Structural model for the $Al_{72}Ni_{20}Co_8$ decagonal quasicrystals

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We propose a structure model for the $Al_{72}Ni_{20}Co_8$ decagonal quasicrystals based on its τ^2-inflated $Al_{13}Co_4$ approximant phase: Applying a 10_5 screw operation on a monolayer obtained from the approximant reproduces almost all features of 2-nm clusters seen in atomic-resolution *Z*-contrast images of $Al_{72}Ni_{20}Co_8$ decagonal quasicrystals. The exception is the central ring, where the symmetry is broken due to chemical ordering of Al and transition metals. By restricting possible overlaps, this enforces the perfect quasiperiodic tiling.

Decagonal quasicrystals can be described by quasiperiodic packing of atomic clusters.[1] For example, all Al-based decagonal quasicrystals (e.g., Al-Ni-Fe, Al-Ni-Co, Al-Cu-Co, ...) comprise distinct 2-nm clusters.[2–5] The detailed determination of the atomic arrangements within the 2-nm clusters is critical for understanding why quasicrystals form. So far, many structural models have been proposed for decagonal quasicrystals based upon x-ray and neutron diffraction, high-resolution electron microscopy, and theoretical calculations.[6–11] However, controversies still remain among these models. It is well known that quasicrystals and their approximant phases have very similar chemical compositions, densities, and electron diffraction patterns, and reversible transformations between the two have been reported.[12] These observations indicate that quasicrystals and their approximant phases have many similar *local* structures. Thus an alternative approach to build the structure of quasicrystals is to understand the differences and relationships between quasicrystals and their approximant phases.

In the present paper, we use this approach to propose a structure model for the 2-nm clusters of the $Al_{72}Ni_{20}Co_8$ decagonal quasicrystal. We take pentagonal structural features present in its closely related τ^2-inflated $Al_{13}Co_4$ approximant phase to propose a cluster monolayer. Applying a 10_5 screw operation to this layer then gives a perfect fit to all features seen in atomic-resolution *Z*-contrast images obtained from the $Al_{72}Ni_{20}Co_8$ decagonal quasicrystal, *except* within the central ring. Here we observe broken symmetry induced by chemical ordering. This ordering restricts possible cluster overlaps and so enforces the perfect quasiperiodic tiling. At the same time, imperfect ordering throughout the structure creates the entropic stabilization necessary to explain why this phase is only stable at high temperatures.

We focus on the $Al_{72}Ni_{20}Co_8$ decagonal quasicrystal because of its high perfection[5] and because the structure of its closely related τ^2-inflated $Al_{13}Co_4$ approximant phase (a phase with *a* and *c* lattice parameters τ^2 times greater than those of monoclinic $Al_{13}Co_4$, where τ is the golden mean) has been well determined.[13] So far, $Al_{72}Ni_{20}Co_8$ is the only high-perfection decagonal quasicrystal ever found, showing no diffuse scattering in electron diffraction. This indicates that it has a periodicity of about 0.4 nm along its periodic axis. Our atomic-resolution *Z*-contrast images[14] [Figs. 1(d)–1(f)] show an important difference from the most popular models for the 2-nm clusters of Al-Ni-Co and Al-Cu-Co de-

