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STM study of the atomic structure of the icosahedral Al-Cu-Fe fivefold surface

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We use scanning tunneling microscopy (STM) to investigate the atomic structure of the icosahedral (*i*-) Al-Cu-Fe fivefold surface in ultra high vacuum (UHV). Studies show that large, atomically flat terraces feature many ten-petal ''flowers'' with internal structure. The observed flower patterns can be associated with features on Al rich dense atomic planes generated from two-dimensional cuts of bulk models based on x-ray and neutron diffraction experiments. The results confirm that the fivefold surface of *i*-Al-Cu-Fe corresponds to a bulk-terminated plane.

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The lack of periodicity within the class of intermetallics known as quasicrystals[1] poses a challenge in determining their surface structure. The most common technique, dynamical theory of electron diffraction, relies very much on the existence of model systems based on periodic structure. Therefore, an exact analysis is not achievable for quasicrystals. Approximations have been introduced successfully into dynamical low-energy electron diffraction (LEED) calculations to determine structures of *i*-Al-Pd-Mn (Refs. 2, 3) and *i*-Al-Cu-Fe (Ref. 4) fivefold ($5f$) surfaces—and the result has been supported in the former case by data from x-ray scattering,[5] low-energy ion scattering,[6] and temperature-programmed desorption.[7] However, these techniques provide only *averaged* information on surface structure. Alternatively, scanning tunneling microscopy (STM) probes the electronic surface structure at atomic scale in real space[8] and thus its application does not require periodicity in the material. In this work, we employ STM as our main technique to probe the surface structure of *i*-Al-Cu-Fe quasicrystal.

STM has been actively used to investigate the structure of the *i*-Al-Pd-Mn $5f$ surface.[9–17] Annealing the sputtered surface at appropriate temperature routinely generates a step-terrace surface structure. In STM studies, an ultimate goal is to obtain high-resolution images displaying the fine structure (at the best, the direct images of the atomic arrangements) on these flat terraces, and to relate the surface structure to the atomic structure of a bulk model. Two facts challenge the achievement of this goal. First, the intrinsic structural and chemical complexity in the quasicrystals undoubtedly engenders a complex geometric and/or electronic surface structure. Second, both the tip specification (the size and the shape) and the scanning conditions greatly influence the resolution and appearance of the STM images. In recent years, several research groups have recorded STM images, with different resolution and at different scales, on flat terraces of *i*-Al-Pd-Mn $5f$ surfaces.[11–15,17] These images are usually dominated by dark ''holes,'' which are sometimes shaped like pentagons and sometimes like fivefold stars, depending upon the resolution of the tip.

Among icosahedral quasicrystals, it is known that *i*-Al-Cu-Fe has a bulk structure very similar to that of *i*-Al-Pd-Mn. It is reasonable to expect that surfaces of these two materials with the same high-order symmetry will exhibit similar structure. In this paper, we test that hypothesis. There has been only one previously published STM image of an *i*-Al-Cu-Fe surface,[18] and it was not possible at that time to attempt interpretation of the observed features, partly due to lack of information about the bulk structure and partly due to the lack of high-resolution in the imaging.

Figure 1 represents the step-terrace structure commonly obtained on a clean, well annealed *i*-Al-Cu-Fe $5f$ surface in UHV, after preparation as described in other publications.[4,19,20] We have discussed the step height measurement and the structural imperfection along the $5f$ axis in detail in a previous paper.[4] The step that separates the two major adjacent terraces in Fig. 1 is 0.40 nm high. The peak-to-peak corrugation across individual terraces is about 0.05 nm. Higher protrusions, about 0.1 nm high (which appear as the brighter bumps on the terrace), are often observed on the surface as well. These may be similar in origin to the larger protrusions that were reported previously in highly resolved STM images of the *i*-Al-Pd-Mn $5f$ surface. There, analysis of their shapes led to the conclusion that they should be regarded as part of the icosahedral structure, and not impurities randomly distributed on the surface.[16]

High-resolution STM [Fig. 2(a)] shows the fine structure

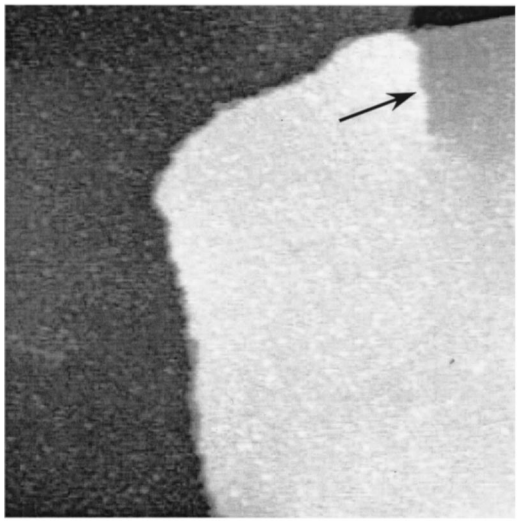

FIG. 1. STM image (100×100 nm^2) showing the typical step-terrace structure. The arrow indicates a screw dislocation; these are often observed on the $5f$ i-Al-Cu-Fe surface.[4]

