Quasi-Unit-Cell Model for an Al-Ni-Co Ideal Quasicrystal based on Clusters with Broken Tenfold Symmetry

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We present new evidence supporting the quasi-unit-cell description of the $Al_{72}Ni_{20}Co_8$ decagonal quasicrystal which shows that the solid is composed of repeating, overlapping decagonal cluster columns with broken tenfold symmetry. We propose an atomic model which gives a significantly improved fit to electron microscopy experiments compared to a previous proposal by us and to alternative proposals with tenfold symmetric clusters.

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The $Al_{72}Ni_{20}Co_8$ decagonal phase is one of the best-characterized quasicrystalline materials [1] and an excellent candidate for comparing structural models of quasicrystals. This ideal, highly perfect quasicrystal is reproducible as a single phase in the $Al_{72}Ni_{20}Co_8$ alloy annealed at 1170 K followed by water quenching.

In a recent paper [2] (henceforth referred to as Paper I), we presented an array of evidence that the atomic structure of $Al_{72}Ni_{20}Co_8$ conforms to the quasi-unit-cell picture [3]. In this picture, the atomic structure can be decomposed into a single, repeating cluster (the quasiunit cell) which shares atoms with neighbor clusters according to specific overlap rules. As first shown by Gummelt [4], overlap rules can be sufficient to insure a unique structure that has perfect quasiperiodic translational order and the same symmetry as the Penrose tile picture based on two repeating tiles with edge-matching rules [5]. However, by reducing the structure to only one repeating unit [2–4,6], the quasi-unit-cell picture leads to a simple description of the atomic structure and requires only simple energetics [2,3] to explain why quasicrystals form and how they grow. Our study showed that, based on high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging [7] which highlights the transition metal (TM) sites [Z(atomic number)-contrast [8]], the quasiunit cell for $Al_{72}Ni_{20}Co_8$ can be constructed from a 2 nm diameter, decagonal cluster column whose atomic arrangement breaks tenfold symmetry. We further proposed a specific atomic structure which cannot be described as a simple decoration of tiles in a Penrose tiling even though it can be described as a "covering" composed of identical, overlapping, decagonal cluster columns [2].

In this paper, we present an improved atomic model [Fig. 1(a)] and new experimental evidence for a key feature arising from the quasi-unit-cell picture: namely, the atomic decoration of the quasiunit cells has broken tenfold symmetry isomorphic to the overlap rules. The improved model is motivated by recent criticisms by Yan and Pennycook (YP) who presented a very high-resolution HAADF-STEM image that revealed some disagreements with our earlier atomic description [9] (this is also criticized recently [10]).

The central issue highlighted by YP is whether the decagonal clusters have "intrinsic" broken symmetry, as we suggest, or whether the fundamental atom cluster is tenfold symmetric similar to some previous structural models [6,11–13] and the broken symmetry is only a consequence of random chemical and occupational (vacancy) disorder due to overlapping of neighbor clusters [6], as YP suggest [9]. (We use the term intrinsic to refer to broken symmetry that is a built-in aspect of the atomic decoration, as opposed to a random disorder effect superposed on a fundamental cluster with tenfold symmetry.) Although both possibilities are consistent with the quasi-unit-cell picture [2] (in the sense that both are described by a single repeating cluster which could obey the same overlap rules; for symmetric clusters, energetics such as interaction between three clusters would prevent wrong overlaps), the question is significant because we have argued that the broken symmetry is fundamental to the structure and a direct manifestation of the overlap rules.

