

Discussion on clusters, phasons, and quasicrystal stabilization

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This paper represents a two-hour discussion that we moderated at the Ninth International Conference on Quasicrystals. The discussion was divided into three parts, concerning (i) the meaning [if any] of clusters in quasicrystals; (ii) phason elasticity, and (iii) thermodynamic stabilization of quasicrystals. To prime the participants, the discussion leaders prepared discussion papers in advance, which are printed separately [3, 2, 1].

The colloquy was rather lively, considering that the topics are probably the most intractable questions in quasicrystals and the ones which have seen the least progress since 1985. There was somewhat less detailed discussion of specific experiments [done, or proposed] than might have been wished, but the discussion made absolutely clear that more experiments are needed in each of the three areas, if we are ever to resolve these questions.

Included in this text are (i) notes from the oral comments taken at the discussion session; and (ii) written comments – about 18, almost evenly divided between theorists and experimentalists – which were sent afterwords by most of the participants who spoke during the session: S. BEN-ABRAHAM, L. BARBIER, T. DOTERA, K. EDAGAWA, F. GÄHLER, Y. GRIN, Y. ISHII, K. KIMURA, R. LÜCK, R. MCGRATH, M. MILALKOVIČ, N. K. MUKHOPADHYAY, G. NAUMIS, D. RABSON, J. ROTH, H.-R. TREBIN, M. WIDOM, AND E. ZIJLSTRA. The order has been rearranged freely so as to gather related points in the same place, and the contributions were intensively edited with the aim of improving clarity.

1. Clusters in quasicrystals

This discussion was led by WALTER STEURER.

1.1. Defining ‘clusters’

The first (and longest) question was the definition of ‘cluster’. Some participants (including W. STEURER thought it was valuable to arrive at an agreed definition. [M. MIHALKOVIČ recalled that in the old days, the community succeeded on one clarification of nomenclature: the distinction between ‘packing’ and ‘matching’ rules.] But others in the discussion took a libertarian attitude that ‘cluster’ can mean anything, so long as the user prefaces his or her use by specifying what sense is meant, e.g. D. GRATIAS said, Let’s each define our own definition of a ‘cluster’, with

a meaning limited to that talk or paper. F. GÄHLER replied, it's just important that each time we use it, we say what we mean. M. MIHALKOVIČ observed that the question of the physical reality of clusters is different from question of synchronizing our dictionaries. We should *not* focus on finding the 'best' definition for 'cluster', but merely on eliminating any clearly misleading concepts or terms.

The main tension was between geometrical definitions – based on purely structural data – and chemical definitions including some criterion about bonding. The practicality of a bonding criterion tends to hang, of course, on the experimental question whether strongly-bonded atom clusters actually exist in quasicrystals, which is discussed later in three micro-reviews (Subsec. 1.4,1.5, and 1.6. [In addition, P. A. THIEL wondered if the results presented at this conference on bulk metglasses related to quasicrystals were evidence in favor of clusters; however W. STEURER cautioned that nanocrystals might be an equally good explanation.]

It is amusing that for some participants, non-overlapping is an automatic attribute of a 'cluster', yet for others, certain 'clusters' are of interest precisely because they completely – and overlappingly – cover the whole quasicrystal structure.

MICHAEL WIDOM: 'a group of atoms that [repeats and] fills space'.

DAVID RABSON: 'a geometric assemblage that maximizes coordination number'.

CHRIS HENLEY: 'a group of atoms which always stay together in some ensemble.'

GERARDO PAY-GOMEZ emended this to 'the largest group of atoms which ...' ['Stay together' was meant here in a geometrical or statistical sense, not bonding sense.]

HENLEY'S point was, the ensemble is implicit whenever we talk about clusters. That is, a 'cluster' must appear in more than one environment, or in more than one structure. [PAY-GOMEZ comments: Finding a cluster on the basis of just (say) the 1/1 approximant of the i-CdTb quasicrystal is like estimating the slope of a curve when you have just one point!] When we are concerned with energetics, this ensemble would be the set of all low-energy structures; when we are concerned with cleavage, the ensemble would be the cleavage surfaces after many trials with equivalent conditions.

HANS-REINER TREBIN: The definition of 'cluster' must incorporate the following (i) these repeating units must *cover* most of the atoms (ii) The cluster centers provide a *coarse-grained* description of the system's physics. (iii) Often clusters are easier to *observe* [as e.g. in electron diffraction]. [This is elaborated later in Subsec. 1.2.]

GERARDO NAUMIS did not have a definition to add, but concurs with the viewpoint of *coarse graining* [as being important in the cluster idea], since usually there is a hierarchy of forces, divided into intra- and inter-cluster forces. THEIS agreed: the reason we need 'clusters', is to implement a new 'coarsened' picture of the system that embodies the physical properties.

YURI GRIN: [The term 'cluster' ought to have a meaning similar to its chemical definition.] That is, the interaction within a cluster differs from [is stronger than] that outside the cluster. Any attempt to define structures geometrically has an arbitrariness. [But until the higher relative stability of the quasicrystal (QC) clusters with respect to their environment can be clearly confirmed, it would be reasonable to state that the term 'QC cluster' is used in the sense of the system of nested polyhedra.]

G. KREINER: As a chemist working in the field of quasicrystals, I openly don't use 'cluster' in its original, chemical sense, which would require us to first solve the problem of bonding [for the material in question]. A working definition would be 'a geometrical entity which can be used for prediction.'

EEUWE ZIJLSTRA expressed support for YURI GRIN'S view: if the standard meaning of 'cluster' in chemistry is 'stable structural unit', he strongly feels that

we should adhere to this definition. Too many words are being used differently by quasicrystal scientists than by all other physicists. To reduce the risk of confusion, let us call these objects, for example ‘quasicrystal clusters’; just as people know ‘herbal tea’ is not really tea, we can assume they will infer that ‘quasicrystal clusters’ are not necessarily real clusters (in the sense of stable structural units). [HENLEY asks: what about the other usages of ‘cluster’ e.g. the ‘Mayer Cluster Expansion’ in statistical mechanics?] It would be great if we distinguished these different meanings by qualifying them as e.g. ‘covering cluster’, ‘stable cluster’, ‘quasicrystal cluster’ (for the polyhedral shells used in structural models), etc.

JOHN CAHN: A definition must be short and it must be easy to test whether it applies in any case. The second criterion leads him to favor a geometrical rather than an energetic definition. A good definition should be fruitful too: e.g. if we find clusters frequently, we can infer or guess them in another material.

