Real-Space Atomic Structure of a Two-Dimensional Decagonal Quasicrystal

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We have imaged for the first time the atomic structure of a quasicrystal using a scanning tunneling microscope. The structure of the decagonal $Al_{65}Co_{20}Cu_{15}$ quasicrystal is described by a pentagon-center-decorated pentagonal quasilattice giving strong evidence for a tiling model. The scanning-tunneling-microscope measurements of the surface are in good agreement with the high-resolution x-ray-diffraction measurements of the bulk.

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The structure of the solid phase is a subject that is central to condensed matter physics, spurring the development of a number of tools designed to elucidate atomic positions. Over the years, the diffraction of x rays and electrons applied to both the bulk and the surfaces of crystalline material has been very successful in the determination of order. Despite the power of these methods, the atomic structure of quasicrystals is yet poorly understood[1] five years after the discovery of a quasiperiodic icosahedral phase in Al_6Mn.[2] The quasiperiodic nature of these materials is itself a stumbling block since most experimental and theoretical methods rely on the periodicity displayed by crystalline compounds. A number of models have been proposed to explain the unusual symmetry of these compounds. The random-packing model[3] of icosahedral units exhibits the basic symmetry but the inherent disorder of the model fails to describe the Al-Cu-Fe class[4] of perfect quasicrystals. Tiling models[5] create a deterministic structure by projecting a six-dimensional hypercubic lattice onto three dimensions and provide a description for a defect-free quasicrystal. The multitwinning model[6] justifies the quasicrystalline diffraction pattern in terms of multiply twinned small crystallites. Small variations on a neighboring crystalline phase may generate icosahedral order according to recent calculations.[7] Additionally, the significance of the entropic terms has been demonstrated using Monte Carlo simulations[8] based on random tiling.

The decagonal quasicrystal phase, discovered by Bendersky,[9] is quasiperiodic in two dimensions and periodic in the third dimension, and is even less understood than the icosahedral phase. This phase appears as intermediate between the icosahedral and the crystalline phases, and, in principle, should be easier to understand due to its reduced dimensionality. Intensive studies[10] of several different decagonal systems have not resulted in a widely accepted model. A further complication is the possible coexistence[11] of decagonal and icosahedral phases. Idziak and Heiney,[12] following their careful study of the Al_6Pd system using both high-resolution x-ray diffraction (HRXD) and transmission electron microscopy (TEM), were unable to make a distinction between a multiply twinned and a quasicrystalline structure. It has been clear that a direct lattice-imaging method is required to provide the insight needed to resolve the quasicrystalline structure. The scanning tunneling microscope (STM) is a unique tool that combines real-space imaging with atomic resolution of surface features. In this Letter we report the first high-resolution STM surface images of the decagonal $Al_{65}Co_{20}Cu_{15}$ quasicrystal, and compare them to the HRXD studies of the bulk. The tunneling images provide strong evidence for the two-dimensional tiling model and rule out multiple twinning as the source for the fivefold symmetry. Moreover, the evidence suggests that the surface structure is a simple termination of the bulk quasiperiodic structure.

Since the decagonal phase of the $Al_{65}Co_{20}Cu_{15}$ compound[13] appears to be thermodynamically stable,[14] we employed conventional techniques[15] to grow several millimeter-sized, faceted single grains. These samples exhibit a columnar decagonal prismatic morphology with the column axis parallel to the periodic direction. The STM sample was oriented with x rays to better than 1° to the tenfold quasicrystalline planes, and cut and polished to optical flatness. The ultrahigh vacuum (UHV) STM used in these experiments has been described elsewhere.[16] The quasicrystal-sample surface was cleaned by repeated cycles of ion bombardment (Ne^+, 1.0 keV) and annealing at temperatures of 700 °C for periods of 10 to 18 h. Analysis of the surface constituents by Auger electron spectroscopy (AES), subsequent to the STM experiments, indicates that the surface stoichiometry is essentially unchanged from the bulk composition. The x-ray-diffraction measurements are carried out on a triple-axes, four-circle goniometer equipped with a 12-kW rotating-anode generator. The performance of this instrument has been previously described.[15]