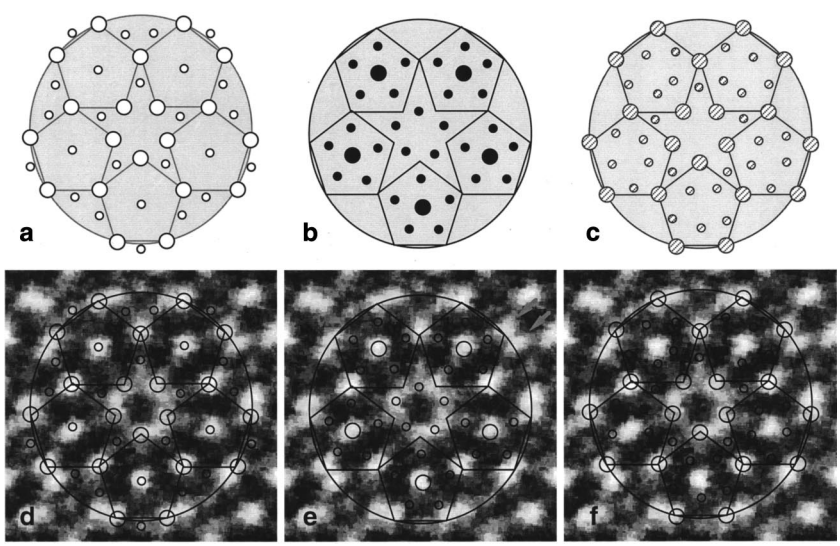

FIG. 1. (a)–(c) Three layers of the 2-nm clusters seen in τ^2-inflated $Al_{13}Co_4$ approximant (from Ref. 13) with (d)–(f) superimposition onto a high-resolution *Z*-contrast image of a 2-nm cluster of the high-perfection decagonal quasicrystal $Al_{72}Ni_{20}Co_8$, viewed along the tenfold axis.

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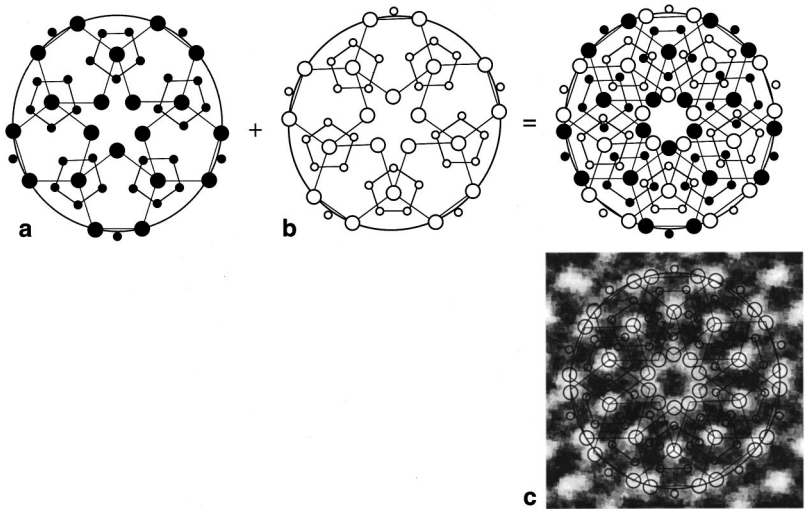

FIG. 2. (a) A layer structure obtained from the $z=0$ layer of the τ^2-inflated $Al_{13}Co_4$ approximant. Only the Al atoms in the third ring are rearranged to form small pentagons. (b) The layer after applying a 10_5 screw operation on (a). (c) Both layers (a) and (b) are superimposed on the *Z*-contrast image. The TM columns are the bright features, while the less intense intensity maxima (gray) are Al columns.

cagonal quasicrystals: These proposed models have one more ring containing transition metals (see, for example, the second outermost ring in the model proposed by Burkov[7]). We now analyze the relationships between the $Al_{72}Ni_{20}Co_8$ decagonal quasicrystal and its τ^2-inflated $Al_{13}Co_4$ approximant phase. It has been reported that the τ^2-inflated $Al_{13}Co_4$ approximant phase consists of fivefold and pseudofivefold 2-nm clusters.[13] The fivefold 2-nm clusters are more similar to the 2-nm clusters seen in the $Al_{72}Ni_{20}Co_8$ decagonal quasicrystal, and their atomic structure has been determined recently.[13] They contain four layers, since the periodicity along the columnar axis is 0.8 nm. The various layers are shown in Fig. 1, (a) corresponding to $z=0$, (b) to $z=1/4,3/4$, and (c) to $z=1/2$, which are stacked in the sequence $a,b,c,b,\ldots$. It is seen that the (a) and (c) layers differ only in the Al atom positions, which are more disordered in (c).

