Chemical Ordering in $Al_{72}Ni_{20}Co_8$ Decagonal Quasicrystals

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First-principles total energy calculations of the 2-nm clusters seen in high-perfection $Al_{72}Ni_{20}Co_8$ decagonal quasicrystals demonstrate that chemical ordering between Al and transition metals in the central ring is energetically highly favorable. The chemical ordering introduces extensive structure relaxation and results in broken decagonal symmetry. Such broken symmetry is sufficient to enforce the perfect quasiperiodic tiling.

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It has been recently demonstrated that ideal decagonal quasicrystals can be effectively described by the Gummelt coverage model, i.e., a tiling formed by asymmetric decagons [1–10]. To understand fully why and how quasicrystals form, it is important to understand not only the atomic structure of the 2-nm clusters but also the *origin* of the broken symmetry.

Currently, there are two major controversial models on the atomic structure of the 2-nm clusters and the origin of the broken symmetry: an intrinsic broken symmetry model proposed by Steinhardt and co-workers [4,5] vs a chemical ordering-induced broken symmetry model proposed by us [6,7]. The intrinsic broken asymmetry model for the 2-nm clusters is composed of three subunits, giving a broken symmetry through the *entire* cluster. The chemical ordering-induced broken symmetry model, however, proposes that the broken symmetry results from chemical ordering that takes place only at the *central ring* of the 2-nm clusters. If there is no chemical ordering, the clusters remain with decagonal symmetry, leading to random tiling. We have recently used this model to explain why quite similar clusters can form either quasiperiodic tiling or random tiling under slightly different conditions, and also how they are related to the approximant phase [7]. However, the *underlying reason* for chemical ordering has not so far been determined. In addition, chemical ordering should induce extensive structural relaxation. It is therefore important to determine the relaxed structure to understand the formation of decagonal quasicrystals.

In this Letter, we first present an improved structure model for the 2-nm cluster of high-perfection $Al_{72}Ni_{20}Co_8$ decagonal quasicrystals based on first-principles total energy calculations. We then demonstrate that it is energetically highly favorable for chemical ordering to occur between Al and transition metals in the central ring of the 2-nm clusters. Extensive structural relaxation then breaks the symmetry of the 2-nm clusters and enforces the perfect quasiperiodic tiling.

The calculations were carried out using density-functional theory, the local density approximation for exchange-correlation, ultrasoft pseudopotentials, and plane waves [11]. In our calculations, we investigated single 2-nm clusters in a $4 \times 4 \times 0.4$ nm^3 (for non-chemical ordering) or a $4 \times 4 \times 0.8$ nm^3 (for chemical ordering) vacuum cube. The energy cutoff for the plane waves used in the calculations was 480 eV. We used a Ni potential for all the transition metals because limitations on computing time made it impossible to differentiate Ni from Co. We have tested a variety of boundary conditions by including more rings, and found that the inner rings were not affected by the choice of which atoms were held fixed at the edge of the cluster. Though the high-perfection $Al_{72}Ni_{20}Co_8$ decagonal quasicrystal is a high-temperature phase (stable above 800 °C) [12], its structure must be a metastable state.

(1) Structure improvement.—We first illustrate an improvement on our previously proposed structure model for the 2-nm clusters [6]. Figure 1(a) shows the atomic structure for the 2-nm clusters without chemical ordering. The structure model was obtained based on its τ^2-inflated $Al_{13}Co_4$ approximant phase [13], and it does not have the broken symmetry, similar to many other models [14–17]. It is thus the model for random tiling. However, we will show that this structure represents a *basic* structure, from which the structure leading to ideal quasiperiodic tiling is obtained just by allowing chemical ordering in the central ring. This breaks the symmetry and restricts the possible overlaps, enforcing the perfect quasiperiodic tiling. We first investigate the stability of the *basic* underlying structure of the 2-nm clusters, with no broken symmetry.