Single-crystal x-ray-diffraction measurements were carried out on grains with well defined facets. A sample volume of approximately 1 mm^3 was illuminated with monochromatic x rays and the reciprocal space was explored to 8 $Å^{-1}$. The reciprocal space consists of planar quasicrystalline reflections stacked periodically with extinctions.[15] The scans along the periodic direction show

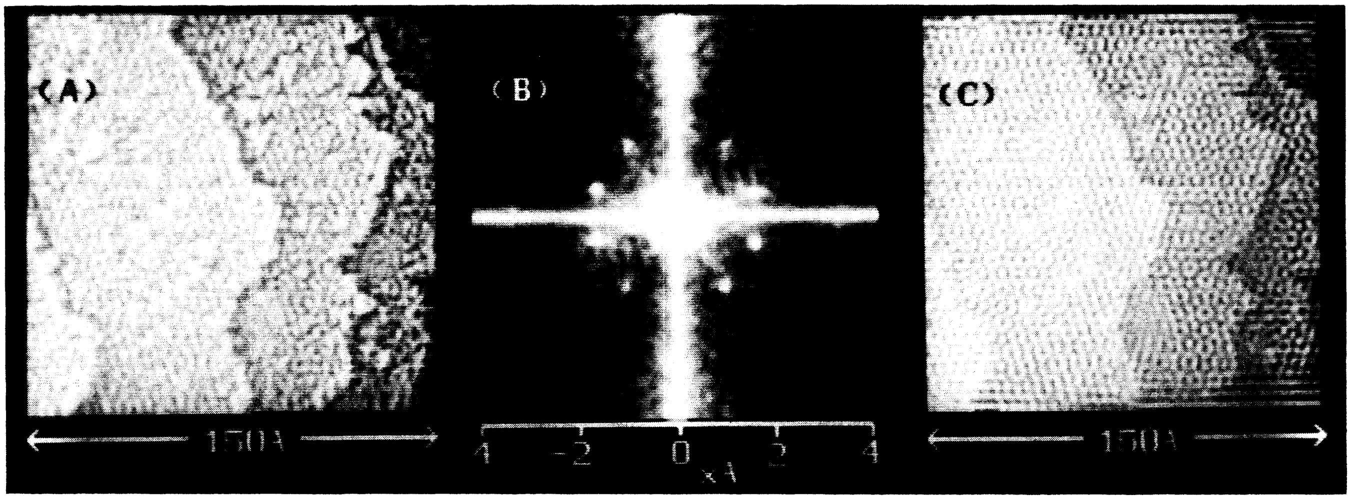

FIG. 1. A tunneling image of the quasiperiodic surface of decagonal $Al_{65}Co_{20}Cu_{15}$. (a) The lateral scale is indicated and the gray scale is derived from local height. (b) Normalized power spectrum of the image, with the wave-vector scale indicated. (c) Small-scale feature enhancement as described in the text.

a fundamental length of 4.13 Å, whereas scans with an in-plane quasicrystalline component in the D pattern[12] reveal that the actual periodicity is 8.26 Å. Complete extinctions of the 00000n (n =odd) reflections indicate that the 4.13-Å layers are identical when viewed along a twofold zone axis. The widths of the in-plane diffraction peaks confirm that the structure is near perfect decagonal with a longitudinal correlation length of 2000 Å.

