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COMMENT

On the band-structure contribution to the stability of the icosahedral quasicrystals and Frank–Kasper phases in the non-transition metal alloys

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Abstract. The electronic contribution to the energy of icosahedral quasicrystals and related crystalline phases is discussed within a nearly-free-electron approximation. The Penrose approximant is used through the Elser and Henley scheme for modelling the Frank–Kasper phase atomic structure. The relative position of the Fermi sphere and the wide-gap reciprocal vectors for both structures is analysed. It is shown that the Jones-like arguments concerning the electronic concentration explain the stability of these phases in systems exhibiting the stable quasicrystal formation. Some assumptions about quasicrystalline alloys of other simple metals are suggested.

In a recent article [1] Mizutani *et al* have reported the results of electronic specific heat measurements for the quasicrystal and Frank–Kasper crystalline phase in Mg–Al–Ag, Mg–Al–Cu, Mg–Al–Zn, Mg–Ga–Zn and Al–Li–Cu alloys. They found that the ratio of the experimentally observed electronic specific heat coefficient to that calculated for the free-electron gas of the same density had a similar dependence on the electronic concentration for the icosahedral quasicrystal and associated Frank–Kasper crystalline phase. For the electronic concentrations corresponding to the formation of the stable quasicrystal in Mg–Ga–Zn and Al–Li–Cu alloys the resulting densities of states at the Fermi level $n(\epsilon_F)$ were found to be considerably smaller than the free-electron values, in agreement with the previously reported data [2, 3].

The $n(\epsilon_F)$ value in the electronic concentration region that provides the formation of the metastable quasicrystals was found to exceed the free-electron one. Similar results were also published previously [3, 4]. Mizutani *et al* have also observed that the chemical composition region corresponding to the formation of the quasicrystalline single phase differed from that corresponding to the Frank–Kasper single-phase formation in the Mg–Ga–Zn and Al–Li–Cu alloys, while in the Mg–Al–Ag, Mg–Al–Cu and Mg–Al–Zn systems, where only metastable quasicrystal can be obtained, these compositional regions are in agreement. In the latter case, upon annealing, the quasicrystals were found to crystallize into the stable Frank–Kasper phase. The difference between the alloy compositions revealing the stable quasicrystal and Frank–Kasper phase formation was previously found in the Al–Li–Cu system [5].

The results of Mizutani *et al*, concerning the electronic specific heat coefficient, confirm the importance of the electronic band-structure contribution to the stability

of the quasicrystals and associated Frank–Kasper phases, at least in the compositional region providing the formation of stable quasicrystals.   However, alternative microscopic mechanisms of quasicrystal stabilization were suggested [6–9], and this issue is still the subject of discussion. In the present comment the relative stability of the icosahedral quasicrystal and associated crystalline Frank–Kasper phase will be analysed from the point of view of the electronic consideration. Here, primarily, in the framework of the nearly-free-electron (NFE) approximation, I study the regions of the chemical composition which correspond to formation of the quasicrystal or Frank–Kasper phases. There are some other factors that determine the alloy stability (e.g. the atomic size ratio, the electronegativity difference), but for the quasicrystal and Frank–Kasper crystalline phases they have the same effect, and can be neglected.

Since Schechtman *et al* [10] observed a quasicrystal in the rapidly quenched Al–Mn alloy, a close relationship between the quasicrystals and the long-period Frank–Kasper phases possessing icosahedral atomic configurations was shown in many cases [11]. A definite similarity of the local atomic structure in two types of phase was observed experimentally [12]. The electronic specific heat measurements [3, 13] give similar density-of-states parameters for these phases.

The close relationship between the atomic structure of the quasicrystal and Frank–Kasper phases can be demonstrated by the projection method. Elser and Henley showed [14] that the lattice of the crystalline Frank–Kasper phase α-AlMnSi can be modelled by means of the Penrose tiling approximant, i.e. using a cut through a 6D cubic lattice with a rational slope. Let us consider three mutually orthogonal 6D vectors of the special kind:

$$l_1 = (p, p, q, 0, 0, q)$$
$$l_2 = (q, -q, 0, p, p, 0)$$
$$l_3 = (0, 0, p, q, -q, -p) \tag{1}$$

where p and q are neighbouring members of the Fibonacci sequence. Then, the atomic structure in the 'physical' 3D space is an icosahedral projection from the 6D cubic lattice of the interior of the 'tube', directed along the vectors $\{l_\alpha\}$. As a result, we have a cubic lattice which consists of two types of Penrose rhombohedra with edge length a_R, just as for the icosahedral quasicrystal. The cubic translation vectors are directed along the images of the 'tube' vectors $\{t_\alpha = \hat{P}_i l_\alpha\}$, where $\hat{P}_i$ is the icosahedral projection operator.