Clusters are clearly well-defined in a vapor phase. And many of these ideas apply to molecular solids, e.g. benzene in a benzene crystal. But metallic bonding has a longer range than chemical bonding. Furthermore, in a truly quasiperiodic structure [e.g. the Penrose tiling with inflation symmetry], we have clusters at all scales. We need to a *useful* definition of ‘cluster’! CAHN asks, must there be a clean separation of a cluster from the matrix which surrounds it?

SHELOMO BEN-ABRAHAM: An isolated cluster of atoms, such as produced for instance by evaporation, is well defined geometrically, chemically and physically. What we are dealing with in the context of quasicrystals, complex (inter)metallic alloys, ‡ and more generally aperiodic condensed matter, is quite another thing. In this context, ‘cluster’ is a flexible conceptual tool, mostly a shorthand expression. We usually designate as a cluster an arrangement of coordination polyhedra, perhaps with some peripheral additions; for the ones with accepted names (‘Bergman’ or ‘Mackay’ clusters) this suffices to specify what is meant by cluster. Such a ‘cluster’ may, in each case, be well defined *geometrically* but has hardly any precise *chemical* and/or *physical* meaning, and perhaps it is not possible to assign one.

Hence, it is impossible and unnecessary to try to establish a formal definition of a cluster. When dealing with an abstract geometrical structure (a packing, a tiling, a covering, a point set) it is preferable, in BEN-ABRAHAM’S humble opinion, to refrain from using the term ‘cluster’ and, instead, to talk about ‘a patch’.

JOHANNES ROTH considered it important to mention that the clusters highlighted appear nearly always to be spherical or [as in decagonals] cylinders of infinite extent in one direction. They are never elongated like an ellipsoid, although that would not be unnatural in certain of the tilings. [That is, perhaps people have an unconscious *a priori* bias towards particular kinds of clusters, and have not necessarily taken alternatives into consideration.] Or should the definition of ‘cluster’ explicitly restrict the shape? N. MUKHOPADHYAY wondered, should we impose a lower bound on the size of a ‘cluster’; does it need to have multiple shells? C. L. HENLEY and M. MIHALKOVIČ noted that, since the interactions responsible for stabilization are long-ranged in metals – and oscillating, as seen in pair-potential modeling – it might even make sense to define a ‘cluster’ in the shape of an annulus or decagonal ring, without including the interior atoms [Those could be in varying configurations, as in ‘pseudo-Mackay’ clusters, or the *i*-CdYb cluster.]

‡ BEN-ABRAHAM suggests the abbreviation CIMA (in place of the now accepted CMA) which (a) is more adequate; (b) can be pronounced as a word; (c) means ‘the top, summit’ in a variety of Romance languages (!).

R. LÜCK agrees that the term ‘cluster’ has been applied with a variety of meanings to different properties of matter. For instance, in Kikuchi’s ‘cluster variation method’ [4], ‘cluster’ means a geometrical construct to compute the configuration entropy of a given material. Again, the term ‘clustering’ is used to describe the atomic arrangement of an alloy when neighboring atoms are observed to be identical species more frequently than in a random arrangement; it describes the opposite of chemical short range order.

These two examples show that there is no general, unique understanding of the term ‘cluster’; in both cases, nothing is said about binding energies within or out of the assumed cluster (as was proposed to be a condition for ‘cluster’ by YU. GRIN). LÜCK, in any article mentioning a ‘cluster’, would define or explain this term in the introduction to avoid confusion, just as any unfamiliar abbreviation or acronym should be defined.

N. K. MUKHOPADHYAY believes we all understand ‘cluster’ to mean some grouping of atoms possessing short- or medium- range order, and having some properties different from rest of the atoms. This can also be considered as a motif or building block in the solid structures. For example, in the T -Mg₃₂(Al,Zn)₄₉ and α -AlMnSi approximants, the motifs are the Bergman and Mackay clusters, respectively. Those clusters are basically non-overlapping and non-touching motifs decorating the unit cell. In respective crystalline, icosahedral, and glassy phases these clusters are arranged periodically, quasiperiodically and randomly. Therefore the clusters can be thought of as a group of atoms acting as non-overlapping motif; they govern the properties that depend on the interplay of short-range (or medium-range) order with the crystal chemistry. structures. [In the T -Mg₃₂(Al,Zn)₄₉ case, the Bergman cluster notion was productive, as it inspired the search for the non-crystalline allomorph.]

1.2. Theorists’ definitions of clusters connected to binding or physical properties

As HANS-REINER TREBIN understands them, clusters are identical groups of atoms which in most cases can be inscribed into spheres or circles, in rare cases into other compact sets. These spheres can also overlap, and there may be more than one type of cluster. The clusters thus usually comprise more than 80% of the atoms. A coarse grained description of complex alloy structures is then given by the positions of the cluster centers and the tilings formed by them.

But clusters must have also a minimum stability, this is one way to interpret ‘stay together’ in the definition proposed by Henley. Hence they are also *physical* entities with adhesiveness in a certain energy range. This definition is suitable e.g. for the pseudo-Mackay clusters of i -AlMnPd. Numerical simulations of crack propagation and comparison with STM investigations strongly indicate that dynamical cracks pass around these clusters [6]. The clusters are present in the icosahedral quasicrystalline forms and the ξ -approximants of Al-Mn-Pd and thus appear to rearrange themselves as whole entities during mutual phase transformations. They also stay together when under plastic deformation partial dislocations and the associated metadislocations are formed and start moving [7]. Such a cluster motion need not necessarily happen by simultaneous motion of all cluster atoms. Indeed, in some instances like Al-Cu-Co motions of a few atoms mimic the motion of entire clusters [8]. Nevertheless TREBIN would call such clusters physical entities. So far clusters are not comparable with molecules although these, too, do dissolve and recombine in dynamical equilibrium.

FRANZ GÄHLER asks, where do draw the boundary of a cluster, and just when can

we call it a cluster at all? Obviously, if a certain arrangement of atoms occurs all over the place, this arrangement must somehow be preferred, energetically or kinetically. But it is highly problematic to demand that the cluster and the rest of the system should be distinguished by the degree of binding. Such a notion would make sense for covalently bound entities, but those are certainly not typical in metals. In metals – including complex intermetallics such as quasicrystals – the binding notion simply does not have a sufficiently localised meaning, as is evident if we try to draw a boundary between the preferred arrangement and the rest of the system: the interactions' effective range is say 6 Å – typically much larger than an interatomic distance. Having a 'cluster' embedded in the rest of the system, it is thus not well-defined which [atomic] interactions are intra-cluster, and which are between the cluster and the rest of the system; and whether a particular 'cluster' of atoms is preferred must depend also on the environment in which that 'cluster' is embedded. If we were to include, in the very definition of 'cluster', an energetic separation from the environment, it would mean that we have to stop using that term!