Figure 1(a) shows a constant-current tunneling image [bias voltage (V_b) 100 meV, demanded tunneling current 1 nA] of a 150-Å square region of the clean surface. Four atomic steps are prominent, along with a network of lines crossing the surface. Closer examination shows that these mass-density lines run along five symmetry directions spaced at 72° and correspond to atomic positions, imaged as a network of points and ringlike structures. The spacing between these mass-density lines is quasiperiodic and will be examined in more detail later. The lines themselves appear to be continuous from terrace to terrace. The terraces are atomically flat, with a measured corrugation of 0.1 Å determined from observations on a number of images. Further perusal of the tunneling image shows that no periodic structures exist. Figure 1(b) is a plot of the normalized power spectrum, $\bar{P}(\bar{q}) = \bar{q}P(\bar{q})$, of the image in 1(a) displayed as a gray scale. $\bar{P}(\bar{q})$ shows ten intense spots at the principle $\bar{q}_0$ of the image, along with a bright inner ring at the next highest harmonic, $1/\tau$ of $\bar{q}_0$ [$\tau = (1+\sqrt{5})/2$]. Other tunneling images show the development of the full tenfold set of spots from images as small as 60 Å in extent. The bright cross in Fig. 1(b) corresponds to momentum transfer where q_x or q_y is small. Large power is present at these values due to nonrepeated features such as the atomic steps. In Fig. 1(c) the features at $\bar{q}_0$ have been amplified by a factor of 2 in order to clarify the atomic-scale features of the surface[17] while retaining important details such as steps and surface imperfections. This amplification necessarily cuts off some of the wave vectors for the principle spot pair with $q_x = 0$, giving rise to Gibbs phenomena visible for two or three periods at the top and bottom of the filtered image, spoiling the edges of Fig. 1(c). An inspection of Fig. 1(a) shows that these features are not contained in the raw data.

Since the full decagonal symmetry is realized on scales as small as 60 Å, and no periodic structures are seen, we can conclude that multitwinning does not adequately describe the features in the STM images. All of the terraces have similar appearance, despite the fact that the step height of ~ 2 Å is a submultiple of the c-axis periodicities of 4.13 and 8.26 Å. When coupled with the continuity of mass-density lines these observations sug-

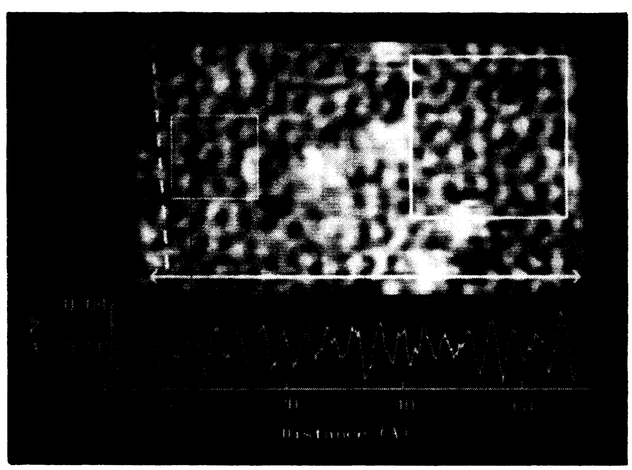

FIG. 2. Tunneling image along with a plot of integrated local heights as described in the text. The small box shows a typical local decagonal feature, while the large box depicts a region tiled in Fig. 3.

gest that the atomic positions in consecutive layers are highly correlated and possibly identical. Finally, the small corrugation on the terraces together with the AES measurements suggest that the surface is not strongly reconstructed.

In Fig. 2 we show a smaller-scale image of the surface, together with the integrated local height, $\bar{Z}$, plotted along a trajectory indicated by the solid line in the figure. The direction of integration is along one of the mass-density waves as indicated by the dashed line. The integrated mass density appears to be nearly periodic, and inspection of the image in Fig. 1(a) shows this to be generally true along all five symmetry directions. Similar to the Ammann lines of a perfect Penrose quasilattice,[18] the continuity of the lines from terrace to terrace strongly suggests defect-free quasicrystallinity, and indicates that any tiling must belong to the Penrose local isomorphism (PLI) class. While no ordered regions can be seen, centers of local fivefold symmetry, as indicated in Fig. 2, exist in numerous places in the tunneling images. In order to explain the near periodicity of the mass-density lines, and the local pentagonal symmetry seen in the STM images, we have tiled a portion of the image in Fig. 2 with a pentagonal quasilattice with pentagon center decoration as shown in Fig. 3. The six distinct tiles[19] of this pentagonal network are similar to those introduced by Onada *et al.*,[20] who use only eight distinct vertices in addition to matching rules to define the local arrangement of Penrose tiles and generate perfect quasicrystals. In the pentagon-center quasilattice, a complete set of mass-density lines comprises four distinct spacings, A, B, C, and D. These are related by $A+C=D$, $B/A=1+\tau$, and $C/(A+B)=\tau$. The small spacings A and B are not resolved in the integrated mass-density plots, instead giving rise to the two averaged lengths of $L=D+B$ and $S=C+1/2(A+B)$, the ratio of which is $2(\tau-1)$ or ~ 1.23. The average mass-density spacing in