All Al-Ni-Co decagonal quasicrystals have been reported to contain a 10_5 screw axis,[2–5] and many of the previously proposed models for the 2-nm clusters have a 10_5 screw axis through their centers.[6–10] Thus the structure of the 2-nm cluster is solved once the structure for a single layer is known. We therefore need to find which layer of the fivefold 2-nm cluster of the τ^2-inflated $Al_{13}Co_4$ approximant phase is similar to the 2-nm clusters of the Al-Ni-Co decagonal quasicrystals. Figures 1(d)–1(f) show superimpositions of the three approximant layers on the *Z*-contrast image of a 2-nm cluster from the $Al_{72}Ni_{20}Co_8$ quasicrystal, taken along the periodic axis. It is seen that all sites in the pentagonal (a) layers match sites in the quasicrystal. All transition-metal (TM) atom sites show brightly in the image corresponding to high intensity, while all Al sites are seen as gray, but are still local maxima or saddle points in the image intensity, consistent with their lower *Z*. Because the (b) layer structure has no atoms in the outermost ring and the (c) layer structure has no Al atoms in the outermost ring, we do not consider these two structures further.

We now construct a cluster monolayer based on the (a) approximant layer. This monolayer must keep the key structural features of the approximant layer, e.g., all the TM atoms located at pentagonal sites. Such pentagonal shapes giving local fivefold symmetry are common in decagonal quasicrystals. We next assume that Al atoms also locate in pentagonal arrangements. The Al atoms in the third ring counting from the center are located at intensity maxima. We thus split these Al sites into two to form small Al pentagons as shown in Fig. 2(a). Now we see that this overlapping array of large TM and small Al pentagonal clusters fits *precisely half* the brightest features in the *Z*-contrast image. If we now apply the 10_5 screw operation to this monolayer, we obtain the layer shown in Fig. 2(b). Superimposing these two rotational variants on the *Z*-contrast image matches *all* image features [Fig. 2(c)].

This 10_5 screw axis can be understood as rotational ordering which occurs under certain conditions, presumably a specific range of chemical composition. The structure explains the origin of the ten columns in the central ring and the ten closely spaced TM column pairs around the 2-nm ring. Our model is similar to the model proposed by Burkov:[7] both have ten TM columns at the central ring and ten closely spaced Al and TM column pairs at the third and outermost rings, respectively. The ten closely spaced TM columns pairs at the outermost ring have also been observed by x-ray diffraction[6] and are predicted in the model of Cockayn and Widom.[10] It is noted that Burkov's model predicts a stoichiometric composition of $Al_{60}M_{40}$, which is low in Al com-

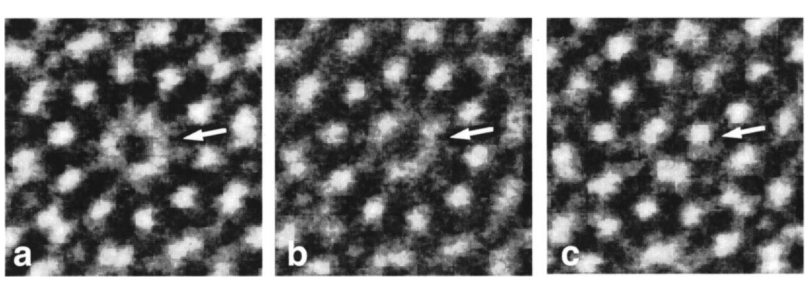

FIG. 3. *Z*-contrast images showing three 2-nm clusters with different degrees of chemical ordering at the central rings: (a) low, (b) medium, and (c) high. Chemical ordering breaks the symmetry of the central rings.