Another point is that clusters often overlap, covering a large portion of the quasicrystal. Where would one draw the boundary [to apply the bonding criterion]. If all of these were to be tightly bound clusters, the quasicrystal would become a single large molecule, with some extra glue atoms in between. GÄHLER doesn't think this is the correct picture.

ZIJLSTRA acknowledges that a problem with the definition of 'stable clusters' as having stronger bonds within the unit than between units, is that in quasicrystals we often see overlapping (interpenetrating) clusters, sometimes covering almost all the atoms. And for [assessing the stability of] clusters that appear in the bulk, interactions with the mainly Al surrounding atoms, at least, must be taken into account. So, the bond strengths should be the target of theoretical and experimental investigations, to determine which building blocks are more stable than others (so they gain more than their present, mainly geometrical, role).

1.3. On clusters and *ico* quasicrystals described by cut-and-project

MARC DE BOISSIEU commented on the application of clusters in quasicrystals (QC). First, for a cluster description to be meaningful it must consist of both a geometrical network (topology) and of a corresponding chemical decoration. Second, for a structure as complex as quasicrystals, one should use all possible descriptions, and consider which is appropriate description for a given problem.

(i) If any physical property is to be deduced from a cluster description of the QC, its chemical decoration (chemical order or disorder) will be crucial. Some answer to this question of chemical decoration can certainly be obtained from the most recent QC structural refinement.

(ii). Besides the topology of the cluster network, there are also tiling descriptions of the structure. The restriction to be a tiling is certainly useful for modeling the atomic structure, but is it really valid for physical properties calculation? Are there any strong experimental evidences for an underlying tiling? [Note that most tilings constructed from HRTEM images end up with quite a lot of disorder.]

(iii). Surface studies of QC is a good example where the cluster description has led to little understanding of the surface structure. A description of the QC structure in term of dense planes (as already evidenced in the early models of *i*-AlLiCu) has been a much more fruitful approach.

(iv). Among the various ‘angles’ from which quasicrystals have been modeled, the hierarchic [inflation] nature of quasicrystals has been little explored for physical properties (except by C. Janot, see e.g. Ref. [5]). Yet this is a striking feature of the diffraction pattern of QC, and DE BOISSIEU suggests it should be better explored from the viewpoint of understanding the physical properties.

LUC BARBIER critiques the entire notion of cluster descriptions. Within the aperiodic structure of quasicrystals (QC), some local atom configurations can be identified: for instance, Bergman or Mackay-like clusters for icosahedral QC (*i*-QC) structures. Are these groups of atoms relevant in the QC structure? Certainly, the symmetry of QCs causes some local configurations to be repeated in the structure. Note the following points:

- (i) One may extract from the *i*-QC structure the aperiodic distribution of Bergman clusters.
- (ii) On the other hand, one could describe the very same atom distribution with Mackay clusters instead.
- (iii) Furthermore, excess atoms (‘glue atoms’), not part of the clusters, are present in the structure.

Thus, [from (i) and (ii)] the cluster description is not unique, and [from (iii)] does not catch the whole structure. [BARBIER instead advocates a structure description completely founded on the hyperspace cut approach, see Sec. 1.6.]

1.4. Evidence for clusters from electron density measurements

In this subsection, KAORU KIMURA addresses the questions posed in STEURER’s discussion paper [1], based on two of his papers (Refs. [10] and [9]), containing experimental data from the 1/1 approximant α -AlReSi of *i*-AlReSi, in which Mackay Icosahedron (MI) clusters are present.

- (i) *How is the distribution of chemical bonds (length, strength, type, anisotropy) between atoms in a geometrical cluster found from structure analysis? Are the strongest bonds between atoms of a shell or between atoms of different shells? Is there a difference between the bonding of different shells (decrease in bond strength from the inner to the outer shells, not every shell consists of atoms in bonding distance to each other)? How does the network of strong bonds look like for concrete examples?*

The electron density distribution in the α -AlReSi 1/1-approximant crystal was measured using synchrotron radiation combined with a fit by the maximum entropy method [9]. The criterion to define bond-strength was the electron density at the bond midpoint. There is a wide distribution of the bond-strengths in α -AlReSi, ranging from strong covalent bonds (near to those in Si) to weak metallic bonds (near to those in fcc Al), which is considered to be one of the features of a structurally complex material.

- (ii) *Is it possible to identify clusters clearly separated from the embedding matrix? What is the size of these clusters, how thick are the matrix parts between clusters? What is the difference between cluster and matrix (chemical bonding)?*

According to the above estimation, the intra-Mackay cluster bonds are stronger than the inter-Mackay cluster bonds, on average. The α -AlReSi and also *i*-AlPdRe quasicrystal are considered to be intermediate states between metals, covalent bonding networks (as in semiconductors) and molecular solids.

- (iii) *Is it possible to model in a first approximation the physical properties (electronic, dynamic) of quasicrystals in terms of clusters embedded in a matrix?*

The thermoelectric figure of merit Z and the effective mass m_* of i -AlPdRe quasicrystals can be increased by strengthening the intra- and weakening the inter-cluster bonds. According to this scenario, Z was improved by substitution of Ru for Re [10].

1.5. Evidence from surface experiments regarding the stability of clusters in quasicrystals

Here RONAN MCGRATH and PAT A. THIEL review the experimental evidence for enhanced stability of clusters from cleavage experiments under ultra-high vacuum conditions. These include:

- (i) the experiments of Ebert, Urban and co-workers on cleavage in ultra-high vacuum conditions of the 2-fold and 5-fold i -AlPdMn surfaces [11, 12, 13];
- (ii) similar experiments by Ebert and co-workers on the 10-fold surface of d -AlNiCo [14];
- (iii) experiments by Cecco and co-workers on the cleaved 10-fold and 2-fold surfaces of d -AlNiCo and the pseudo-10-fold surface of the ξ' -AlPdMn approximant [15].

Scanning tunneling microscopy (STM) measurements of all of these surfaces formed by cleavage showed the presence of approximately nanometre size protrusions in STM measurements. These surface experiments are practically the only experimental evidences of the physical reality of clusters in quasicrystals.

Considering first the cleavage of AlPdMn surfaces, the ≈ 1 nm protrusions seen on the 10-fold and 2-fold surfaces of i -AlPdMn were linked by Ebert *et al.* to the enhanced structural stability of Mackay-type clusters. For the 2-fold surface, autocorrelation patterns of the images showed some order in the arrangements; none was found for the 5-fold surface. On the other hand Cecco *et al.* found that the cleaved pseudo-10-fold surface of ξ' -AlPdMn showed protrusions of order 4–8 nm in size, with no evident preferential orientation and no periodicity. As the unit cell parameters of ξ' -AlPdMn are $a=2.3541$ nm and $c=1.2339$ nm, the authors conclude that there is no evident correlation to the underlying structure, which contains partial Mackay icosahedra [16].