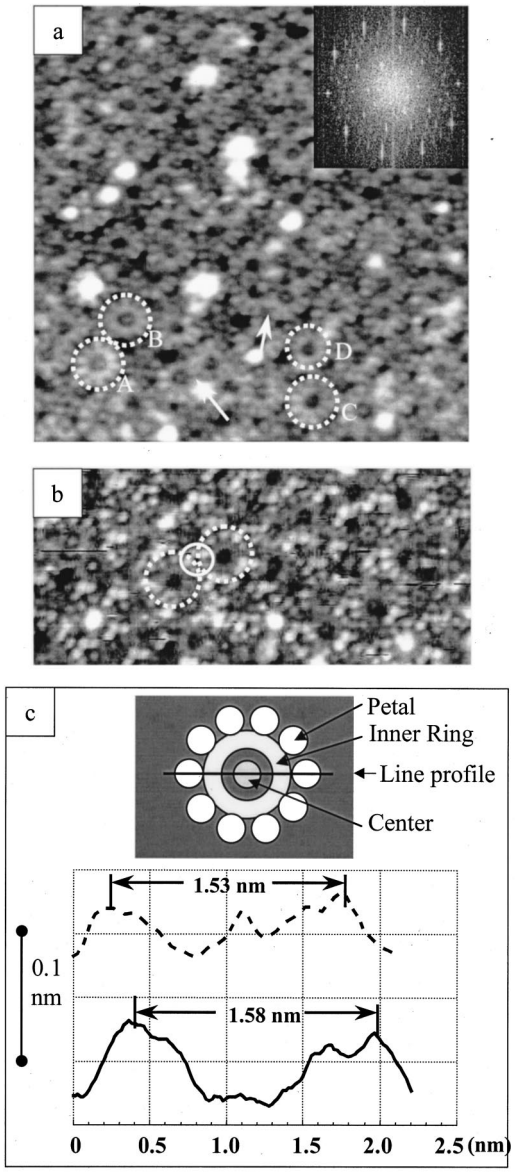

FIG. 2. (a) High resolution STM image ($20\times20\ \mathrm{nm}^2$) of an atomically flat terrace. Inset: Fourier transform of an image of $50\times50\ \mathrm{nm}^2$ on a terrace. A: complete flower with ten petals and filled center. B: flower with one missing petal and filled center. C: flower with empty center. D: nearly petal-free flower. Arrows: overlapping of neighboring flowers. (b) High resolution STM image ($10\times20\ \mathrm{nm}^2$) showing small pentagons gluing two adjacent flowers. Large circles: flower patterns. Small circle: outlines of small gluing pentagons. (c) Schematic of a flower, together with line scans of a flower with filled center (top curve in box), and an empty center (lower curve in box).

on the flat terraces. The Fourier transform from such a image of $50\times50\ \mathrm{nm}^2$ [see inset in Fig. 2(a)] exhibits tenfold symmetry, consistent with the $5f$ quasiperiodic order on the terrace. The most notable features in the image are the ''flowers'' that are approximately 1.5 nm in diameter, measured from peak to peak of the outermost petals, as shown in Fig. 2(c). Several flowers are outlined in Fig. 2(a), and labeled A–C. In their pioneering STM work on *i*-Al-Cu-Fe $5f$ surface, Becker *et al.*[18] also reported some ''daisy''-like structures that appeared like central spots surrounded by a series of ring- or U-shaped features. However, features in their STM image were not sufficiently resolved. We have obtained STM images at higher resolution, which makes it possible to analyze the structural features of the flowers. The ''complete'' flowers [Fig. 2(a), A–C] consist of ten petals. Despite the distortion of the STM scan, the ten petals appear to be uniformly distributed (as far as both intensities and positions are concerned, e.g., flower A) in a circle, which gives local tenfold symmetry. However, some flowers are missing parts of petals (e.g., flower B). The center of the flowers is either filled (e.g., flowers A and B) or empty (e.g., flower C). Between the center and the ring of ten petals in each flower, there is clearly another ring of bright contrast, which, however, is not well resolved in the STM images. These features are clarified in the schematic sketches of Fig. 2(c).