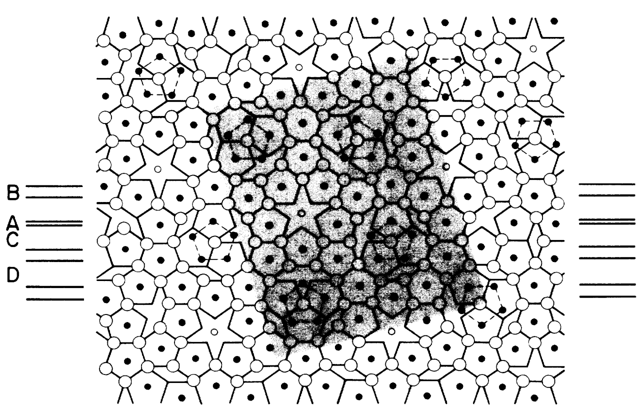

FIG. 3. A pentagonal quasilattice model that simulates the STM image. The shaded region designates the area outlined by the large box in Fig. 2. Atoms shown by solid circles are at an elevated position and are imaged by STM.

Fig. 2 is 3.9 Å, giving $L=4.3$ Å and $S=3.5$ Å, a difference of only 0.8 Å. While we have been able to distinguish the L and S mass-density spacings in smaller, pristine surface regions, the presence of surface defects, possibly oxygen induced, tend to degrade the lateral determination of position. Nonetheless, the pentagon-center-decorated quasilattice adequately accounts for the near periodicity of the mass-density lines. In the normalized power spectrum displayed in Fig. 1(b) the strong peaks occur at 1.62 ± 0.10 Å^{-1}, in very good agreement with the position of the most intense peak in HRXD at 1.6489 Å^{-1}. This momentum corresponds to a periodicity of 3.89 Å and also reflects the average of the quasiperiodic spacings of the line features of the image.

The experimental step height of 1.94 ± 0.10 Å is approximately one-fourth of the 8.26-Å c-axis periodicity and one-half of the fundamental length of 4.13 Å measured by HXRD. This suggests that the terraces are in fact slices of the bulk structure, with the quasiperiodic arrangement of each atomic layer revealed at its respective surface. Further, the principle structural unit, with a periodicity of 4.13 Å must be easily decomposed into $\sim$2-Å subunits. We assign the 4.13 Å to the height of an icosahedron made up of two Al pentagons stacked with a relative rotation of 36° with Co atoms capping the top and the bottom. This assignment is based on the dimensions of subunits of related crystalline phases.[21] We noted that the uninterrupted extension of the mass-density lines across the terraces in all five distinct directions implies that the local atomic structure is highly correlated along the c axis from layer to layer. This condition may be met by positioning pentagons in adjacent layers to overlap with a relative rotation of 36°, maximizing the packing and matching the measured step height. Starting from a pentagonal quasilattice layer and constructing the next layer using optimally packed, rotated Al pentagons we see that the epitaxial layer is also a pentagonal quasilattice in the PLI class, with a local structure identical to the starting layer. The two layers are in fact related by an inflation.[22] The positional invariance of the ringlike features from layer to layer is then understood as periodically stacked icosahedrons, forming a chain structure along the c axis. Similarly stacked Al icosahedra have also been suggested[23] for the Al_4Mn decagonal phase. The quasicrystalline layers imaged as terraces in Fig. 1 then consist of a primarily Al pentagonal quasilattice frame with Co and Cu atoms as decoration. We propose that the adjacent Al quasilattice layers are complementary as described above, with a pentagon edge length of 2.90 Å, typical of Al-Al interatomic distances.[21]