Turning to the 10-fold surface of d -AlNiCo, the 1–2 nm size protrusions seen on this surface were interpreted differently by the two groups that observed them: Ebert *et al* [14] saw them as evidence for the existence of columnar clusters in d -AlNiCo. On the other hand, Cecco *et al* [15] could find no correlation between the protrusions seen in their images from the 10-fold surface and the underlying structure.

What are the corresponding results when *simple* metal crystals are fractured? Although the literature does not appear to be extensive, STM measurements from cleaved Bi(0001) [17] and Sb(0001) [18] show these surfaces as being atomically flat over large areas.

To summarise, therefore, all evidence is that cleaved quasicrystal surfaces are rough on the nanometer scale (also found in the approximant ξ' -AlPdMn), but there is disagreement as to whether this indicates enhanced stability of pseudo-spherical (or columnar) clusters. The roughness might also be explained in terms of the non-existence of natural cleavage planes in these complex alloys: in the bulk structure

of *i*-AlPdMn and *i*-AlCuFe the largest ‘gaps’ perpendicular to the five-fold direction (evident in Yamamoto’s structure model) are of the order of 1 Å thick [19], which is just half of the (0001) interplanar spacing (≈ 2 Å) that occurs in Bi or Sb [17, 18].

The limited data available need to be augmented through further experiments. These might include fracture of other refractory metal surfaces along high index planes, and fracture of other complex metallic alloy giant unit cell structures. These materials, although periodic, have a cluster sub-structure, and are the focus of a new ‘Network of Excellence’ funded by the European Union and coordinated by J. M. Dubois [this was described in the presentation of Dubois on the first afternoon of this conference.] As to repeating the fracture experiments on quasicrystals, it should be kept in mind that these samples are very precious [and are destroyed by the experiment].

As a final remark, MCGRATH and THIEL echo the comments in C. L. Henley’s discussion paper [3], that regardless of whether clusters have a physical reality ‘they are inescapable as a framework to organise our understanding of a structure’. In STM measurements of the icosahedral five-fold surfaces, truncated pseudo-Mackay and pseudo-Bergman clusters appear as identifiable characteristic motifs, which also turn out to be important in adsorption and nucleation processes. Clusters, whether stable or not, can provide a common language between the experimental bulk, experimental surface and theoretical communities.

1.6. Clusters: surface science and 6D-cuts

This subsection consists of a critique by LUC BARBIER, who believes surface studies furnish additional arguments about the role of clusters [See his comments in subsec. 1.3, above.]

Let’s first recall the height correlation function

$$G(\mathbf{r}) \equiv \langle [h(\mathbf{r}) - h(0)]^2 \rangle \quad (1)$$

used to characterize the roughness of any surface. On terraces of a well equilibrated [facet] surface, $G(\mathbf{r})$ saturates at large distances, which means the terraces are *flat*. On the other hand, a thermally *rough* surface (as it is generally the case for low index vicinal surfaces of usual crystals) has a long-range height correlation divergent as $G(\mathbf{r}) \sim \ln(r)$ (and no faster: that is a universal property of *equilibrium* 2d interfaces).

1.6.1. Well equilibrated quasicrystal surfaces

For the 2- 3- and 5-fold surfaces at thermal equilibrium, STM observations show wide flat terraces; the helium diffraction experiment shows that this is valid for the whole surface. Analysis of the surface structure shows that the terrace planes cut the Bergman and Mackay clusters [20].

As in the bulk, on extended flat terraces of icosahedral quasicrystals (*i*-QC), e.g. *i*-AlPdMn [20] or *i*-AlCuFe [21], well-defined patterns are seen which could define surface clusters: filled (or empty) flower-like patterns, 10-fold rings of pentagons. These are useful as a guide for the eye to perceive the QC symmetry (pentagonal structures, aperiodicity, rows following Fibonacci sequences), yet one cannot describe the surface structure solely on this basis. A much more fruitful approach is the 6-d description of *i*-QC structures. Given one unique periodic (within the 6-d space) unit cell, all possible configurations within the real 3-d space can be obtained allowing a complete description of both terrace structures and step height distributions.

1.6.2. Cleavage

It has been proposed that fracture surfaces found in experiments on quasicrystals [11, 14] exhibit at the lowest scale a cluster-like pattern.

In fact, experiments on all materials have found a universal behaviour of the roughness of relaxed fracture surfaces [22]. All fracture surfaces exhibit a self similar roughness within the range ξ_c , the elementary grain scale, up to R_c , the limit at which linear continuous mechanics applies. Within this range, the height correlation of the self-affine morphology follows a power law: $G(r) \propto r^\alpha$ with the universal exponent $\alpha = 0.8$. [This is a greater roughness as compared to the thermally rough surface.] Furthermore, this exponent α is found to be independent of the material structure [22]: it is the same in glass, intermetallic alloys, composite materials like concrete... even in *single crystals* [23].

Up to now, measurement of ξ_c has not been performed for QC. Only a scale analysis of the roughness of cleavage surfaces over several decades of length scales would allow concluding in favour of a possible relevant cluster morphology in cleavage surfaces.

1.6.3. Hyperspace description

Thus, leaving the various attempts of a surface cluster description, surface studies better contribute to unambiguously define the unit cell within the associated hyperspace [20, 21]. Only this unique and unambiguous (even if not yet definitely fixed) unit cell allows to capture all the richness of the QC structure. The origin of the stability of icosahedral QC structures necessitates a better understanding of what is allowed in the decoration of the 6-dimensional unit cell (the geometry being fixed by the symmetry properties). The energetic balance that would be deduced within the hyper space description is still lacking.

Reducing the QC description to the distribution of some clusters would miss the fundamental [defining] property of QC: their aperiodicity as a consequence of the symmetry [of their atomic structure], which can only be completely represented in the hyper space geometry. Clusters of *various* positions and sizes can be built from this well-defined [hyperspace] unit cell. Though they are useful for immediate comparison of structures with different local configurations (thus for revealing whether the 6-d unit cell has different contents) they cannot catch the essence of the QC structures. Within a QC structure clusters cannot be defined in a unique way; whereas, as for usual crystals, unique definitions of both symmetry and hyperspace unit cell satisfy the crystallographer.

1.6.4. Conclusion

To summarize the main points:

(i) Though a cluster view may be useful for a quick comparison of various surface (or bulk?) structures of QC, it is useless (or misleading ...) in a description of the whole structure.

