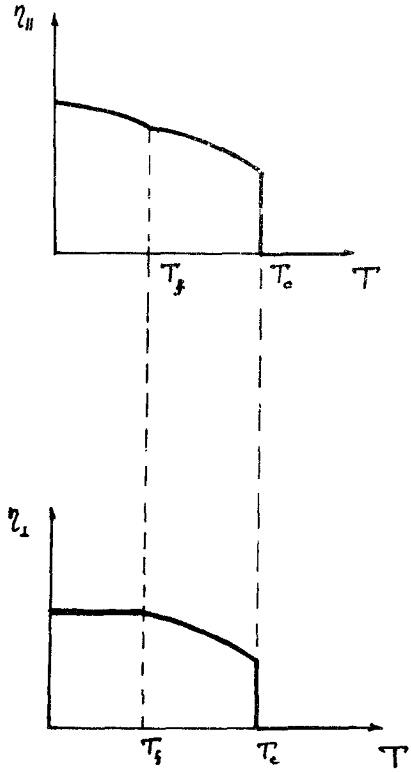

FIG. 1. Temperature dependence of the phonon and phason components of the spontaneous strain, which determine the proportionality factors relating the width of a diffraction peak to the longitudinal and transverse components of the corresponding wave vector.

In place of expansion (1) we then need to write a Ginzburg-Landau functional $\Delta\mathcal{F}\{\eta_{\parallel}(\vec{r}),\ \eta_{\perp}(\vec{r})\}$, which describes the free energy as a function of all the components of the strain tensor of the quasicrystal. The mixed term in the expansion of the elastic energy is

$$\Delta\mathcal{F}_{int} = C_{int}\int d^3\vec{r}\sum_k \eta^k_{\parallel 5}(\vec{r})\eta^k_{\perp 5}(\vec{r}), \tag{7}$$

where $\eta_{\parallel 5}$ and $\eta_{\perp 5}$ are the phonon and phason components, respectively, of the strain. These components transform in accordance with a five-dimensional irreducible representation of the icosahedral symmetry group.[15] The equilibrium phonon strain, found from the conditions

$$\frac{\delta}{\delta\eta_{\parallel}(\vec{r})}(\Delta\mathcal{F}\{\eta_{\parallel}(\vec{r}),\ \eta_{\perp}(\vec{r})\}) = 0; \qquad \eta_{\perp}(\vec{r}) = \eta^f_{\perp}(\vec{r}), \tag{8}$$

is then nonzero in the case $\eta^f_{\perp}(\vec{r})\neq 0$, regardless of the temperature. The instability of the quasicrystal is suppressed. This situation may prevail during rapid growth of a quasicrystal, since the arrangement of the atoms at the growing surface must be correlated over large distances if a nondefective structure is to form.

In the case of annealing or slow cooling, a stable quasicrystal containing no phason displacements can be obtained.[8] By virtue of the condition $\eta^f_{\perp}(\vec{r})\equiv 0$, expansion (1) then becomes a single-component expression which leads to a purely phonon spontaneous strain; this strain is manifested as a linear behavior of the width of a peak on the diffraction pattern as a function of the longitudinal component of the corresponding wave vector. This case is realized in the Al–Cu–Ru quasicrystal,[17] in which a freshly quenched sample exhibits a topological disorder which converts, after an annealing and a subsequent cooling, into a slight broadening of the peaks. This broadening depends on only the phonon component of the wave vector.[8]

In summary, this new model for phason displacements, which are associated with a phonon strain in the critical region of the elastic-instability phase transition, satisfactorily reproduces the topological disorder which is observed in diffraction experiments on stable icosahedral quasicrystals.

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