So far, the resolution of available Z-constant images does not enable us to resolve precisely the Al columns inside the 2-nm ring. However, the positions of all transition metal columns and the Al columns in the 2-nm ring can be resolved without any doubt [9,10]. Thus, all the transition metals should still fit the Z-contrast images after first-principles relaxation. Most columns of our model [Fig. 1(a)] fit the Z-contrast image very well, except the Al pair columns in the third ring counting from the center. After relaxation, we found that all transition metals and

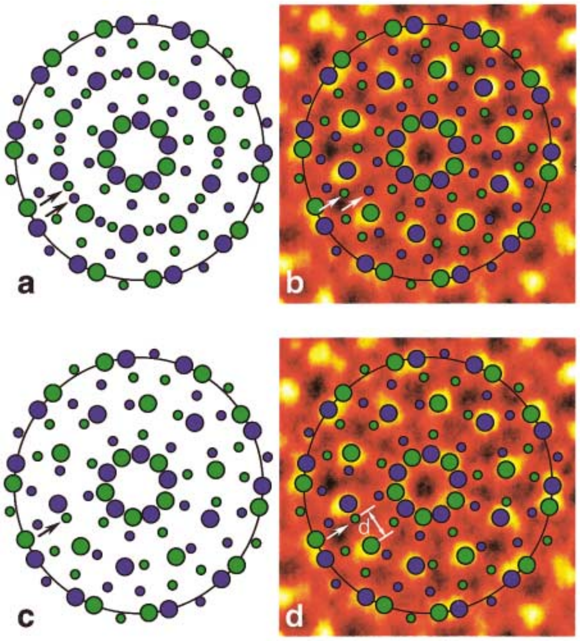

FIG. 1 (color). Previously proposed structure model for the 2-nm clusters in random Al-Ni-Co decagonal quasicrystals, (a) before and (b) after first-principles relaxation. Green represents $c = 0$ and blue $c = \frac{1}{2}$ along the periodic c axis. The large circles denote transition metals and the small circles Al atoms. (c) The improved structure model without broken symmetry. After relaxation, the structure is an excellent fit to the Z-contrast image (d).

most Al did not move far, except for the Al pair columns indicated by double arrows in Fig. 1(a) in the third ring. The two Al atoms of each pair repel strongly, one Al atom relaxing significantly inwards and the other outwards, giving the structure shown in Fig. 1(b). This relaxation results in a total energy reduction of about 10 eV, indicating that the Al pair columns are highly unstable. In addition, these relaxed Al columns also do not fit the Z-contrast image, as seen in Fig. 1(b). Thus, the Al pair columns should be refined.

The unreasonable Al pair columns resulted because we split each Al into two in the third ring to avoid having them sit at intensity maxima in the Z-contrast image when we construct the model from the τ^2-inflated $Al_{13}Co_4$ approximant phase (see Ref. [6] for details). This can also be realized by simply shifting those Al away from the intensity maxima instead of splitting them, giving a modified structure without the Al pair columns, as shown in Fig. 1(c). This modified structure is now a metastable state. After relaxation, no atom moved significantly from the initial positions. In Fig. 1(d), the relaxed modified structure model is superimposed on the Z-contrast image taken along the periodic axis. It is seen that it now fits the Z-contrast image very well.

(2) Chemical ordering.—In the high-perfection $Al_{78}Ni_{20}Co_8$ decagonal quasicrystals, most central rings of the 2-nm clusters show broken symmetry, with *five* transition metal columns in the form of one single and two pair columns [see Fig. 3(c) in Ref. [6]]. We proposed that the broken symmetry is due to chemical ordering between Al and transition metals at the central ring [6]. The transition metal pairs have been used as a source of matching rules in other models [15,18]. Here, we confirm that such chemical ordering is energetically highly favorable through first-principles total energy calculations.

It is known from the Z-contrast images that the ideal chemical ordering has five pure transition metal columns and five pure Al columns in the central ring. In this case, the central ring contains 50% transition metal sites and 50% Al sites. We considered three structures in our calculations: (1) No chemical ordering. Each column in the central ring is a mixture of transition metals and Al, as shown in Fig. 2(a). (2) With chemical ordering but without broken symmetry, as shown in Fig. 2(b). (3) With chemical ordering *and* broken symmetry as seen in Z-contrast images, as shown in Fig. 2(c). Note that the three structures in the calculations have the same unit cell dimension and the same number of each atom species, so that their total energies can be directly compared.

