Quasi-Unit Cell Model for an Al-Ni-Co Ideal Quasicrystal based on Clusters with Broken 10-fold Symmetry

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We present new evidence supporting the quasi-unit cell description of the $\text{Al}_{72}\text{Ni}_{20}\text{Co}_8$ decagonal quasicrystal which shows that the solid is composed of repeatedly, overlapping decagonal cluster columns with broken 10-fold symmetry. We propose an atomic model which gives a significantly improved fit to electron microscopy experiments compared to previous proposals by us and to alternative proposals with 10-fold symmetric clusters.

The $\text{Al}_{72}\text{Ni}_{20}\text{Co}_8$ decagonal phase is one of the best-characterized quasicrystalline materials and an excellent candidate for comparing structural models of quasicrystals. This ideal, highly perfect quasicrystal is reproducible as a single phase in the $\text{Al}_{72}\text{Ni}_{20}\text{Co}_8$ alloy annealed at 1170K followed by water-quenching.

In a recent paper (henceforth referred to as Paper I), we presented an array of evidence that the atomic structure of $\text{Al}_{72}\text{Ni}_{20}\text{Co}_8$ conforms to the quasi-unit cell picture. In this paper, the atomic structure can be decomposed into a single, repeating cluster (the quasi-unit cell) which shares atoms with neighbor clusters according to specific overlap rules. As first shown by P. Gummelt, overlap rules can be sufficient to ensure a unique structure that has perfect quasi-periodic translational order and the same symmetry as the Penrose tile picture based on two repeating tiles with edge-matching rules. However, by reducing the structure to only one repeating unit, the quasi-unit cell picture leads to a simple description of the atomic structure and requires only simple energetics 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 which highlights the transition metal (TM) sites (Z-contrast), the quasi-unit cell for $\text{Al}_{72}\text{Ni}_{20}\text{Co}_8$ can be constructed from a 2 nm diameter, decagonal cluster column whose atomic arrangement breaks 10-fold symmetry. We further proposed a specific atomic decoration which satisfies the observed centrosymmetric $P10_5/mmc$ symmetry and the measured density and stoichiometry. An interesting feature is that the resulting atomic structure 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.

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 quasi-unit cells has broken 10-fold symmetry isomorphic to the broken symmetry of 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. YP advocate an alternative structure which conforms to the quasi-unit cell picture in that it is composed of a single, decagonal cluster column obeying the same overlap rules. However, the YP proposal for the atomic decoration of the cluster (Fig. 1(b)) exhibits perfect 10-fold symmetry, similar to some previous structural models of Al-Ni(Cu)-Co quasicrystals.

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 10-fold symmetric and the broken symmetry is only a consequence of random chemical and occupational (vacancy) disorder, as YP suggest. (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 10-fold symmetry.) Although both possibilities are consistent with the quasi-unit cell picture, the question is significant because we have argued that the broken symmetry is a direct manifestation of the overlap rules or energetics of the ground state. According to this point of view, the appearance of the broken symmetry clusters in images is fundamental to the structure and a sign that the sample is nearly ideal. In contrast, YP conclude that any broken symmetry is accidental, due to random chemical and occupational disorder.

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 quasi-unit cell; see Fig. 1(a). The changes from the previous model are: (1) 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 (2) add three Al atoms in the central kite interior. As in our ear-
lier model, the quasi-unit cell has an atomic decoration that breaks 10-fold symmetry in a pattern isomorphic to the configuration of kites inscribed in the decagon, which represent the overlap rules. (The “kite” is the convex polygon inscribed with light-blue in the decagon of Fig. 1(a), which is a mnemonic for representing the overlap rules; neighbor decagons can overlap only if any kite-regions in the overlap region lay precisely on top of one another.) Also, as before, the atomic model cannot be interpreted as a simple Penrose tile decoration. The improved model now fits all TEM imaging data (Figs. 2-4), reproduces the observed $P10_5/mmc$ 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 (3.94 g/cm$^3$ and $Al_{72}Ni_{20}Co_{8}$, with uncertainty < 2%).

FIG. 1. Two competing models for the atomic decoration of the decagonal (2 nm) quasi-unit cell for $Al_{72}Ni_{20}Co$: (a) our proposed model with broken 10-fold symmetry and (b) an alternative model with unbroken 10-fold 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 of neighbor clusters (encircled in black).