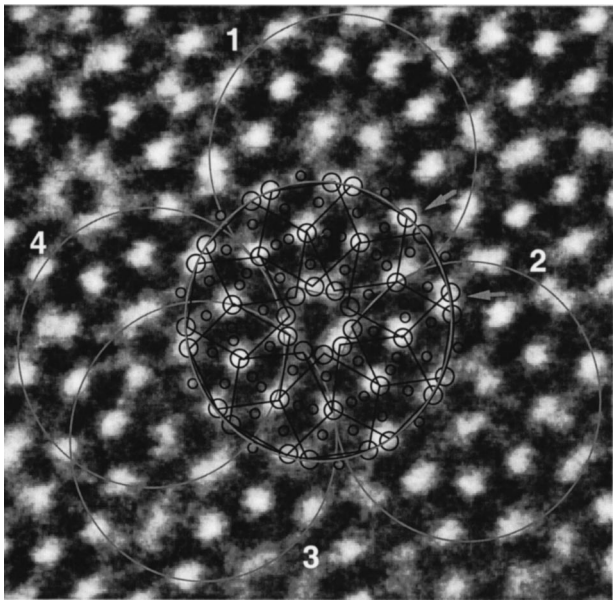

FIG. 4. *Z*-contrast image showing the four intercluster separations. The central circle shows a cluster with only four neighbors nucleated due to the broken symmetry of the central ring. These four clusters now show all the intercluster separations necessary for quasiperiodic tiling: clusters 1, 3 and 2, 4 show the 3.44-nm separation. Clusters 1 and 2 are 2.06 nm apart, as are 2 and 3 and also 1 and 4. Clusters 1, 2, 3, and 4 all show a 1.23-nm separation from the central cluster, while a 0.74-nm separation is seen between clusters 3 and 4.

pared to the $Al_{72}Ni_{20}Co_8$ decagonal quasicrystal. A major difference between our model and Burkov's model is the absence of the ten TM atoms in the fourth ring counting from the center in our model (for which there is no evidence in our *Z*-contrast images). Thus our model significantly improves the stoichiometry.

It is important to note that none of the central rings show the uniform strong intensity characteristic of ten TM columns. In Fig. 3(a), the central ring shows a relatively uniform and high intensity, but in comparison to the ring of ten TM columns, the intensity is clearly not high enough to correspond to ten full TM columns. Partial substitution by Al has taken place, which we referred to previously as chemical disorder and proposed as the source of entropy to stabilize the phase at high temperatures.[16] Chemical ordering has also been reported in other icosahedral quasicrystals.[17] The central rings of some clusters show much stronger broken symmetry, as shown in Fig. 3(c). Similar broken symmetry has also been reported previously.[3,4,15] In our images we can see that *five* columns show an intensity sufficiently high (bright) to correspond to full TM columns, one being a single column, the others forming closely spaced column pairs. The other five columns have lower intensity (gray), indicating high Al occupancy. The average composition of the ordered ring is therefore 50% TM and 50% Al. In Fig. 3(b), the central ring shows an intermediate case, also with some broken symmetry. In the disordered case, the intensities are consistent with the *same* average composition for the ring, 50% TM and 50% Al. Assuming this to be the case, the stoichiometry of our model becomes $Al_{73}M_{27}$, which is very close to the nominal composition $Al_{72}M_{28}$.

The intermediately ordered cases might also be interpreted as resulting from phason flips within individual ordered cluster columns.[18] However, we find no correlation between these different degrees of order and the configuration of overlapping clusters, as would be expected in this case. We propose therefore that these more uniform rings represent true chemical disorder. Further evidence of chemical disorder is seen in Fig. 4, where large intensity variations exist between different TM sites. These intensity variations are many times too large to be attributed to statistical noise in the image. They must represent real variations in composition in particular atomic columns, another indication of a high chemical entropy contribution.

Atomistic explanations for the overlapping cluster network in quasicrystals have been proposed previously.[19] In our case, the closely spaced pairs of TM columns that are present in the ordered central rings and in the outer rings of the clusters provide an ideal atomistic mechanism to interlink clusters and explain the matching rules.[20] Such a growth process naturally produces overlaps with intercluster separations in the ratio τ, exactly the 0.74-, 1.23-, 2.06-, and 3.44-nm spacings seen in the Gummelt coverage model of the ideal quasicrystal.[21–23] If there is no chemical ordering occurring, each 2-nm cluster will have many different ways to overlap with the next. Thus the clusters will form a random tiling. However, chemical ordering breaks the symmetry in the central rings and limits the freedom in forming overlaps. As seen from Fig. 4, the ordered central cluster has only four possible overlaps, which are in precisely the configuration of the Gummelt coverage model for the ideal quasicrystal. The overall structure would therefore show ideal quasicrystalline coverage only when complete chemical ordering occurs at the center of *all* the 2-nm clusters.

In the case of the approximant phase, if we try to overlap its clusters without the rotational variants, the density of common sites is very low. The approximant phase therefore grows only by the addition of *individual* small pentagonal units around its basic 2-nm cluster, as found by Saitoh *et al.*[3] in the case of the τ^2-inflated $Al_{13}Co_4$ approximant. Thus we believe that rotational ordering of 2-nm clusters, with chemical ordering in the central rings, is fundamental to stabilizing the quasicrystalline form. At the same time, substantial variations in site occupation occur throughout the cluster, which explains the entropic stabilization. Order and disorder coexist.

