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Enforcement of matching rules by chemical ordering in the decagonal AlCuCo quasicrystal

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An atomic structure model of the decagonal AlCuCo quasicrystal is proposed. The matching rules recently found by R. Klitzing *et al.* [Int. J. Mod. Phys. B (to be published)] for an abstract triangle tiling are enforced by specific Cu (Co) ordering, reducing the symmetry to $P10_5/m$. The model renders very simple Kalugin's homology indices of (1,0) for Al and (0,1) for Cu (Co) and the "magic" Al composition of $\tau^{-1} \approx 0.618$. Coupling of the chemical and phason disorders is suggested.

An atomic structure model of decagonal AlCuCo and AlNiCo was proposed by the author[1] and then slightly amended.[2] It has been in good agreement with experimental data (high resolution electron microscopy images[3] and x-ray diffracto-grams[4−6]) available until recently. Here I communicate further refinement of the model and discuss its compliance with the latest experiments, namely thorough examinations of equilibrium phase diagrams of the decagonal AlCuCo (Ref. 7) and AlNiCo,[8] as well as the icosahedral AlCuFe.[9] These studies show that though at elevated temperature the quasicrystalline phase is stable in a rather wide region of compositions (usually, about 10%), with the temperature lowered the region shrinks to virtually a point (as small as 1% at 550 °C, the lowest reported temperature). This suggests existence of a single magic composition, below referred to as "stoichiometric," where the stability persists down to $T = 0$. Many recent experiments indicate that specifically quasicrystalline properties, from structural perfection to low conductivity, are the most salient at this magic composition, making it the best candidate for the composition of the ideal, defectless, "theoretical" quasicrystal. Accordingly, below the consideration will be restricted mainly to this stoichiometric composition.

(1) AlCuCo and AlNiCo are not completely isostructural. Until recently they have been believed isostructural because their reciprocal lattices are identical and even intensities similar.[4−6] In fact, the two alloys could be isostructural if one did not care about which atomic positions are occupied by which chemical species. However, recent experiments point to at least systematic Al to Cu (Co) substitutions, which violate full equivalence. Indeed, the stoichiometric composition of AlNiCo (Ref. 8) seems to be $Al_{73}(Cu,Co)_{27}$. The Al content, 0.73, is closely approximated by $5\tau/(5\tau+3)$, leading to Kalugin's homology indices of (5,0) for Al, (0,3) for Cu (Co) and (5,3) overall (the latter is corroborated by the density data[1,10]). In AlCuCo the stoichiometric Al content was isolated

within the 0.62–0.64 interval,[7] suggesting the true value to be $\tau^{-1} = 0.618$. (Incidentally, the same τ^{-1} value for the Al content was recently reported by Bancel in the icosahedral AlCuFe.[9]) Combining previously obtained (1,1) overall homology indices[1,2] with the τ^{-1} composition one could suggest (1,0) for Al and (0,1) for Cu (Co), which are obviously different from the analogous numbers of AlNiCo. [Recall that (1,1) is equivalent to (5,3),[10] leaving a chance for partial isotypism, up to Al–Cu (Co) substitution.] Kalugin's homology indices are a fundamental characteristic of a perfect quasicrystal (in simplified terms, they show how many times atomic motifs wind over the hypertorus[10]); they are almost as fundamental as the space group. In any event, two perfect quasicrystals cannot be equivalent if their homology indices differ. Thus, despite apparently identical indexing the two quasicrystals, AlCuCo and AlNiCo, are characterized by different hyperspace atomic motifs. The further refinement of the model[1,2] reported below is applicable only to the structure of AlCuCo; no ideas have been suggested about AlNiCo.

(2) From binary tiling to Klotz triangle tiling. The previous version of the model[2] viewed the structure as a specifically decorated binary tiling.[11] The tiling sites were occupied by two decagonal clusters, small and large.[1,2] The model gave reasonable (1,1) overall Kalugin's indices (which agree with the density data), but unrealistic (13,7) for Al and (8,6) for Cu (Co) (further denoted as M); the Al content was 60%. This prompted me to pick certain M atomic positions and place Al atoms there, changing individual indices to (13,8) and (8,5), which are equivalent to reasonable values of (1,0) and (0,1) under τ^3 deflation.[10] In the perpendicular space this substitution should correspond to minor redrawing of the Al-M border. This task can be achieved in several manners, but one method looks preferable, as will be seen from what follows. These new atomic motifs are shown in Figs. 1(b) and 1(c), accompanied with a corresponding