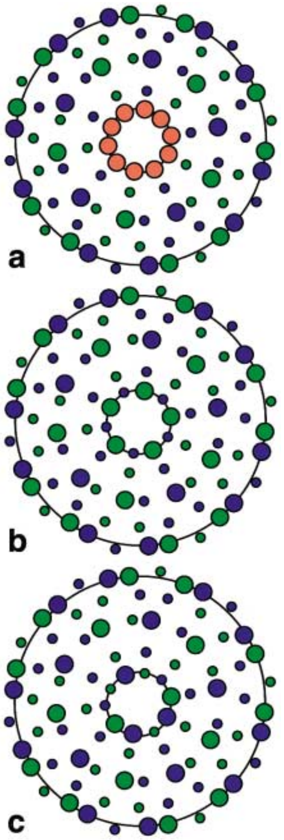

FIG. 2 (color). Three structures with the central ring containing 50% transition metal sites and 50% Al sites. (a) Basic structure without chemical ordering with each column (red color) containing 50% transition metals and 50% Al. (b) With chemical ordering, but without broken symmetry. (c) With chemical ordering and the broken symmetry seen in Z-contrast images.

We find that the structure with chemical ordering and broken symmetry has the lowest energy, about 12 eV lower than the structure without chemical ordering, and 5 eV lower than the structure with chemical ordering but without broken symmetry. Such large energy differences indicate that the chemical ordering between Al and transition metals in the central ring with broken symmetry is energetically highly preferred, *even when the surrounding atomic configuration is symmetric.* This confirms that chemical ordering in the central ring is the origin of the broken symmetry, and, hence, the quasicrystalline order. We have also considered other structures showing chemical ordering but with different broken symmetry, i.e., the five transition metals are not in the form of one single and two pairs, but their total energies are always higher. Thus, when the chemical composition is satisfied, chemical ordering and the broken symmetry shown in Fig. 3(a) will take place in the 2-nm clusters. We have also investigated the contribution to the symmetry breaking from Ni-Co ordering for a cluster with the same amount of Ni and Co, but we found that Ni-Co ordering has a much smaller effect on the total energy than Al–transition-metal (TM) ordering.

We further found that both the structure without chemical ordering and the structure with chemical ordering but without broken symmetry did not have extensive relaxation. However, extensive relaxation did occur in the structure with both chemical ordering and broken symmetry [Fig. 2(c)]. After relaxation, three Al atoms in the central ring moved inwards, giving the final structure as shown in Fig. 3(a). This relaxation, i.e., from Figs. 2(c) to 3(a), reduces the total energy by 8 eV, indicating that the movements of the three Al columns are energetically highly favorable. Figure 3(b) shows the superimposition of the relaxed structure on a Z-contrast image where broken symmetry is seen in the central ring, giving a very good fit. Figure 3(c) shows a Z-contrast image at lower magnification. The structure of all 2 nm clusters is similar to that shown with higher magnification in Fig. 3(b), except for the central rings, which show variable degrees of chemical ordering. Clearly, our model fits well everywhere in our Z-contrast images.

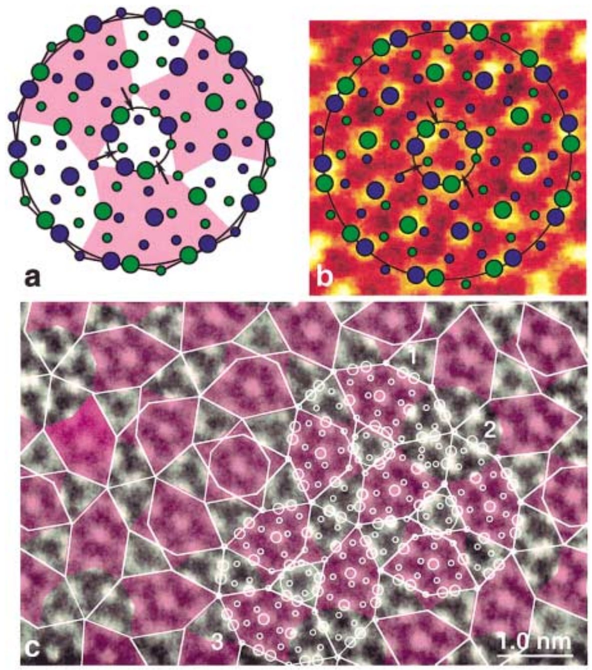

FIG. 3 (color). (a) Structure with chemical ordering and broken symmetry after total energy relaxation. The three arrows indicate the three Al columns that moved towards the center. The broken symmetry is represented by the pink subtiles. (b) The relaxed structure superimposed on a Z-contrast image. (c) A Z-contrast image with lower magnification showing more 2 nm clusters. The layout shows the overlaps of 2 nm clusters, giving the same tiling as the Gummelt coverage model.