Fig. 1(b) shows a competing, 10-fold symmetric decoration, similar to the suggestion by YP. The 10-fold symmetry may not be apparent because YP must introduce chemical and occupational (vacancy) disorder in the central ring of atoms, typically 5 TM and 5 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 10-fold symmetric as proposed by YP and in earlier models.

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 for the 10-fold symmetric model to obtain a reasonable stoichiometry and density (assuming fully occupied sites, the atomic density, approximately 0.073Å$^{-3}$ is too high for a densely-packed 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 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 (b) are only representative; depending on neighbors. The configuration inside the decagon in our model can have three (minor) variations, 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 10-fold symmetry (a triangle of TM spots, as shown in Fig. 2(c)) in the center-most 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). YP propose to produce a similar triangle through chemical disorder, as shown in Fig. 1(b). Even if one accepts the notion that chemical disorder would somehow produce a similar triangular pattern in nearly all clusters, 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. The orientational correlation suggests 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 is that it is difficult to explain why highly perfect samples of AlNiCo only occur for a narrow composition range. The highly perfect AlNiCo phase appears to reveal diffuse streaks or superlattice reflections when its composition deviates from the $Al_{72}Ni_{20}Co_{8}$ stoichiometry by only a few (atomic) percent for all constituent elements. Note that the perfection of the sample is even sensitive to the ratio of Ni to Co, suggesting that the two TM atoms, also, may lie at specific positions in the structure as proposed in our model (a variant Ni/Co ordering could also be considered, as discussed later). 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 10-fold symmetry breaking clusters, then one would expect that the single phase region would extend to a wider composition range than a order of a few atomic percent, but it does not.

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 and close to its ideal stoichiometry. Some alternative models presume that the structure must be significantly disordered because
the phase is thermodynamically stable only at high temperature. However, we would suggest that the situation need not be different from the case of crystalline phases which are thermodynamically stable only at high temperature. In either case, that state of lowest free energy (at finite temperature) can be described in terms of an ideal ordered state even though, upon quenching, there exist some defects and disorder, as discussed later.

FIG. 2. (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 rectangular region used for comparing real versus predicted image contrasts (see Fig. 3). The model in Fig. 1(a) superimposed on HAADF-STEM image, confirming a validity of the TM sites.

A third argument for intrinsic broken symmetry is based on new, direct evidence from HRTEM by a 400kV 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 MacTempas program (Total Resolution, Inc.) whose calculation is based on the multislice method.

Fig. 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. 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 10-fold symmetry. Similar symmetry breaking is found in each of the decagon regions in Fig. 2(a).

FIG. 3. 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).

These images should be compared to Figs. 3(a) and (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, (10-fold 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) and 3(a) and 3(b): the residual intensities are shown in Figs. 3(c) and (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 of 3 Al atoms at the core (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 are phonon 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, which are relatively rare compared to the 10-fold symmetry breaking clusters, may be explained by this effect.

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

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 (a low-pass filter effect to select a desired diffracted beam to be the major contribution for imaging.) The systematic change in the image contrasts with changing focus must be reproduced by the atomic model. The top row of Fig. 4 shows HRTEM images taken at smaller (Δf = −25 nm) and larger (Δf = −70 nm) defocus values than the Scherzer value, −45 nm. The corresponding calculated images are shown for the broken symmetry model in the second row and for the 10-fold symmetric model in the third row. Clearly, the observed defocused images exhibit the 10-fold symmetry breaking contrasts, confirming the result with Sherzer defocus (Fig. 3) and supporting models intrinsic broken 10-fold symmetry.

Recently, M. Widom and coworkers have completed a total energy based prediction of the structure of AlNiCo, in which 2 nm decagonal clusters with broken 10-fold symmetry emerge in the lowest energy configuration with nearly identical assignments of Al and TM positions as shown Fig.1(a). (The total energy, they find, prefers Ni – Ni pairs to our Ni – Co pairs; switching the Co with isolated Ni in Fig.1(a) produces a variant model that also gives a reasonable fit.) The convergence between our experimental test of the quasi-unit cell picture and the recent theoretical analysis suggests that there is real hope for obtaining a definitive atomic model for AlNiCo from a further structural refinement (by diffraction method) on the present ideal model. This implies that a theoretical understanding of the structure may guide the discovery of new quasicrystals.

This research was supported by CREST of Japan Science and Technology Corporation, US Department of Energy grant DE-FG02-91ER40671 (Princeton) and by the Korea Research Foundation Grant KRF-IDR98-B0001.
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