real space image of Fig. 1(a). (At the current stage, one pays no attention to symbols distinguishing Cu from Co; their significance becomes apparent later; here Cu and Co are still randomly mixed, as in Refs. 1 and 2.) The structure so defined possesses the desired (1,0) and (0,1) indices for Al and M, respectively, and the Al content becomes $\tau^{-1} \approx 0.618$. However, the small cluster loses its decagonal symmetry and the present structure [Fig. 1(a)] is not a binary tiling anymore. It can be viewed as a decorated tiling of the plane by two Robinson triangles, with large clusters sitting at the tiling sites. The current tiling, as a mathematical object, without any reference to atomic decoration, was introduced and extensively studied in Ref. 12 and will be called below Klotz triangle tiling (KTT), because it was obtained by "Klotz construction."[22] KTT is not equivalent to the canonical Penrose tiling[13] and, in a sense, is even simpler than the latter: the vertices of this triangle tiling are generated by a single atomic motif, a regular decagon.[12] The above statement concerning the equivalence of this tiling decorated as in Fig. 1(a) and the quasicrystal generated by the atomic motifs of Figs. 1(b) and 1(c) is not just a result of a speculation or a computer simulation, but a mathematically rigorous statement (the proof will be presented elsewhere). Lastly, it is worth noting that the equivalence
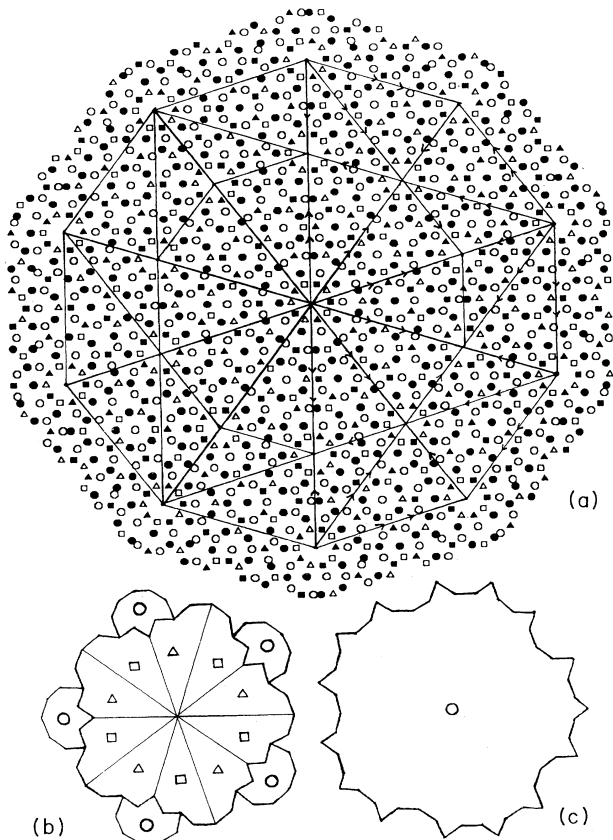
guarantees the uniqueness of the decomposition of a given projected atomic pattern into triangle tiles, as in Fig. 1(a). (The same property holds for other models discussed below.)

(3) Matching rules for Klotz triangle tiling and distinguishing Cu from Co. The mathematical concept of matching rules was introduced by Penrose[13] and later applied and further developed (see, e.g., Refs. 14–17). The matching rules mechanism is regarded as a possible mechanism of expanding specific local order over the whole quasicrystal, thus establishing true long-range quasiperiodic order. Though the undecorated Klotz triangle tiling possesses many properties of "perfect" tilings,[12] it lacks the local matching rules. (Technically, even undecorated KTT can be obtained by matching rules in Levitov's formulation[16] by specifying an atlas of allowed local configurations; however, physical implementation of these rules looks quite implausible due to the rather large size of the configurations, which would, in turn, require nonvanishing interatomic interactions between, say, 100th neighbors.) However, complementing sides and vertices of triangles with arrows, Klitzing *et al.* recently managed to prove the existence of matching rules for the arrow-decorated KTT.[18] These rules are shown in Fig. 3: when two triangles share a side, the ar-
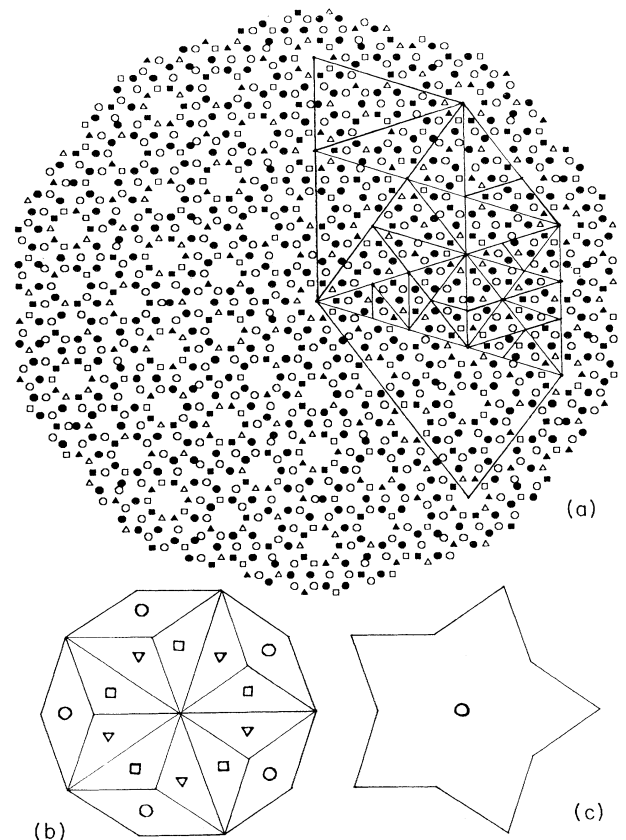