In a variety of systems the atomic structure of the Frank–Kasper phase was successfully described by means of a $(1, 1)$ Penrose approximant with $p = q = 1$ [15]. In this case the BCC lattice parameter is

$$t = a_R \tau (2 + 2/\sqrt{5})^{1/2} \tag{2}$$

where $\tau = (\sqrt{5} + 1)/2$ is the 'golden mean', and the ratio of the occurrence of two types of rhombohedra is 5/3 (in the Penrose tiling for icosahedral quasicrystal this ratio is equal to τ).

The suggestion of an atomic structure relationship for the quasicrystal and Frank–Kasper phases allows us to evaluate the structure-dependent terms in the electronic contribution to the energy of phases. It is this part of the electronic energy that is most important because of the small atomic volume difference between these phases.

This contribution within the NFE approximation is determined by the presence of a band gap in the electronic spectrum near the Fermi surface. Despite the near-complete close filling of the reciprocal space by the quasicrystal wavevectors, sufficiently wide gaps are found to appear at a discrete set of icosahedral spots, which have small values for the complementary component $G_\perp$ [16–18]. Thus the Jones theory of the Hume-Rothery alloys, which consists in considering the relative positions of the Brillouin zone face and the Fermi sphere, is adequate for use in quasicrystal stability analysis [18–20]. As pointed out by Friedel [19], the symmetry multiplicities of the wide-gap reciprocal vectors for quasicrystal and associated Frank–Kasper phases are large as compared with those for simpler crystal structures. Hence, the Fermi vector falling in the region near this gap should enhance stability.

Let us consider the reciprocal space. Elser [21] found the expression for the quasicrystal reciprocal vectors:

$$G^Q = \frac{\pi}{a_R} \sum_{j=1}^{6} m_j n_j \tag{3}$$

where n_j are unit vectors directed along the icosahedral fivefold axis and m_j are arbitrary integers. If the coordinate axes are directed along the vectors $\{t_\alpha\}$ of the $(1, 1)$ Penrose approximant lattice we then have:

$$G_x^Q = (\pi/a_R)(\tau + 2)^{-1/2}((m_1 + m_2)\tau + (m_3 + m_6))$$
$$G_y^Q = (\pi/a_R)(\tau + 2)^{1/2}((m_4 + m_5)\tau + (m_1 - m_2))$$
$$G_z^Q = (\pi/a_R)(\tau + 2)^{1/2}((m_3 - m_6)\tau + (m_4 - m_5)). \tag{4}$$

The reciprocal lattice of the BCC $(1, 1)$ approximant is a FCC lattice:

$$G^C = (\pi/a_R)\left[\sqrt{\tau + 2}/(\tau + 1)\right](k_1, k_2, k_3) \tag{5}$$

with the sum $k_1 + k_2 + k_3$ even.

There are some reciprocal vectors which are included in both sets $\{G^Q\}$ and $\{G^C\}$. They have indexes:

$$m_1 = (3k_2 - k_1)/2$$
$$m_2 = -(3k_2 + k_1)/2$$
$$m_3 = (3k_1 - k_3)/2$$
$$m_4 = (3k_3 - k_2)/2$$
$$m_5 = -(3k_3 + k_2)/2$$
$$m_6 = (3k_1 + k_3)/2.$$

But such vectors in the icosahedral reciprocal 'lattice' have a large value of the orthogonal component $G_\perp$. Hence [17], the corresponding band gaps have a small width, and can be ignored in our consideration. Thus, the stability of the definite phase (quasicrystal or Frank–Kasper) will be determined by the type of reciprocal

vector (G^Q or G^C, respectively) that is closest to the real value of $2k_F$, calculated from the electronic concentration:

$$k_F = (3\pi^2 n_{at} z)^{1/3} \tag{6}$$

where n_{at} and z are the mean atomic density of the alloy and the electronic concentration (electrons per atom), respectively [22].

Let us consider the case of the Al–Li–Cu system, where depending on the alloy composition, a BCC R phase or a stable quasicrystal can be obtained. The crystalline lattice parameter and the edge length of the quasicrystal rhombohedra satisfy relation (2) [23]. Thus, we can treat the reciprocal space using the above scheme. There is experimental evidence of the mass density and the composition of the R phase [24]. In order to calculate z we have to know the valency of the alloy constituents. Unlike simple metals such as Al and Li, where the number of electrons in the conduction band is evident, Cu is a complicated case, because some of the d electrons may be delocalized and hence, involved in z. Considering the Cu valency renormalized according to Vaks *et al* [18], one can calculate the Fermi vector length:

$$2k_F = 5.027\pi/a_R. \tag{7}$$

This value is fairly close to the length of the $(1,1)$ approximant reciprocal vector $G^C_{444} = 5.034\pi/a_R$, whereas the nearest icosahedral vector is $G^Q_{222100} = 5.052\pi/a_R$.