(ii) Experimental proof of the existence of clusters by cleavage experiments is far from proven, so long as a scale analysis of the surface height correlation function is lacking.

(iii) Assuming the unit cell within the hyperspace description is a reality, the following definition of QC clusters would be implied:

‘QC Clusters’ are various assemblies of atoms that can be generated and are distributed according to the associated Bravais hyperspace lattice decorated by one single unique unit cell.

This means that a cluster approach to describe QC structures will remain necessarily ambiguous.

2. Phason fluctuations

This discussion was led by MARC DE BOISSIEU.

2.1. Definition of ‘phason’?

This term probably occasions even more confusion than ‘cluster’ in the field of quasicrystals. M. WIDOM began with a question: what is DE BOISSIEU’S meaning for ‘phason hopping’? If an atom hops back and forth [between the same two places], would you call it a ‘phason’? [See DE BOISSIEU’S discussion paper [2].]

2.1.1. A critique of the ‘-on’ in ‘phason’

SHELOMO BEN-ABRAHAM emphasized that strictly speaking, ‘X-on’ is a quantum of excitation X. Thus, a ‘phonon’ is one quantum of a quantized lattice vibration mode. That is manifestly evident in the occupation number representation. However, it is commonplace to refer, by metonymy, to the lattice vibration mode itself as a ‘a phonon’. That is not quite correct, but acceptable and generally also accepted.

In the context of aperiodic crystals we deal with excitations called ‘phasons’. In incommensurate structures these are precisely defined and well named. In more general cases perhaps less so. Yet they clearly refer to the extra degrees of freedom present in aperiodic crystals. Flips are, of course, their elementary manifestations. Nevertheless, it is grossly misleading to call the single flips ‘phasons’. (R. LÜCK concurred with S. I. BEN-ABRAHAM’S comment that the term ‘phason’ is misleading due to the ending ‘-on’.)

In the early days, BAAKE, BEN-ABRAHAM, and the Tübingen group used to call these flips ‘simpleton flips’ as they occurred in the simplest hexagonal vertex (= local environment); we now know that they occur in more complex environments, too. To conclude, everyone knows what is meant by a flip in a quasicrystal. So, BEN-ABRAHAM proposes, let us call it just ‘a flip’. It does not need the *epitheton ornans* (superfluous adjective) of ‘phason’ in front of it.

C. L. HENLEY offered a polemic about nomenclature that is introduced carelessly. The late Per Bak first used the term ‘phason’ for quasicrystals [24] but afterwards, at least once he claimed he meant to write ‘phase’, e.g. ‘phase stiffness’. Thus for us, ‘phason’ is properly only an adjective, e.g. ‘phason mode’ or ‘phason coordinate’, and is similar in meaning to ‘perp-space’ or ‘complementary-space’. Yet the *name* ending in ‘-on’ suggested a discrete, countable object, so some people attached it to the matching-rule violations or to dynamic tile flips, which implement phason modes in discrete models.

2.1.2. Phason defects: point, line, or wall?

REINHARD LÜCK comments on the the geometry and observations of *phasonic defects* as described in 1988 and subsequently [25, 26, 27]. [In this viewpoint, a

phason-free quasicrystal would result from an flat cut at the correct slope through the appropriate hyperspace crystal. A ‘phason’ refers to an elementary violation of a local rule, such that furthermore a closeness condition in complementary space is fulfilled. [27].]

In 3D, a phasonic defect is a *line defect* forming a closed loop or terminating at the surface or at a dislocation line; only in 2D is it a point defect described by a jog in the so-called ‘Conway worm’. Movement of phasonic defects requires phason flips, usually realized by jumps of atoms (or groups of atoms), as described in the discussion paper by M. de Boissieu [2].

The remarks in this discussion by H.-R. TREBIN and detailed investigations of M. FEUERBACHER *et al* [28] the mentioned interaction of dislocations and phasonic defects as line defects. Details concerning the healing of phasonic defects formed in plastic deformation were discussed in a collaboration with David Warrington [29]. The formation of ‘phason walls’ is definitely compatible with the required property of a line defect. A high concentration of phasonic defects may destroy the line character of phasons due to the high density. However, there is no reason that a phason is regarded as a point defect.

2.2. Theorists’ viewpoints on phason elasticity and dynamics

2.2.1. Hydrodynamics: need to model short wavelengths

HANS-RAINER TREBIN distinguishes *phason flips*, which correspond to jumps of one atom or a localized group of atoms between split positions, and *phason excitations*, which consist of correlated phason flips over large distances, that together make the macroscopic shift.

Long-wavelength phason excitations are well described by the hydrodynamical equations established by Lubensky *et al* [30] and others. Some phenomena like phason-induced diffuse scattering and diffusion of phason fluctuations [31] [seen in X-ray speckle imaging of diffuse wings], and also ‘phason walls’ [32] [created by moving dislocations], have been studied experimentally. The decay time constant in the mechanical experiments is similar to that for fluctuations in the diffuse scattering experiments [on similar length scales]. Thus the existence of the phason degree of freedom in quasicrystals is well established.

What is missing up to date are studies of phason dynamics beyond the hydrodynamical limit, i.e. phason excitations of shorter wavelengths, phason damping mechanisms and the freezing of phason kinetics or ‘phason pinning’. For the study of these phenomena discrete models are required [33] and – TREBIN speculates – concepts from the theories of the glass transition.

N. RIVIER: Years ago, there was an interesting theory by Kalugin and Katz, about how the brittle-ductile transition in quasicrystals was due to a percolation of phason flips. D. GRATIAS: Experiments contradicted that theory: they didn’t actually show the catastrophic change of atomic diffusion at high temperatures, which it predicted.

2.2.2. Hydrodynamics: need to measure long wavelengths

YASUSHI ISHII would expect different behaviours, or even different physics, for phasons in the short and long wavelength regimes. I would like to stress here the *dynamic* aspects of phasons in these different regimes. An ideal quasiperiodic structure

is obtained by a flat cut ($\mathbf{h}_\perp = \text{constant}$) of higher-dimensional lattice but a cut for real samples is inevitably corrugated somewhat. Such corrugation or fluctuation in the perp space is induced, for example, due to uncontrollable experimental conditions such as inhomogeneities in temperature and compositions at the growth front.

According to the hydrodynamic theory, spatial Fourier components of the phason fluctuation with wavevector \mathbf{q} relax with a time constant proportional to $1/|\mathbf{q}|^2$. The short-wavelength (large $|\mathbf{q}|$) component is thus rapidly relaxed whereas the long-wavelength one cannot be relaxed completely. Such unrelaxed fluctuation is a kind of disorder and yields diffuse scatterings around Bragg peaks. Depending on the phason elastic constants (so-called K_1 , K_2 and K_3 for the icosahedral case, where K_3 is the phonon-phason coupling) one particular mode of the fluctuation has a larger time constant than others and eventually dominates the phason disorder. This is a scenario proposed by Widom and Ishii [35] and is exactly what de Boissieu observed in *i*-AlPdMn [36].