FIG. 1. (a) Decoration of the Klotz triangle tiling (l, the long bond, is 19.6 Å): $\bigcirc$, Al, $\triangle$, Cu, $\square$, Co; empty symbols mark $z = +1/4$ layer, full $z = -1/4$. The hyperspace atomic motifs of the $z = +1/4$ layer: (b) $\triangle = +2$; (c) $\triangle = -1$ [$\triangle$ gives the coordinate along the commensurate hyperspace direction (Ref. 1)].

FIG. 2. Decoration of the tiling with $l = 7.5$ Å (the τ^2 deflation of the KTT of Fig. 1), same notations as in Fig. 1. True elementary cells are the smallest triangles; composite tiles of the three subsequent inflatory steps are also shown. The decagon side length in b is 2.44 Å, the quasilattice constant.
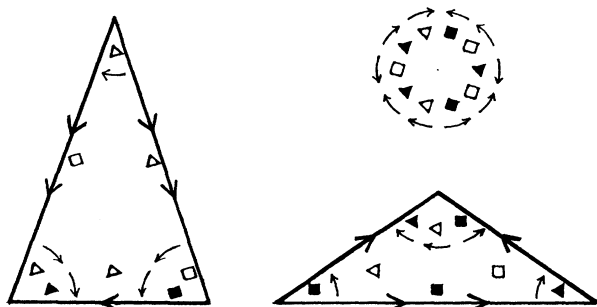
FIG. 3. Arrow matching rules and their representation by Cu (Co) ordering (same notations as in Fig. 1). Only those M atoms relevant to the matching rules are shown.

rows must be codirectional and the rim of arrows around every vertex must be as in Fig. 3 (up to a rotation). If an arbitrary triangle tiling satisfies these rules it is inevitably a perfect quasiperiodic tiling which lifts up to the decagonal atomic motif with sharp boundaries. In other words, local matching rules establish the long-range quasiperiodic order. One is tempted to decorate triangles with real atoms, so as (i) the atomic decoration is equivalent to the arrow decoration of Fig. 3, (ii) the hyperspace motifs *for individual atoms* are still simple and not numerous[1] and (iii) the structure agrees with the experiment. This appears to be possible; one such decoration is shown in Fig. 1(a): just the above introduced atomic structure but with a special chemical ordering of Cu and Co. The mapping to the arrow decoration is seen in Fig. 3: clockwise arrows correspond to Cu, counterclockwise to Co (or vice versa, opening the way for antiphase domain formation). Note that the matching of the on-side arrows translates into the requirement: Two neighboring M atoms adjacent to the shared side must be unlike [Fig. 1(a)], which reduces the number of short Co-Co bonds, the feature often believed to lower the cohesive energy. The compliance with the criterion (ii) above should be further discussed. What happens when one lifts individual atoms up into the hyperspace? It turns out (read: the proof will be published elsewhere) that Cu and Co separate from each other simply occupying 36° wedges [Figs. 1(b) and 1(c)].

(4) Alternative decorations and inflation-deflation. The decoration of Fig. 1 is not the only one consistent with the matching rules of the KTT; several more have been developed. Modifications could include systematic Al-M permutations (no more substitutions, to maintain the τ^{-1} Al content) as well as relatively small atomic displacements (not to be mixed up with atomic relaxations, the atoms must hop from one site of a Penrose-like network to another, to preserve simple hyperspace motifs for individual atoms[1]). Certain M atomic positions are not vital for the matching rules and, therefore, allow Cu-Co substitutions. Along with such redecorations which leave the tiles unchanged the inflations or deflations of the triangles themselves could be considered. Figure 2 exemplifies an atomic structure, which is also a decoration of the same KTT, but the triangles are τ^2 deflated compared to those of Fig. 1(a), $l = \tau^{-2} 19.6$ Å$=7.5$ Å. (Further