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[1] P. Guyot, and M. Audier, Philos. Mag. B **52**, L15 (1985); V. Elser and C. L. Henley, Phys. Rev. Lett. **55**, 2883 (1985); W. Steurer, Acta Crystallogr., Sect. B: Struct. Sci. **B45**, 534 (1989); H.-C. Jeong and S. J. Steinhardt, Phys. Rev. Lett. **73**, 1943 (1994).
[2] K. Hiraga, F. J. Lincoln, and W. Sun, Mater. Trans., JIM **32**, 308 (1991).
[3] K. Saitoh, K. Tsuda, M. Tanaka, A.-P. Tsai, A. Inoue, and T. Masumoto, Philos. Mag. A **73**, 387 (1996); K. Saitoh, K. Tsuda, M. Tanaka, K. Kaneko, and A.-P. Tsai, Jpn. J. Appl. Phys., Part 2 **36**, L1400 (1998).
[4] K. Tsuda, Y. Nishida, K. Saitoh, M. Tanaka, A. P. Tsai, A. Inoue, and T. Masumoto, Philos. Mag. A **74**, 697 (1996).
[5] S. Ritsch, C. Beeli, H.-U. Nissen, T. Godecke, M. Scheffer, and R. Luck, Philos. Mag. Lett. **74**, 99 (1996).
[6] W. Steurer and K. H. Kuo, Acta Crystallogr., Sect. B: Struct. Sci. **B46**, 703 (1990).
[7] S. E. Burkov, Phys. Rev. Lett. **67**, 614 (1991).
[8] A. Yamamoto, Sci. Rep. Res. Inst. Tohoku Univ. A **42**, 207 (1996).
[9] K. Saitoh, K. Tsuda, and M. Tanaka, Philos. Mag. A **76**, 135 (1997).
[10] E. Cockayne and M. Widom, Phys. Rev. Lett. **81**, 598 (1998).
[11] P. J. Steinhardt, H.-C. Jeong, K. Saitoh, M. Tanaka, E. Abe, and A. P. Tsai, Nature (London) **396**, 55 (1998).
[12] P. A. Bancel, Phys. Rev. Lett. **63**, 2741 (1989); E. R. Abe and A. P. Tsai, *ibid.* **83**, 753 (1999).
[13] K. Saitoh, T. Yokosawa, M. Tanaka, and A.-P. Tsai, J. Electron Microsc. **48**, 105 (1999).
[14] S. J. Pennycook and D. E. Jesson, Phys. Rev. Lett. **64**, 938 (1990); D. E. Jesson and S. J. Pennycook, Proc. R. Soc. London, Ser. A **449**, 273 (1995).
[15] C. Beeli and S. Horiuchi, Philos. Mag. B **70**, 215 (1994).
[16] Y. Yan, S. J. Pennycook, and A.-P. Tsai, Phys. Rev. Lett. **81**, 5145 (1998).
[17] M. Boudard, M. de Boissieut, C. Janot, G. Heger, C. Beeli, H.-U. Nissen, H. Vincent, R. Ibberson, M. Audier, and J. M. Dubois, J. Phys.: Condens. Matter **4**, 10149 (1992).
[18] S. Ritsch, H.-U. Nissen, and C. Beeli, Phys. Rev. Lett. **76**, 2507 (1996).
[19] C. Janot and M. de Boissieu, Phys. Rev. Lett. **72**, 1674 (1994); C. Janot, J. Phys.: Condens. Matter **9**, 1493 (1997).
[20] The Burkov and Cockayne-Widom models use Cu/Co ordering as a source of matching rules.
[21] P. Gummelt, Geom. Dedicata **62**, 1 (1996).
[22] M. Duneau, in *Proceedings of the Fifth International Conference on Quasicrystals*, edited by C. Janot and R. Mosseri (World Scientific, Singapore, 1995), p. 116.
[23] P. J. Steinhardt and H.-C. Jeong, Nature (London) **382**, 433 (1996).