In this case of the long-wavelength phason fluctuation, individual phason flips, which are local rearrangements of underlying tiles or atomic jumps, correlate at a long distance because the same Fourier mode is responsible for them. This correlation is an important consequence of the quasiperiodic order in the system.

Edagawa observed local phason flips in high-resolution electron microscopy [34]. It would be very nice if he also observed that long-wavelength components of the phasons remain unrelaxed in the sample after long-time measurement, but apparently this has not yet been tested. For the jumps observed by EDAGAWA (also Coddens's time-of-flight measurements [37]), ISHII believes the short-wavelength component of the fluctuation and its fast dynamics play primary roles. The hydrodynamic description is not appropriate enough for such flips localized in real space. *In situ* observation of the relaxation process, if possible, would be interesting and important for further understanding of the phason degrees of freedom in quasicrystals.

2.2.3. Phason elasticity from other models?

MIKE WIDOM calls attention to issue of the derivation of phason elasticity from the various stabilization models. To date the square-gradient elasticity has been derived only for random tiling models, and appears to be valid for matching rule models in their high temperature "random tiling" phases. I am not aware of the status of elasticity properties for models based on either pseudogaps or on cluster density maximization. I would encourage people advancing such models to determine their elastic properties. At the same time, WIDOM would appreciate a survey of the experimental support for square-gradient elasticity and an assessment of whether it should be considered as experimentally proven.

2.3. Experiments on phason dynamics

K. EDAGAWA: It appears that a large phason mode occurs, which is a combination of many elementary flips. But it is not sure this is part of a long-wavelength phason mode.

In this subsection, KEIICHI EDAGAWA addresses M. WIDOM'S question, – is there agreement as to what Edagawa observed in the [video] HRTEM experiments [34], that claimed to see phason hopping? – and some related issues. Note that in this work, we can construct a tiling structure from the image without ambiguity. The tile vertices can be lifted up to the high-dimensional lattice, from which we can define the spatially

varying phason displacement $\mathbf{h}_\perp(\mathbf{r})$ (a smoothed function obtained from the staircase structure in the high-dimensional space).

Question 1. What is observed by us?

It is a going-back-and-forth phason flip in a tiling with edge length 2 nm. Of course it is not a long-range phason fluctuation itself but a localized phason flip.

Question 2. The term 'phason' should be used only for long-range mode (many theoretician may think so). Therefore, should such a localized flip be called just 'flip' or 'flippon'?

EDAGAWA does not think so. The flip we observed is not just a flip but a flip leading to the change in the local value of $\mathbf{h}_\perp(\mathbf{r})$ [constructed as explained above]. Hence, such a flip is properly called 'phason flip'.

Question 3. How can one relate such a local phason flip to the long-range phason mode?

First of all, such a long-range phason fluctuation must consist of a combination of local phason flips. It is not sure whether the particular phason flip we observed is part of a long-range phason mode fluctuation. We attempted to deduce spatial and temporal correlations from our movie, but we could obtain no clear result due to limited area-size and time-duration in the observation. However, we can safely say at least that what we observed is a local fluctuation of $h(\mathbf{r})$, as Prof. ISHII pointed out.

Question 4. The time scale in the phason flip we observed is by many orders longer than those observed using neutron and Mössbauer by Coddens et al. Why?

What they observed is an elemental phason flip involving only a single atom (or a few atoms). What we observed is a larger-scale phason flip in a 2nm tiling in HRTEM images, which are a projection of the structure (through a thickness of maybe 30nm): this flip consists of a combination of many elementary phason flips. That seems to explain qualitatively the large difference in the time-scale, though no quantitative evaluation has been made.

2.4. Phasons and electronic structure

In this subsection, GERARDO NAUMIS has elaborated the connections between notions of average lattice, phason disorder, clusters, and the electronic stability of quasicrystals [39]. Since we know that phasons exist, and assuming that quasicrystals are stabilized electronically via the Hume-Rothery mechanism, somehow the electronic structure must remain the same when phasons are introduced. How is this possible?

2.4.1. Phasons and inflation/deflation

The first question is whether phasons are local jumps or coherent? In Refs. [40] and [41], we showed that even if the [cut] window is shaken at random in the higher dimensional space, there is a spatial correlation in the sites where phasons are observed. The picture for phasons was found to be to that for vacancies: at small scales, one can describe them as jumps, but at large scales, conservation laws determine the behavior.

What is really correlated for phasons is the *probability* of having phason jumps [40], which is different for different sites. The sites with a bigger probability of jumps are in the edges of the window [39]; then the probability of phason jumps depends on the perp-space coordinate in a way related to the deflation rules of the quasicrystal.

Indeed, it was observed experimentally [38], that phasons occur in deflated structures. Namely, sites at the center of the cut band, or window, are very unlikely to flip-flop, since the window would need a huge fluctuation in order to not include such a site. So, one can define an ‘effective band width’ [of these unlikely sites], a reduced window which turns out to be just a deflation.

2.4.2. Consequences for electronic structure

Next we must prove that phasons in the sites where they are likeliest to happen, do not compromise the density of electronic states and this do not destroy [destabilize] the quasicrystal. In a Fibonacci chain this was confirmed and in high dimensions it also seems to be true [39]: sites that are far from the center of the cut window do not contribute so much to the diffraction bright spots, which are what determine the electronic gaps [42]. Another way to express this is that the stable points, corresponding to the center of the cut window, are more likely to belong to the ‘average lattice’ points, which contribute the most to the bright diffraction spots [43] and thus determine the electronic structure.

3. Stabilization of quasicrystals

Most participants were aware that there are two general viewpoints on quasicrystal stabilization – energetic stabilization of an ideal quasiperiodic structure, versus random-tiling ensembles which are presumed to be stabilized (but only at higher temperatures) by tiling configurational entropy. This is taken up in HENLEY’s discussion paper [3]. [It also forms one subtext of the phason discussions, since it is claimed that the hydrodynamic elasticity observed in diffraction experiments [36, 31], is realizable only in a random-tiling-type state.] But relatively little of the discussion was devoted directly to this dichotomy, perhaps because there was little new to say.