Our first step is to address the criticisms of our earlier model by YP based on HAADF-STEM images. We modify the atomic decoration of the quasiunit cell; see Fig. 1(a). The changes from the previous model are as follows: (i) switch Co atoms from the interior of kite-shaped regions (near the acute corner) with Al on the edges of the kite-shaped region in Fig. 1(a); and (ii) add three Al atoms in the central kite interior. As in our earlier model, the quasiunit cell has an atomic decoration that breaks tenfold symmetry in a pattern isomorphic to the configuration of kites inscribed in the decagon, which represent the overlap rules [2–4]. (The "kite" is the convex polygon inscribed with light-blue in the decagon of Fig. 1(a); neighbor decagons can overlap only if any kite regions in the overlap region lay precisely on top of one another.) The improved model now fits all TEM imaging data (Figs. 2–4), reproduces the observed $P10_5/mmc$

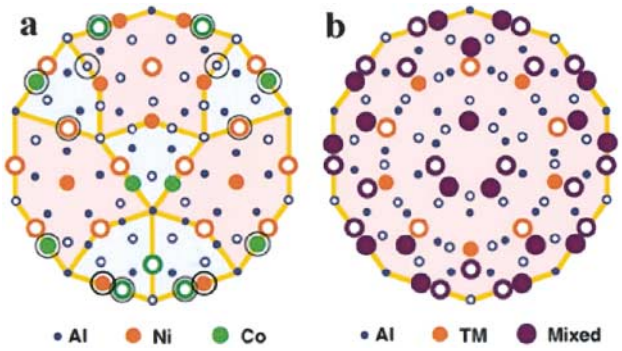

FIG. 1 (color). Two competing models for the atomic decoration of the decagonal (2 nm) quasiunit cell for $Al_{72}Ni_{20}Co_8$: (a) our proposed model with broken tenfold symmetry and (b) an alternative model with unbroken tenfold symmetry but with accidental symmetry breaking introduced in the central region due to chemical and occupational (vacancy) disordering. Solid circles represent level $c = 0$ and open circles represent $c = 1/2$ along periodic c axis. Figure (a) also includes atoms added by overlap [2–4] of neighbor clusters (encircled in black).

symmetry, and has density (3.98 g/cm^3) and stoichiometry $Al_{71.2}Ni_{20.5}Co_{8.2}$ consistent with the measured values [2] (3.94 g/cm^3, with uncertainty $<2\%$).

Figure 1(b) shows a competing, tenfold symmetric decoration, similar to the suggestion by YP [9]. The tenfold symmetry may not be apparent because YP must introduce chemical and occupational (vacancy) disorder in the central ring of atoms, typically five TM and five Al sites shown in Fig. 1(b), in order to produce an acceptable fit to the HAADF-STEM imaging. The result produces TM cluster pairs similar to Fig. 1(a). Nevertheless, it is important to note for the present high-resolution transmission electron microscopy (HRTEM) study that the configuration of atomic positions—ignoring whether they are occupied by Al or TM—is tenfold symmetric as proposed by YP and in earlier models [6,9,11–13].

Another feature of Fig. 1(b) is that most sites are "mixed," having fractional occupancy by Al, TM, or vacancy depending on random disorder. Mixed and statistically occupied atomic sites are required essentially for the tenfold symmetric model to obtain a reasonable stoichiometry and density (assuming fully occupied sites, the atomic density of approximately 0.073 Å^{-3} [6] is too high to be a real metallic structure, corresponding to 4.35 g/cm^3 if one assumes the observed stoichiometry). In our model, Fig. 1(a), each site is purely Al, Ni, or Co. It is possible for a vacancy in one decagon to be a filled site in another decagon due to additional atoms contributed by overlap of neighbors in one case and not the other (this feature was interpreted as a nonsimple Penrose tile decoration [2]). This effect is not random, though; the distribution of filled (or unfilled) sites is quasiperiodically correlated in the ideal limit. In this sense, both Figs. 1(a) and 1(b) are only representative, depending on neighbors. The configuration inside the decagon in our model can have three (minor) variations [14], and many more variations are possible in the chemical and occupational disorder model. Here, though, we have intentionally shown examples of clusters from each model that are most nearly the same to show how even they can be distinguished.