The pentagonal quasilattice correctly describes the STM images except inside the local decagonal features. Here STM images generally show a complete ring of atoms (indicated by dashed pentagon in Fig. 3), whereas the pentagon-center-decorated quasilattice shows only

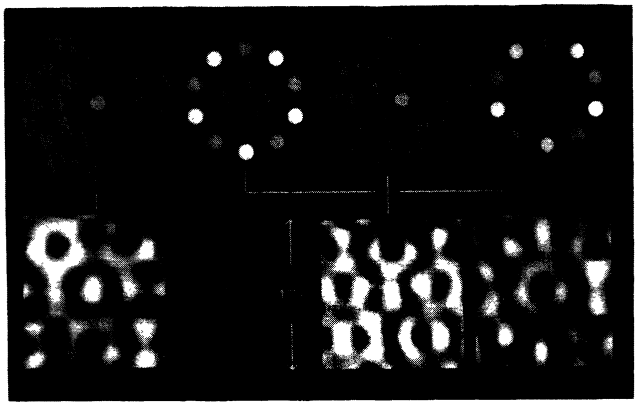

FIG. 4. Local decagonal structure of atoms in the 2D quasilattice and their proposed stacking along the periodic direction. These are compared to small-scale decagonal features in the tunneling images.

three atoms. While it is plain that the STM is resolving single features separated by ∼4 Å, it is unclear that a five-atom ring 4 Å in extent will be cleanly resolved. We suspect the ringlike features are by and large composed of five atoms. We conclude that the pentagonal tiles are not decorated identically but are in fact context dependent, possibly with some substitution of Co and Cu for Al. This model predicts that center sites between two rotated pentagons in adjacent layers are occupied by smaller size transition-metal atoms in an ideal surface termination. These transition-metal atoms (as shown by solid circles in Fig. 3) occupy an elevated position and are imaged by STM.

The proposed stacking structure for the decagonal phase is shown in Fig. 4 for a typical decagon pattern and compared to local decagonal features in the STM images. The four layers shown correspond to the fundamental length of 4.13 Å along the periodic axis. On each terrace decagonal elements of the layered quasilattice are seen. Inspection of the data shows that the patterns labeled 1 and 3 are quite rare in the tunneling images. These may be decagon stacks where the final layer of transition-metal atoms are missing, resulting in imaging of the principally Al pentagons.

In summary, the combined high-resolution x-ray and tunneling-microscope measurements of the atomic structure on a length scale from a fraction of an angstrom to a few thousand angstroms of decagonal $Al_{65}Co_{20}Cu_{15}$ are satisfactorily described by the quasiperiodic order inherent in 2D tiling models and are inconsistent with atomic structure detailed by multiple twinning. No evidence for disorder in the quasilattice is visible in the small-scale STM images. The bulk structure consists of a complementary stacking of individual pentagonal quasilattices, each related by an inflation to those above and below. We thank L. C. Kimerling, Y. Kuk, and V. Elser for helpful discussions.