3.1. Mechanisms of stabilization: miscellaneous remarks

3.1.1. Role of diffraction (structural) experiments

DENIS GRATIAS: Ideal models make specific predictions [about the atomic structure as it appears in 6D]. M. WIDOM: The phason Debye-Waller factor that appears in all refinements [has the physical meaning of random fluctuations of the phason coordinate]. In effect, this is incorporating random-tiling effects in your ideal models. M. DE BOISSIEU notes that the fitted [phason or perp space] Debye-Waller factor, DW_{\perp} is in agreement with the measured diffuse scattering. He wonders [2] if this parameter is just another way to [accomodate chemical disorders of the atoms]? [W. STEURER ag

H.-R. TREBIN: We need to look for the temperature dependence of the phason elastic constants [as a way to distinguish whether its origin is mainly energetic or entropic]; it would respectively be decreasing or increasing with temperature. M. DE BOISSIEU: This experiment was already done by my group, and it shows the phason elastic constant *increases* with temperature.

3.1.2. Random tilings vs. line compounds?

There exist ‘line compound’ quasicrystals e.g. i -CdYb; MUKHOPADHYAY (with others) has wondered whether a random tiling can possibly have a definite

stoichiometry (and thus touches the applicability of the entropic stabilization model). CHRIS HENLEY clarified that the random tiling model is still applicable to line compound quasicrystals, if the stoichiometry is maintained when tiles are interchanged.

3.1.3. Hume-Rothery stabilization

To G. NAUMIS, we must start by considering that quasicrystals are electronically stabilized via the Hume-Rothery mechanism, i.e., the electronic density of states must develop a pseudogap at the Fermi energy to lower the kinetic energy per electron. (This is similar to the Peierls instability of one-dimensional metals, a static lattice deformation that breaks the periodicity.) This poses interesting questions concerning the interaction of phasons and the electronic structure, which he elaborated in that part of the discussion (Sec. 2.4). [WIDOM (Subsec. 2.2.3, above) asked practically the reverse question: what implications does the pseudogap mechanism have for phason fluctuations?]

EEUWE ZIJLSTRA has been confused by the frequent reference to 'Hume-Rothery stabilization' in quasicrystals, since he understands this term to be reserved for *sp*-type materials, such as *i*-AlZnMg [in which plane waves are mixed by potential scattering so as to split a gap right on the free-electron Fermi surface, thus lowering the energy since only the bonding state is occupied.] In icosahedral Al-TM-TM quasicrystals (and some crystals such as Al₆Mn), it appears instead that the large hybridization between the TM *d*-states and the free-electron like *sp*-states is the main contribution towards stability [44]; this is visible in the plots of Trambly de Laissardiere and Mayou [45] If the *sp-d* hybridization is turned off by hand in the LMTO Hamiltonian [45], the pseudogap vanishes (to within numerical accuracy).

3.1.4. Stabilization and soft matter quasicrystals

TOMONARI DOTERA addressed the question,

Can quasicrystals be universal over different length scales? If so, do they form with the same origin?

A general belief that, if they exist, all quasicrystalline phases are high temperature phases, may be reconsidered when one considers the new frontier of soft-matter quasicrystals. In the 'liquid quasicrystal' system reported by Ungar [46] at this conference, the dodecagonal quasicrystal phase is the *low* temperature phase, lower than other 3D spherical micellar phases such as $P4_2/mnm$ (tetragonal) corresponding to the σ phase in the Frank-Kasper family. [The hexagonal columnar phase is even lower in temperature; but that case is a different story since the spherical micelles made up of dendrons get broken up and are reconstructed into cylinders.] Chemical disorder and tiling entropies discussed in the literature may be quite different in soft matter. And the length scales grow larger – the tiling edge of the σ phases are respectively: [47]. metallic alloy ($\sim 0.5\text{nm}$), chalcogenide ($\sim 2\text{nm}$), dendron ($\sim 10\text{nm}$), and star block copolymer ($\sim 80\text{nm}$)

3.2. Mathematical question of ground-state stabilization

JOHN CAHN: Some years ago, Charles Radin *proved* that, for 'almost all' potentials in a certain mathematical sense, the ground state is non-periodic. [M. WIDOM notes that

the condition was just L^2 normalizable potentials; they are not physically reasonable, in that the potential is near zero for most distances but on a sequence of large and ever-more-widely spaced distances it has relatively large values.]

DAVID RABSON avers that to prove, mathematically, that a quasicrystal is the ground state of any realistic system (that is, not of a simplified pair potential designed to have a quasiperiodic ground state) is likely to be very difficult. Even for *periodic* compounds, has any real structure has been proven (mathematically) to be the ground state? Think how long it took just to prove Kepler’s conjecture about the close packing of spheres. Aside from the mathematical difficulties, the temperatures one would like to probe in order to say with some confidence that a system has a periodic or quasiperiodic ground state are too low for equilibration; diamond, at room temperature and pressure, is famously merely metastable.

RABSON also comments that periodic systems have one advantage in securing our faith that they really are periodic: Bloch’s theorem and all that follows from it (band structure and *e.g.*, optical and electronic properties) are so successful at describing and predicting the behaviour of periodic metals, semiconductors, and insulators that it is difficult to conceive of these materials as other than (essentially) periodic. [Of course one can still apply Bloch’s theorem to quasicrystals considered as the limiting case of a sequence of approximants, but the predictive value is less.] What we need are a theoretical framework to replace Bloch’s theorem, and a set of experimental observations that make the replacement relevant.

3.3. Thermodynamic and mechanical experiments

3.3.1. Stability of quasicrystals from the viewpoint of phase equilibria

REINHARD V. LÜCK observes that we know two main reasons for stability of quasicrystals. One reason is kinetic stabilization, the other is thermodynamic stabilization. Kinetically stabilized states, such as the original quasicrystalline state [48] (a melt-quenched Al-Mn alloy) are often termed ‘metastable’. This term does not fix the mechanism of stabilization, it only implies that there is an energy barrier to be overcome for transition into the stable state – which was measured by extensive investigations early in the history of the metastable quasicrystals.

For thermodynamic stability of materials, as pointed out in de Boissieu’s discussion paper [2], there are two different possibilities. One is stability as a ground state of matter, at zero Kelvin, which can only be determined by heat of formation or enthalpy ΔH . In any (theoretical) model several contributions to ΔH should be taken into account. Only pure metals and perfectly ordered intermetallics can be the ground state of matter according to the second law of thermodynamics; this rules out the possibility of a random tiling model as a ground state.