We now consider the experimental evidence for intrinsic broken symmetry [Fig. 1(a)] based on a combination of HAADF-STEM imaging (highlights the TM sites) and HRTEM (total projected potential).

First, in our analysis of a large HAADF-STEM image in Paper I, we found that essentially all clusters exhibit the same broken tenfold symmetry [a triangle of TM spots, as shown in Fig. 2(c)] in the centermost region of each cluster. Some spots are elongated, suggesting closely spaced, column pairs of TM atoms, as occurs in both models in Fig. 1. The triangle of spots breaks the symmetry within a decagon in a manner isomorphic to the overlap rules, which are represented by kite-shaped decorations inside each decagon; see Fig. 1(a). (Both our model and the YP model predict that the triangle of spots deviates slightly from equilateral, which defines a mirror symmetry axis for each cluster. This deviation is difficult to resolve in the experimental images, though; for the purposes of this discussion, it suffices to treat the triangles as equilateral.) In the YP picture, one must suppose that chemical disorder somehow produces a similar triangular pattern in nearly all clusters, but that is not enough. The problem arises that the orientation of the triangle of spots is correlated across the image in accord with the overlap rules. This correlation is apparent in the HAADF-STEM figure in Paper I which shows that every kite-shaped region in the overlap pattern of decagons corresponds to a triangle of spots with matching orientation, suggesting strongly a chemical ordering between the Al and TM atoms and is inconsistent with random chemical disorder.

A second problem with the chemical and occupational disorder proposal [Fig. 1(b)] is that it is difficult to explain why highly perfect samples of AlNiCo occur only for a narrow composition range. The highly perfect AlNiCo phase changes to a (much) less perfect quasicrystal phase which reveals diffuse streaks or superlattice reflections when the composition deviates from the $Al_{72}Ni_{20}Co_8$ stoichiometry by more than approximately 1–2 atomic percent for the Al content [15]. This clearly indicates that a disorder between Al and TM atoms is very unlikely to occur in the perfect AlNiCo phase. Additionally, the ratio of Co to Ni is constrained to lie within a few atomic percent of the cited stoichiometry [15], suggesting that the two different TM atoms may also be assigned to distinct positions in the structure as proposed in our model. (A similar configuration of TM atoms is predicted for the nearly isostructural AlCuCo phase [16]). We note, however, that Ni and Co are quite similar in atomic numbers and TEM cannot distinguish them.

The above two discussions lead to a conclusion that $Al_{72}Ni_{20}Co_8$ is a quasiperiodic intermetallic compound

with nearly perfect atomic order (between Al and TM) and close to its ideal stoichiometry. Some alternative models presume that the structure could be significantly disordered because the phase is thermodynamically stable only at high temperature [6,9,11–13]. If the structure could tolerate sufficient disorder [a large number of mixed sites in Fig. 1(b)] to transform all or nearly all decagonal clusters to tenfold symmetry breaking clusters, then one would expect that the single phase region would extend to a wider composition range (at high temperature) than an order of a few atomic percent, but it evidently does not. It is worth mentioning that a disordering only between Ni and Co might contribute a substantial entropy term to the free energy sufficient to stabilize the present high-temperature AlNiCo phase [17].

A third argument for intrinsic broken symmetry is based on new, direct evidence from HRTEM by a 400 kV TEM with a resolution of 0.17 nm. For HRTEM observation, samples were crushed and then dispersed on perforated carbon films supported on Cu grids. Simulation of image contrasts was performed using the MACTEMPAS program with the multislice method (Total Resolution, Inc.).