We now illustrate how our chemical ordering-induced broken symmetry [Fig. 3(a)] will restrict the possible overlaps and give the same overlap rules as the Gummelt coverage model. The central rings of the clusters contain pairs of columns similar to the pairs present in the outer ring. This naturally suggests how one cluster can nucleate a second, resulting in two types of overlap as shown in Figs. 4(a) (type *A*) and 4(b) (type *B*). For the overlap shown, most of the sites for the second clusters already exist in the first. In type *A* overlap, only two A1 column pairs and four TM pairs are not coincident as indicated by the white and black arrows, respectively. In type *B* overlap, beside the four Al column pairs (indicated by the white arrows), there are

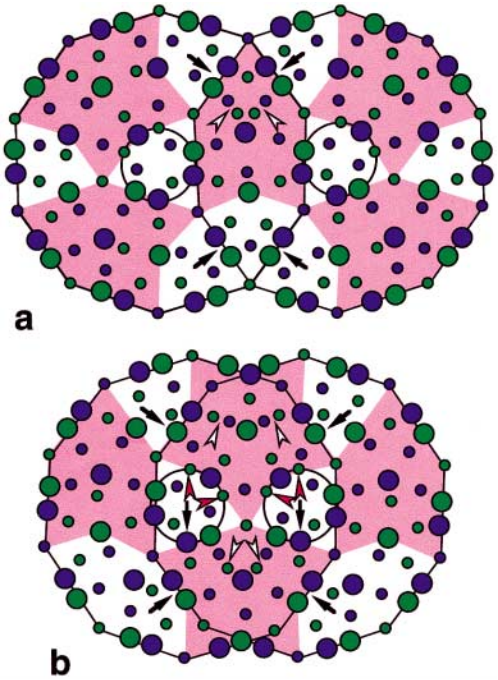

FIG. 4 (color). The details of the (a) type *A* and (b) type *B* overlaps.

four Al columns (indicated by the red arrows) and six TM columns (indicated by the black arrows) that are not coincident. Other variants are also possible since the cluster shown in Fig. 3(a) is chiral; in the third ring only one of the two possible Al sites between neighboring TM sites is occupied, so left-hand (LH) and right-hand (RH) variants could coexist with no effect on the TM sites. If LH and RH clusters overlap, the noncoincident Al sites appear at different positions. A random superposition of LH and RH clusters would contribute to the diffuse scattering, and is consistent with the low but symmetric intensity observed in the Z-contrast images.

Accommodating these noncoincident sites is presumably easier at high temperatures, when the TM columns could be either vacant or occupied by Al. In fact, we have observed in our Z-contrast images that some of the column pairs in the outer rings have single TM columns. If there is no chemical ordering, i.e., there is no broken symmetry at the central rings, there are ten possible ways for both type A and type B overlap. This, of course, results in a random tiling. When chemical ordering occurs in the central ring, it has the broken symmetry shown in Fig. 3(a), and the possibility for type A and B overlaps is restricted to four and two, respectively, mainly due to the inward relaxation of the three Al columns. These restricted overlaps are equivalent to breaking the symmetry by coloring the cluster in the pink subtiles shown in Fig. 3(a) and allowing only the colored area to overlap. This is the same subtile used in the Gummelt coverage model and gives the same overlap rule. In Fig. 3(c), we have colored all the clusters in the Z-contrast image. We see that all clusters obey the overlap rule, i.e., *the overlap is controlled by the central rings.* The resulting tiling perfectly matches the Gummelt coverage.

It is important to note that the chemical ordering takes place only when the chemical composition is satisfied. If, for example, the central ring contains 100% transition metals or 100% Al, the 2-nm clusters take the structure without broken symmetry shown in Fig. 1(b). The large variety of possible overlaps will result in ideal random tiling. We emphasize that, apart from the central ring, our chemical ordering-induced broken symmetry model has significant differences from the intrinsic broken symmetry model. In our model, *only* the central ring has broken symmetry; whereas, in the intrinsic broken symmetry model, additional rings have broken symmetry.

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