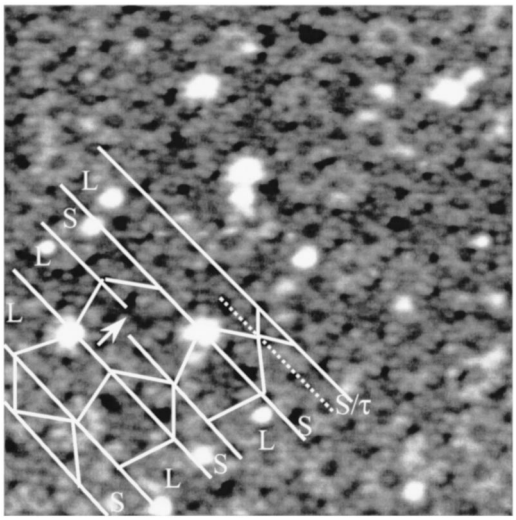

FIG. 3. Same high resolution STM image as in Fig. 2. Pentagons are drawn to illustrate the local $5f$ arrangements of flowers. Parallel lines separated by different spacings align the flowers. The arrow indicates where a displacement takes place. The splitting of a wider spacing into two smaller ones is shown in the upper-rightmost spacing.

It is clear that there is also a wealth of features between the intact flowers, which we call the ''glue'' area. In some cases, four close petals from two neighboring flowers (two petals from each flower) constitute four vertices of a pentagon, with an additional atom that does not belong to any flowers fulfilling the fifth vertex. Such pentagons appear much more clearly in Fig. 2(b). Another type of glue object is a nearly petal-free inner ring, with a diameter of 1.05 nm, shown in Fig. 2(a). Such a ring can be resolved into ten separate spots, defining axes parallel to the axes of the petal-rich flowers, suggesting that the inner rings have this symmetry in the full flowers as well. Overlapping is another possible configuration for adjacent flowers, as indicated by the white arrows in Fig. 2(a).

Some groups of five flowers form large pentagons, as outlined in Fig. 3. Noting that the lines linking the center and one of the ten petals of each flower define five directions, we connect the flowers by five sets of parallel lines in the five

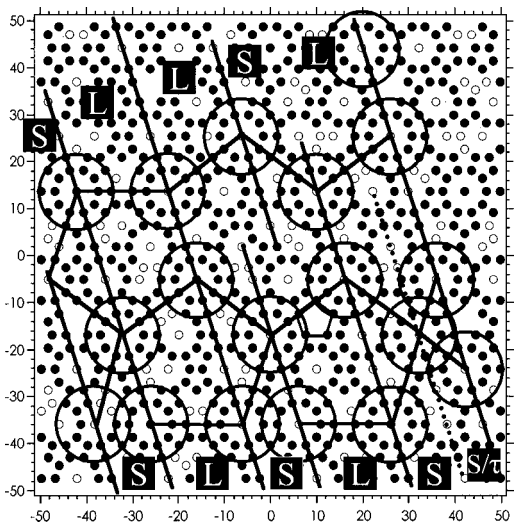

FIG. 4. Atomic positions in a plane (10×10 nm^2) generated from experimental bulk structure model. Filled circles: Al atoms. Unfilled circles: Fe atoms. The sketched contour illustrates the matching part of the STM image outlined in Fig. 3.

directions defined above. Figure 3 shows only part of one set of parallel lines to illustrate the idea. Analysis shows that these lines are mainly separated by two different spacings: $L=1.88$ nm for the wider spacings and $S=1.17$ nm for the narrower ones. The ratio $L/S=1.61$ is close to the ''golden mean'' $\tau=(\sqrt{5}+1)/2\approx1.618$.

The arrow in Fig. 3 indicates a location where one parallel line stops and shifts at right angles. Such discontinuity and displacement changes the sequence of the consecutive spacings, e.g., from a *LLS* sequence to a *LSL* one, which makes it impossible to identify the exact sequence of successive spacings. Another reason why it is difficult to identify exact sequences is because one could also identify other, more closely spaced lines connecting flower centers, particularly when dealing with extended images of larger area. An example is shown by the upper-right-most spacing in Fig. 3. The wider spacing (L) then would be reasonably split into two shorter spacings of S and S/τ (note $L=S+S/\tau$).

Based on x-ray and neutron diffraction measurements, Boudard *et al.*[21] derived a bulk model for *i*-Al-Pd-Mn. The bulk structure can be described as atomically dense planes, quasiperiodically stacked along the $5f$ axis, and separated by less dense planes. The atomically dense planes can be separated into a small number of groups, each group encompassing only a small range of variations in composition and local order.

Similar experiments have been carried out on the *i*-Al-Cu-Fe alloy,[22] and a similar structure model can be used to describe its *bulk* structure. Based on this model, dynamic LEED calculations[4] concluded that the outermost layer perpendicular to the $5f$ axis is Al-rich with a fraction of Fe atoms. Figure 4 presents a 10×10 nm^2 section of such a plane, generated from the bulk model. This atomically dense plane contains 85% Al atoms and 15% Fe atoms.