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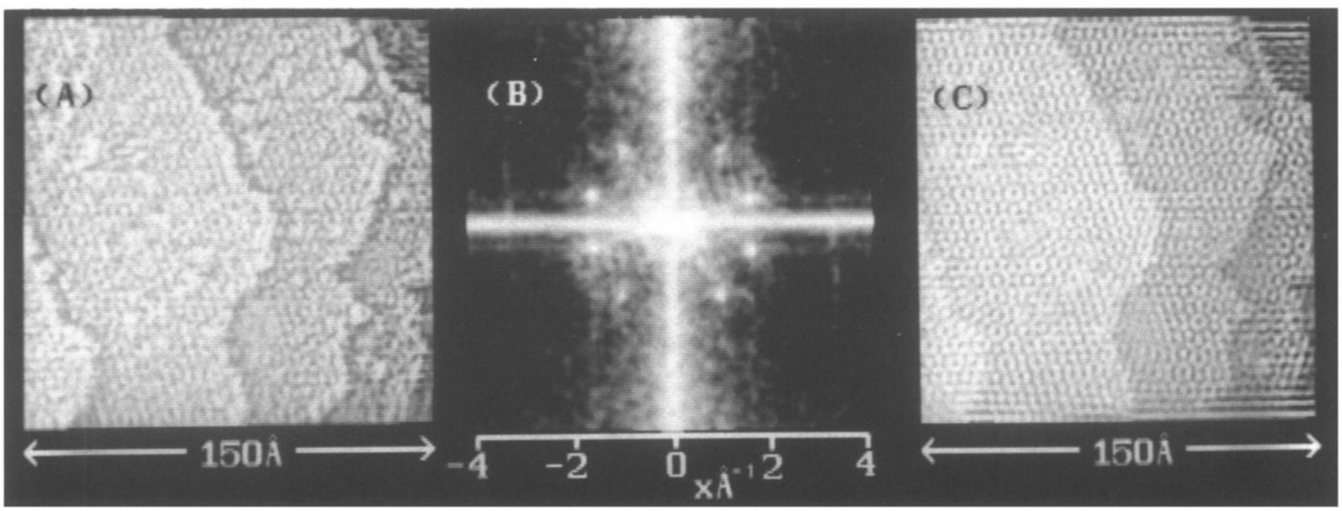

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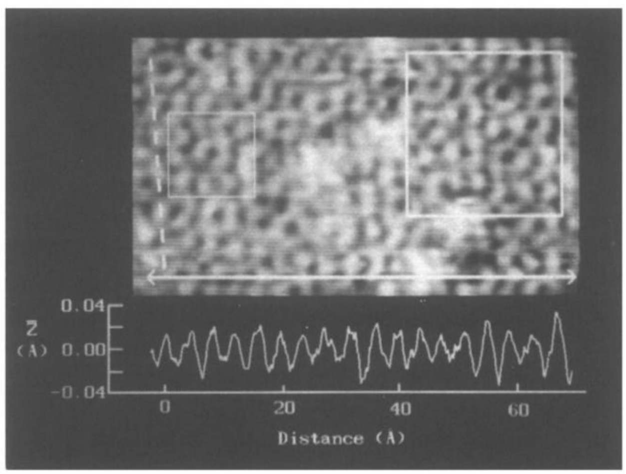

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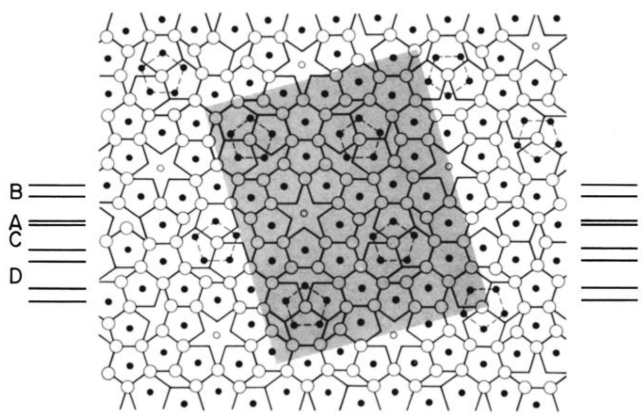

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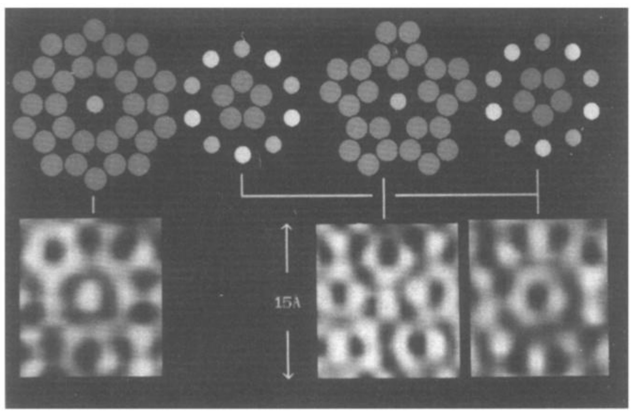

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