The other possibility is stability at ambient and high temperature; this is determined by the Gibbs [free] energy ΔG , which includes (as is well known) an entropy term. Contributions to configurational entropy may arise from topological and chemical disorder: they include, in pure metals, vacancies, interstitials and vibrations; in solid solutions, also the entropy of mixing; and in intermetallics and ordered alloys, anti-structural atoms and chemical disorder. Quasicrystals have yet another contribution to entropy, which is based on phasonic disorder or (for short) ‘phasons’, which can be topological or chemical or a combination of the two types. At present it seems to be quite certain that quasicrystals can be found in a thermodynamic stable state at high temperature. Certain quasicrystalline modifications are only stable at

high temperatures, e.g. the ‘basic Ni’ i.e. Ni-rich d -AlCoNi stabilized by the entropy of mixing Ni/Co [50], also other decagonal or five-fold variants.

LÜCK considers it a still open question if quasicrystals can exist as a ground state of matter. Direct measurement of the heat of formation requires investigation of all competing phases of the alloy system, e.g. by Saâdi *et al* [51] in the Al-Cu-Fe system. A conclusion was hard to reach, since the differences of measured ΔH values were small; a second paper [52] stressed that the icosahedral phase can be the ground state, since the values of ΔH versus concentration form a convex configurational polyhedron.

Experimental attempts to clear up this point require great care to overcome kinetic difficulties at low temperature, e.g. slow diffusion, so the equilibration time exceeds a human lifetime. There is evidence that many found states, especially some of the so-called approximants, are not sufficiently in thermodynamic equilibrium. Even the most perfect quasicrystals exhibit phasonic defects, and it seems very difficult to get rid of them.

Several projects have pointed up the quite important role of diffusion in quasicrystals; failure to allow sufficient time for this results in metastable states. But if experiments are performed at a micro or nano scale in order to reduce equilibration time, the surface energy may falsify the results. As most quasicrystals are formed from the liquid state in a peritectic reaction (often extremely incongruent), the role of diffusion during single crystal preparation must be considered. As-cast states formed under usual cooling rates and even after moderate cooling rates may be metastable states, due to undercooling or low diffusion rates. Therefore, LÜCK and collaborators have discussed the as-cast states of Al-Cu-Fe [53] separately from the equilibrium states [54].

3.3.2. Probing stabilization by non-equilibrium processing

Regarding the low temperature stability of quasicrystals, N. K. MUKHOPADHYAY pointed out that at low or even room temperature, it is extremely difficult to achieve the equilibrium condition in ternary and quaternary compounds, as the kinetics is too sluggish due to the low diffusivity: it is a frozen state. However, we can adopt non-equilibrium processing techniques (such as electron irradiation [58], ion milling, mechanical milling [59, 60, 61] etc.) to energize the system by inducing defects, thus driving it towards a stable or metastable configuration.

With these techniques, we gain the help of ballistic diffusion to overcome the problem of low thermal diffusivity. In fact it may be possible to achieve the equilibrium state by suitably controlling the process parameters. It is therefore instructive to exhaust the possibilities by optimizing the experimental condition.

Furthermore, while adopting these techniques there is also a possibility of obtaining a nanophase microstructure, in which case the overall thermal diffusivity is enhanced, and the diffusion distance is reduced. As a result, the equilibration can be achieved at a faster rate even at lower or intermediate temperature range during the annealing/thermal treatment followed after the non-equilibrium processing techniques. However extreme precaution needs to be taken to avoid the contamination or compositional changes during these processes; otherwise artifacts may lead to incorrect conclusions.

Many examples of phase transformations were found (by e-beam irradiation/mechanical milling) in Al-transition metal quasicrystals by the groups of URBAN [58] and MUKHOPADHYAY [59].

Thus it appears that these quasicrystals are *not* stable at room temperature. Therefore, careful experiments of the kind mentioned above are worth pursuing in order to ascertain the relative stability/instability of the quasicrystal phase at lower temperature. However, what is the stable configuration in the (true) ground state phase is still an open question, and needs further studies on both the theoretical and experimental fronts.

3.4. Role of *ab-initio* calculations

MIKE WIDOM asserted that, in fact, highly accurate and reasonably efficient first-principles calculations are starting to give us a real possibility to know answer [whether there is a quasicrystal ground state] from theory rather than experiment. He recommended the ‘CALPHAD’ method to resolve the stability of quasicrystals. In brief, that means we combine experiments (e.g. on heat capacity) with first-principles calculation (mainly at $T = 0$) – putting together every scrap of known information – to obtain $G(T, x)$ at low temperatures.

The problem of quasicrystal stabilization is essentially a question of alloy phase diagram topology. The equilibrium phase diagram in the (x, T) composition/temperature space must be derivable from a free energy function $G(x, T)$. Published phase diagrams drawn solely on the basis of empirical observation, without reference to the underlying free energy, often have the embarrassment of details that are thermodynamically improbable, or even impossible [55]. Such pitfalls are avoided through use of the CALPHAD method, which utilizes databases of thermodynamic functions. This method suffers from a shortage of accurate data for quasicrystal-forming alloys, but filling in the missing information can be a helpful common focus for metallurgical research efforts that will result in significant advances in our understanding.

A newly developing approach seeks to incorporate data from first principles calculations [56]. By a happy coincidence, first principles methods are at their most powerful at very low temperatures, where traditional experimental methods suffer from long equilibration times. This approach can help refine complex alloy structures and also distinguish low temperature stability from metastability [57]. Demanding $G(x, T)$ be consistent simultaneously with reliable experimental observations and with accurate calculations provides useful checks on both experiment and theory. WIDOM recommends that quasicrystal researchers wishing to address thermodynamic stability consider CALPHAD as an organizing principle for their efforts. [M. DE BOISSIEU reminds that calorimetric experiments are needed as one kind of input. [2].]

J. CAHN: Have you ever correctly predicted the melting temperature of a single compound? M. WIDOM: No, but that isn’t necessary. The proposal is not only to use first-principles calculations, but also thermodynamic data. The former methods are surprisingly good at low temperatures; [the latter data are easy to obtain near melting].

JOHN CAHN: How does the calculated total energy scale with the order of the approximant? M. MIHALKOVIČ: Not enough example approximants have been computed for us to extract the scaling.

K. F. KELTON brought up the paper of R. G. Hennig *et al* [62] which suggested that *i*-TiZrNi might be an equilibrium quasicrystal. The best decoration model for the quasicrystals had an *ab-initio* energy lying only 3 meV/atom above the tie-lines of competing crystalline phases. [But, in recent *ab-initio* calculations of phase diagrams

by M. WIDOM and collaborators, which use comparatively large approximants to model decagonal quasicrystals, that energy would be considered a sizeable difference. C. L. HENLEY, a coauthor of Hennig and Kelton, notes that the *i*-TiZrNi calculation was limited to smallish approximants each containing only one kind of ‘canonical cell’ (or ~ 200 atoms after decoration). That energy probably gets smaller if we take into account that different kinds of canonical cells are mixed, but quite possibly a moderate-sized approximant would beat the quasicrystal.]

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