Many flowerlike patterns, with size similar to those that dominate the STM images, are easily identified in the plane (Fig. 4). Each flower consists of two concentric rings with a filled center. Each ring possesses ten atoms. However, the choice of atoms to form such flower patterns in the plane is not unique. We have chosen the flowers in Fig. 4 in such a way that their arrangement matches the pattern of flowers drawn in the STM image of Fig. 3, and vice versa. As observed in the STM images, local ''glue'' configurations that connect the neighboring flowers, such as the small pentagons, overlapping flowers, and intermediate-sized rings, are also identified in the plane, as indicated by the constructions in Fig. 4. The size of the features identified in the model (Fig. 4) compares very well with the size of the features measured with STM, as indicated in Table I.

TABLE I. Experimental and model-based sizes of characteristic features.

Feature	Size in STM data (nm)	Size in model(nm)
Full flowers (petal to petal)	1.57 ± 0.06	1.52
Inner ring	1.05 ± 0.04	0.94
Small pentagon (edge length)	0.46 ± 0.02	0.47
Large pentagon (edge length)	2.04 ± 0.08	1.99
L (defined in Fig. 3)	1.88 ± 0.07	1.89
S (defined in Fig. 3)	1.17 ± 0.05	1.17
L/S	1.61 ± 0.06	1.61

Furthermore, we note that the center of the patterns identified in Fig. 4 is either occupied by Al atom or Fe atom. In addition, some flower patterns have Fe atoms, instead of only Al atoms, occupying the atomic positions in the petals. Comparing the obtained STM image (Fig. 3) where the flowers are either filled or empty at the center and some flowers exhibit missing petals, we speculate that Fe and Al atoms contribute differently to the electronic structure at the surface and thus respond differently to the tunneling conditions used to acquire the presented STM images. Another possible in-

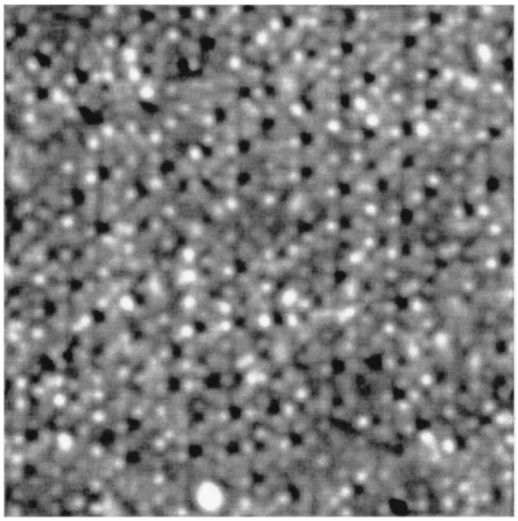

FIG. 5. High resolution STM image (20×20 nm^2) of an *i*-Al-Pd-Mn $5f$ surface, obtained under experimental conditions very similar to those of Figs. 2 and 3, and with the same experimental apparatus.

terpretation for the missing parts (both the empty center and the missing petals) is local defects on the surface.

Finally, we point out that the atomic-resolution STM images of *i*-Al-Cu-Fe presented in this paper are quite different than those for the *i*-Al-Pd-Mn $5f$ surface. On the latter surface, pentagonal or star-shaped holes are the predominant features reported to date.[11–14,17] We have ruled out differences in experimental conditions in various laboratories as being responsible for the differences, as follows: in the same chamber, we acquired a 30×30 nm^2 high-resolution STM image on an *i*-Al-Pd-Mn $5f$ surface (Fig. 5) with the same tip under similar tunneling conditions. The most notable features in Fig. 5 are the pentagonal depressions aligned in parallel directions. Nonetheless, images for both alloys can be interpreted in terms of features expected for the bulk-terminated surfaces.[17] Hence, it is puzzling why the surface STM images are very different, when the bulk structures of the two quasicrystals are very similar. Perhaps subtle differences in the electronic structure simply serve to emphasize the pentagonal holes in one alloy, and the flowers in the other.

In summary, we have obtained atomic resolution STM images on the atomically flat terraces of *i*-Al-Cu-Fe $5f$ surface. The analysis of the images shows that the flat terraces exhibit local $5f$ symmetry, consistent with the quasiperiodicity on the surface. The acquired STM images display the atomic arrangements on the surface with sufficient resolution so that it is possible to compare the STM image directly with the atomically dense planes generated from the experimental bulk structure. The comparison shows a good match. We conclude that these images are consistent with the description of the $5f$ surface of *i*-Al-Cu-Fe as Al-rich, bulk-terminated planes.

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