Relative stability of quasicrystals and Frank-Kasper phases of similar composition

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

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The electron component of the energy of quasicrystals and of crystalline phases of approximately the same composition, whose structure is described by a rational cross section of a six-dimensional space, is analyzed in the approximation of nearly free electrons. The mechanism proposed here can explain the stability of such phases in the Al-Li-Cu system.

Quasicrystal alloys often lie adjacent to periodic phases of similar composition, with a large unit cell, on the phase diagram.[1] Diffraction experiments[2] show that the local structure of these phases (which are Frank-Kasper phases) differs only slightly from that observed in quasicrystals. It has been shown[3] that the structure of such alloys can be obtained through an icosahedral projection onto the three-dimensional "physical" space of the points of a six-dimensional cubic lattice which lie within a "tube" which runs in a rational direction along the vectors $\mathbf{l}_1 = (p,p,q,0,0,q)$, $\mathbf{l}_2 = (q,-q,0,p,p,0)$, $\mathbf{l}_3 = (0,0,p,q,-q,-p)$, where p and q are successive terms of the Fibonacci sequence. The result is a cubic lattice with translation vectors $\{\mathbf{t}_\alpha = \hat{P}_1\mathbf{l}_\alpha\}$ ($\hat{P}_1$ is the icosahedral projection operator) which is made up of the same two rhombohedra, with an edge of length a_R, as the quasicrystal.

Many Frank-Kasper phases are described by the (I,I) projection with $p = q = 1$ (Ref. 4). In this case the period of the bcc lattice which results is $t = a_R\tau(2 + 2\sqrt{5})^{1/2}$, where $\tau = (\sqrt{5}+1)/2$ is the golden section, and the ratio of the numbers of large and small rhombohedra (which is τ in a quasicrystal) takes on the value 5/3.

Let us examine the electron component of the energy of a quasicrystal and of a Frank-Kasper phase. In the approximation of nearly free electrons, this component is determined by the appearance of energy gaps in the band spectrum near the Fermi surface. The approximation of nearly free electrons was used to analyze the electronic structure of quasicrystals in Refs. 5–7. It was found that although the wave vectors of

the quasicrystal fill the inverse space densely, gaps of fairly large width arise on a discrete set of reflections which lie a finite distance from each other. We can thus evaluate the stability of a quasicrystal on the basis of the Jones theory of Hume-Rothery alloys,[7,8] in which the positions of reciprocal-lattice vectors with respect to a sphere of radius $2k_F$ are analyzed.

For a quasicrystal, recriprocal vectors can be written in the form[9]

$$\mathbf{G}^Q = \frac{\pi}{a_R} \sum_{j=1}^{6} m_j \mathbf{n}_j,$$

where $\mathbf{n}_j$ are unit vectors which are directed toward the vertices of the icosahedron, and m_j are arbitrary integers.

In a cubic unit basis with axes along the vectors $\mathbf{t}_\alpha$ we have

$$\mathbf{G}^Q = \frac{\pi}{a_R} \frac{1}{\sqrt{\tau+2}} ((m_1+m_2)\tau + (m_3+m_6);\ (m_4+m_5)\tau + (m_1-m_2);(m_3-m_6)\tau + (m_4-m_5)).$$

The reciprocal vectors of the (I,I) projection form an fcc lattice in this vasis:

$$\mathbf{G}^C = \frac{\pi}{a_R} \frac{\sqrt{\tau+2}}{\tau+1} (k_1, k_2, k_3).$$

The sum of indices $k_1 + k_2 + k_3$ must be even.

Using the renormalization of the copper valence[7] for the R Frank-Kasper phase of AlLiCu, which was studied in Ref. 10, we can find an expression for the Fermi momentum:

$$2k_F = 5.027 \frac{\pi}{a_R}.$$

The value is close to the reciprocal-lattice vector of the (I,I) projection with indices (444):

$$G^C_{444} = 5.034 \frac{\pi}{a_R}.$$

Chen *et al.*[11] have found that in the series of alloys Al_xLi_3Cu a quasicrystal corresponds to $x = 5.1$ and a cubic R phase to $x = 4.8$. The ratio of the average number of electrons per atom of the quasicrystal, Z_Q, to that for the R phase, Z_C, turns out to be $Z_Q/Z_C = 1.013$. If we assume that the R phase stabilizes at $2k_F = G^C_{444}$, while the quasicrystal stabilizes in the vicinity of the nearest of the reciprocal vectors with a wide gap, $2k_F = G^Q_{222100} = 5.052\,\pi/a_R$, we find $Z_Q/Z_C = (G^Q_{222100}/C^C_{444})^3 (n^C_{at}/n^Q_{at})$, where n^Q_{at} and n^C_{at} are the atomic densities of the quasicrystal and of the Frank-Kasper phase. Kalugin[12] has shown that we have

$$n_{at}^{Q} \sim \frac{\Lambda_1 + \tau\Lambda_2}{1+\tau^2},$$

where Λ_1 and Λ_2 are the total numbers of atoms in the small and large rhombohedra, respectively. Since the ratio of the numbers of large and small rhombohedra in the R phase is 5/3, we find, correspondingly,

$$n_{at}^{C} \sim \frac{\Lambda_1 + \frac{5}{3}\Lambda_2}{1+\frac{5}{3}\tau}.$$

Taking the values of Λ_1 and Λ_2 from Ref. 12, we finally find $Z_Q/Z_C = 1.012$; this value is nearly the same as the experimental value.

The appproximation of nearly free electrons thus yields a satisfactory description of the relative stability of a quasicrystal and of a cubic R phase in the Al-Li-Cu system.

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