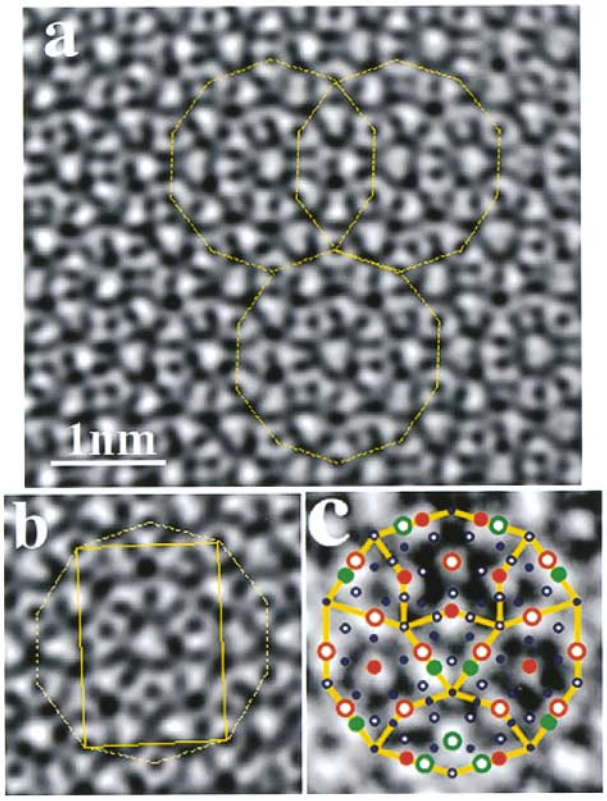

FIG. 2 (color). (a) HRTEM image of the high quality sample of $Al_{72}Ni_{20}Co_8$, taken at near edge of a cleavage grain (Fourier filtering was made to subtract the background). (b) A decagonal region showing a rectangular region used for comparing real versus predicted image contrasts (see Fig. 3). (c) The model in Fig. 1(a) superimposed on HAADF-STEM image, confirming a validity of the TM sites.

Figure 2(a) shows the HRTEM structure image of the $Al_{72}Ni_{20}Co_8$ taken from the tenfold symmetry axis under nearly the Scherzer defocus (−45 nm for the present microscope), which reflects the projected electrostatic potential: dark regions correspond to the projected atomic positions [11]. Some 2 nm decagonal clusters have been outlined in the image to guide the eye. Viewing carefully the interior of the decagon [rectangle region of Fig. 2(b)], one notices that the contrasts appear to break tenfold symmetry. Similar symmetry breaking is found in each of the decagon regions in Fig. 2(a).

These images should be compared to Figs. 3(a) and 3(b), which show the calculated HRTEM image contrasts for the two models in Fig. 1. Note that the decagon center in Fig. 3(a) exhibits a triangle feature (tenfold symmetry breaking), while Fig. 3(b) reveals a nearly perfect circle. The introduction of chemical disorder in the central decagonal ring in Fig. 1(b) to match the HAADF-STEM image has not significantly affected the HRTEM image. The observed image in Fig. 2(a) is more similar to the broken symmetry model in Fig. 3(a). To confirm this, we have computed the difference between the observed and calculated images over the rectangular region outlined in Figs. 2(b), 3(a), and 3(b); the residual intensities after nonlinear least square fitting are shown in Figs. 3(c) and 3(d). Clearly, the model with intrinsic broken symmetry fits better. We emphasize that the difference originates from symmetry breaking in the arrangement of atomic sites (regardless of Al or TM), such as a slight displacement (0.95 Å shift) of three Al atoms at the core [18] [see arrows in atomic models in Fig. 3(c)] that breaks the symmetry of the decagonal ring in Fig. 3(d). Note that the image contrasts at the core will appear to be more symmetric if there