Chen *et al* [5] found that the most stable quasicrystal among the $Al_x Li_3 Cu$ alloys appears at $x = 5.1$, while the Frank–Kasper R phase corresponds to $x = 4.8$. The electronic concentration ratio $z^Q/z^C = 1.013$. Let us suggest that the Frank–Kasper R phase and the quasicrystal are stabilized when the $2k_F$-sphere in reciprocal space just touches the G^C_{444} vector or the nearest of the wide-gap icosahedral vectors, i.e. G^Q_{222100}, respectively. Then, for the mean electronic concentrations we obtain

$$z^Q/z^C = (G^Q/G^C)^3 (n^C_{at}/n^Q_{at}) \tag{8}$$

where n^C_{at} and n^Q_{at} are the mean atomic densities of the crystalline Frank–Kasper phase and the quasicrystal respectively.

As shown by Kalugin [25], the quasicrystal atomic density is proportional to

$$n^Q_{at} \propto (\Lambda_1 + \tau\Lambda_2)/(1 + \tau^2) \tag{9}$$

where Λ_1 and Λ_2 are the numbers of atoms in the 'prolate' and 'oblate' rhombohedra respectively. Changing τ to the occurrence-of-rhombohedra ratio in the $(1,1)$ Penrose approximant (i.e. 5/3), for the Frank–Kasper R phase one can obtain analogously

$$n^C_{at} \propto [(\Lambda_1 + 5\Lambda_2/3)/(1 + 5\tau/3)]. \tag{10}$$

Taking the $\Lambda_{1,2}$ from [25], finally we have $z^Q/z^C = 1.012$. This ratio is in good agreement with the experimental one.

It is worth mentioning that the suggested mechanism of the phase stabilization leads to a lower value of the electronic density of states at the Fermi level as compared with the free-electron one. The reduced value of $n(\epsilon_F)$ was found in the stable quasicrystals as well as in crystalline Frank–Kasper phases of the alloys of the Al–Li–Cu and Mg–Zn–Ga systems [2–4]. It is this case that concerns the observable

difference in alloy chemical composition between the single-phase quasicrystal and Frank–Kasper crystal [1]. Thus, the difference corresponds to sufficient separation of the locations of the G_{444}^C and G_{22100}^Q vectors in the reciprocal space.

However, the compositional regions providing the formation of the Frank–Kasper phase and metastable quasicrystal in the Al–Mg–Ag, Al–Mg–Cu and Al–Mg–Zn alloys are in agreement [1]. There is a more complicated situation in the reciprocal space region near $G_{311111}^Q = 5.236\pi/a_R$ related to the electronic concentration in this case. There is a reciprocal vector of the (1, 1) approximant $G_{046}^C = 5.239\pi/a_R$ that is very close to G_{311111}^Q. So, there is no electronic concentration region with a value of $2k_F$ that touches the G_{311111}^Q vector in reciprocal space, and is sufficiently separated from the Brillouin zone face of the crystalline Frank–Kasper phase. Hence, in this case, the electronic band energy contribution to the total energy of the Frank–Kasper phase cannot be much larger than that of the quasicrystal and, thus, electronic stabilization of the quasicrystalline phase is not feasible.

As Vaks *et al* showed [18], all simple-metal quasicrystals known at present have compositions associated with electronic concentration $z^Q = 2.17$ or $z^Q = 2.45$, which correspond to G_{22100}^Q and G_{311111}^Q, respectively. However, for both of the stable quasicrystals (Al–Li–Cu and Mg–Zn–Ga) $z^Q = 2.17$. So, the above considerations explain this to some extent. However, the electronic density of states at the Fermi level in the case where $z^Q = 2.45$ is not reduced as compared with the free-electron one. This indicates that for such alloys the band-structure contribution, originating from the Fermi surface–Brillouin cell face interaction, does not play a crucial role in the stabilization of both the icosahedral quasicrystal and the Frank–Kasper crystalline phases. Hence, some other factors should be taken into account. However, the mean electronic concentration of an alloy can still be valid as a basis for the analysis of the relative stability, because the contribution is small compared with the phase cohesive energy, but not with the small energy difference between two phases (quasicrystal and Frank–Kasper crystal) of similar structures.

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