deflations lead to physically implausible atomic configurations.) The true building blocks of the new tiling are small triangles of Fig. 2(a); however, inflated composite triangles are clearly visible, in full accordance with the inflation-deflation rules proved in Ref. 12. Note that the decoration of the tiles of $l = 19.6$ Å can be viewed as a special redecoration of the tiles of Fig. 1(a). However, in Fig. 1(a) the 19.6-Å tiles *are* the elementary cells, they cannot be decomposed, whereas in Fig. 2(a) the 19.6-Å tiles are composed of 7.5-Å tiles, the true elementary cells of this tiling. From the point of view of local environments the atomic structure of Fig. 2(a) is no worse, as well as no better, than that of Fig. 1(a): no large cavities, no interatomic distance shorter than 2.3 Å, etc.; it is hard to prefer one to another without detailed cohesive energy calculations or comparison with the x-ray data (see below). However, the model of Fig. 2 has one advantage over that of Fig. 1: the phason flip in the former is much simpler, and can be achieved mainly by small atomic displacements, without long jumps, which are required for a couple of atomic positions in the model of Fig. 1. This property is thought to be important for enabling the material to get rid of phason defects introduced during the solidification. Lastly, lifting into the hyperspace results in extremely simple motifs of Figs. 2(b) and 2(c) (the proof will be given elsewhere).

(5) Space group, extinctions, and the experiment. Unfortunately, the general belief that AlCuCo and AlNiCo are isostructural served us badly. The best experimental results are obtained for AlNiCo.[5,6,19] The data on AlCuCo is limited to the HREM of Ref. 3 and the single-crystal x-ray analysis of Ref. 4. The accuracy of both is insufficient to distinguish between the three models proposed above or the old version,[2] neither is it enough to confirm or rule out even a random binary tiling. Indeed, the calculated R factor quantifying the difference between, say, the structure of Figs. 1 and 2 is only 4%; at the same time the effect of the shift in composition is much more pronounced, as well as the effect of the crystal imperfection. The set of the x-ray intensities was collected in Ref. 4 from an as-cast sample of $Al_{65}Cu_{20}Co_{15}$ composition, whereas we need Al_{62}. Moreover, such as-cast samples were recently shown[20] to be structurally inferior: compositionally inhomogeneous, strongly supersaturated, and unstable under heat treatment; they even give the wrong space group (see below). For this reason the standard comparison of the calculated diffraction patterns for the above introduced models with those measured in Ref. 4 is pointless; more experiments on good quality samples, which have become available since the completion of Ref. 4, are needed. Experimental verification of the Cu-Co chemical ordering, suggested above, looks even less plausible than distinguishing between different decorations: the calculated R factor between chemically ordered and disordered versions of, say, Fig. 1 is less than 1%; anomalous x-ray or neutron scattering is needed to resolve very low x-ray contrast between Cu and Co ($Z = 27$ and 29, respectively). Nevertheless, circumstantial evidence could be obtained from the extinctions. The separation of Cu and Co, as in both Figs. 1 and 2, is inconsistent with the 20 mirrors which

were present in the chemically disordered version. Recalling the atomic arrangement along the periodic Z direction, the space group becomes $P10_5/m$ or $V(r^{1/2},h)_{10}$ in notations proposed by Mermin and co-workers.[21] A chemically disordered version gave $P10_5/mmc$ or $V(r^{1/2},h,m)_{10}$, as in Refs. 1 and 2. Note that the point group of the reciprocal lattice remains unaffected by the chemical ordering: it is $10/mmm$ for both ordered and disordered versions. Characteristic extinctions for the two space groups are $(0000n)$, odd n, for the ordered structure (the last index marks the periodic Z direction) and, for the disordered structure, the whole lines *between* the star vectors in odd-n layers are extinct.[21] These extinctions are the subject of the old controversy: most diffractograms (both x-ray and electron) available until recently showed these lines extinct,[3−6] testifying for $P10_5/mmc$, whereas Yamamoto *et al.*[19] saw these forbidden reflections. However, it has been recently shown that whereas in as-cast samples the referred lines are extinct, in properly cooked samples of well controlled and homogeneous composition they rekindle, though very dim.[20]

Summary. A structure of Fig. 1 should be preferred over that previously suggested[2] on the grounds of better Kalugin's homology indices, more realistic stoichiometric composition (namely, the τ^{-1} Al content), and better compliance with the density data (both measured and calculated are 4.7 g/cm^3). However, this structure is not the only one consistent with available experimental data; several more, such as one of Fig. 2, could be developed. To distinguish between them more experiments on better quality samples are required. The recently discovered matching rules for the Klotz triangle tiling[18] could be enforced by a special chemical ordering of Cu and Co. This mechanism implies strong coupling between the phason and chemical disorders: no chemical order, no matching rules, no exact quasiperiodicity (i.e., smeared boundaries of atomic motifs). Atomic coordinates in parallel space as well as calculated diffraction patterns are available upon request (burkov@physun.physics.mcmaster.ca).

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