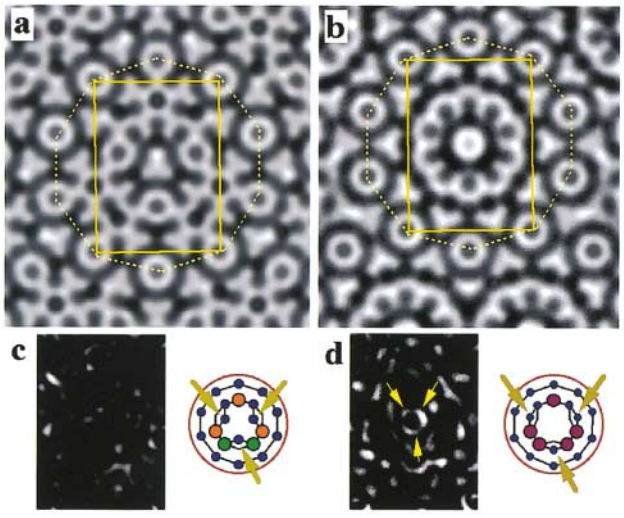

FIG. 3 (color). Simulated images of the atomic models in Fig. 1 are shown in (a) and (b), respectively. Both were calculated with −45 nm defocus and 3.6 nm thickness. Differences between the observed and simulated image contrasts of the rectangle regions are shown in (c) and (d).

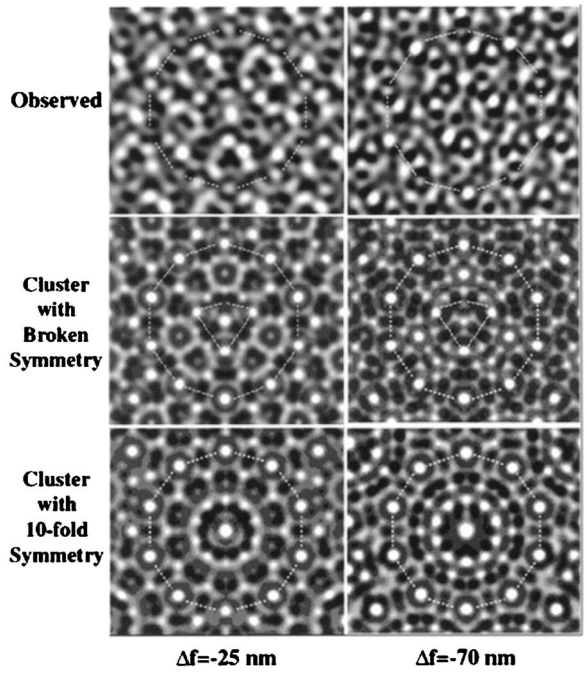

FIG. 4. Observed and computed (with 3.6 nm thickness) through-focus HRTEM images at different defocus values.

are phason defects which flip decagons on some layers but not others within the thickness observed. The more symmetric "*b*" clusters in the HAADF images shown by YP [9], which are relatively rare compared to the tenfold symmetry breaking clusters, may be explained by this effect.

We have also performed a through-focus HRTEM study. Since the phase difference between direct and diffracted beams is altered by changing the focus value in HRTEM, the image contrasts appear to be different depending on the focus values [19]. The systematic change in the contrasts with changing focus must be reproduced by the atomic model. The top row of Fig. 4 shows HRTEM images taken at smaller ($\Delta f = -25$ nm) and larger ($\Delta f = -70$ nm) defocus values than the Scherzer value, -45 nm. The corresponding calculated images are shown for the broken symmetry model [Fig. 1(a)] in the second row and for the tenfold symmetric model [Fig. 1(b)] in the third row. Clearly, the observed defocused images exhibit the tenfold symmetry breaking contrasts, confirming the result with Sherzer defocus (Fig. 3) and supporting models with intrinsic broken tenfold symmetry.

It is also supporting the fact that, in the structural models predicted by total energy calculation [16], the 2 nm decagonal clusters emerge in the lowest energy configuration with nearly identical assignments of Al and TM positions as shown Fig. 1(a). The convergence between our experimental test of the quasi-unit-cell picture and the theoretical analysis suggests that a definitive AlNiCo quasicrystal structure can be obtained from a further structural refinement (by diffraction method) on the present ideal model, providing an important hint about the energetics responsible for quasicrystal formation.

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Note added.—Recently, our previous AlNiCo model has been criticized by Yan and Pennycook [20].

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