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Structural aspects of the fivefold quasicrystalline Al-Cu-Fe surface from STM and dynamical LEED studies

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Abstract

We investigate the atomic structure of the fivefold surface of an icosahedral Al-Cu-Fe alloy, using scanning tunneling microscopy (STM) imaging and a special dynamical low energy-electron diffraction (LEED) method. STM indicates that the step heights adopt (primarily) two values in the ratio of tau, but the spatial distribution of these two values does not follow a Fibonacci sequence, thus breaking the ideal bulk-like quasicrystalline layer stacking order perpendicular to the surface. The appearance of screw dislocations in the STM images is another indication of imperfect quasicrystallinity. On the other hand, the LEED analysis, which was successfully applied to Al-Pd-Mn in a previous study, is equally successful for Al-Cu-Fe. Similar structural features are found for both materials, in particular for interlayer relaxations and surface terminations. Although there is no structural periodicity, there are clear atomic planes in the bulk of the quasicrystal, some of which can be grouped in recurring patterns. The surface tends to form between these grouped layers in both alloys. For Al-Cu-Fe, the step heights measured by STM are consistent with the thicknesses of the grouped layers favored in LEED. These results suggest that the fivefold Al-Cu-Fe surface exhibits a quasicrystalline layering structure, but with stacking defects.

Keywords:

Theoretical methods, models & techniques:

1. Electron-solid interactions, scattering, diffraction

Experimental sample preparation and characterization methods:

2. Scanning Tunneling Microscopy (STM)
3. Electron-solid diffraction--Low Energy Electron Diffraction

Phenomena:

4. Step formation and bunching

Elemental and chemical identity:

5. Aluminum

Compounds:

6. Alloys

Surfaces:

7. Single crystal surfaces--Low index single crystal surfaces

1. Introduction

The atomic structure at the surfaces of quasicrystals is a matter both of technological and fundamental interest. On the technological side, the highly-ordered but non-periodic bulk structure of these metallic alloys is tied to an unusual combination of physical properties. These properties have already led to some applications as coatings and composites, and may lead to more.[1, 2] On the fundamental side, a basic question is how the bulk structure of the three-dimensional quasicrystals (i.e., the icosahedral phases) responds to the two-dimensional truncation enforced by a surface. Another is how the bulk and surface structures relate to the macroscopic physical properties.

In the present paper, we employ two techniques to gain insights into the atomic structure at the surface of one particular quasicrystal, icosahedral (i-) Al-Cu-Fe.

The first technique used here is STM, which provides real-space information on some aspects of surface structure. The first report of an STM image of the 5f surface of this particular alloy, i-Al-Cu-Fe, was given by Becker et al., [3]. However, all subsequent work on surfaces of icosahedral materials was done with i-Al-Pd-Mn, and in these later studies a very detailed level of analysis emerged. Schaub, et al.[4-6] observed a step-terrace structure that displayed geometric characteristics expected for a bulk-terminated surface, namely, arrangements of features, both lateral and vertical, in Fibonacci sequences. Later, we provided an interpretation of the fine structure on the terraces in terms of the cluster structure of the bulk.[7] Very recently, Ledieu et al. have analyzed the fine structure in terms of bulk tilings.[8] While these approaches and analyses differ, there is one main conclusion common to all of the three more recent studies (Schaub's, ours, and Ledieu's): The fine structure on the terraces of i-Al-Pd-Mn is consistent with bulk structural models. Hence, the *horizontal* structure, i.e. the structure within the surface plane, must be close or identical to that of the bulk.

The step heights measured via STM present a different situation. While Schaub et al. reported only two values of step heights on i-Al-Pd-Mn, we found three; furthermore, we found the frequency of step heights as a function of height to be much different (qualitatively) than did Schaub et al., suggesting a significant difference in the layer-stacking in the two studies. [4-7] Analysis of step height data are important for two reasons: First, they are a test of the *vertical* 'perfection' of the quasicrystalline surface, i.e. of whether the layers are stacked in a bulk-like sequence; and second, the LEED I-V model predicts specific step heights by predicting separations between favored terminations. Hence, the step heights measured in STM can be cross-checked against the results of the LEED structure model. In this paper, we will report and analyze the step heights on 5f i-Al-Cu-Fe.

In the second technique, we exploit the fact that surfaces of the icosahedral quasicrystals display sharp and dense LEED patterns.[5, 6, 9-16] Dynamical LEED analysis of experimental intensity-voltage (IV) curves can then be used to derive atomic structure, but for quasicrystals a special challenge comes from the non-periodic ordering of the atoms in the bulk. (A number of techniques, including LEED, have confirmed that the fivefold surfaces retain fivefold symmetry.[5-7, 9-20] Hence, it is reasonable to assume that a bulk-terminated surface is a good starting point in the structural analysis.)

It is impossible to define a unit cell as in periodic crystals; instead there is an infinite variety of local structures. Therefore an exact dynamical calculation of LEED IV curves for quasicrystals is not feasible, and certain approximations are required to make the analysis possible.

Our previous study of the fivefold surface of i-Al-Pd-Mn [12, 21] showed that a successful dynamical analysis of a fivefold (5f) surface could be achieved. The main modification to the LEED theory was the "average neighborhood approximation," according to which the scattering properties of atoms with similar neighborhoods were assumed to be identical. The success of the approximation was partly due to the fact that a few types of local structures repeat throughout a quasicrystal and thus dominate in the diffraction. For example, more than 50% of the atoms on the 5f surfaces of Al-Pd-Mn form pentagons. In addition, the structure of LEED IV curves primarily reflects local structure, mainly because of the short free mean path of the diffracting electrons. [22]

It is reasonable to expect that the same analysis will work for i-Al-Cu-Fe. The bulk structures of i-Al-Cu-Fe and i-Al-Pd-Mn are very similar, with minor deviations due mainly to differences in composition: the changed composition fractions result primarily in substitution of chemical identities, and secondarily in a small number of added or deleted atoms in some sites. This paper presents the outcome of that analysis, for the 5f surface.

The organization of the paper follows. First, experimental details, both of LEED and STM, are presented in Sec. 2. The theory of the dynamical LEED of quasicrystals is summarized in Sec. 3. In Sec. 4, the experimental STM data, including step height distributions, are presented. In Sec. 5, the dynamical LEED analysis on Al-Cu-Fe is described. In Sec. 6, the results are compared with those for Al-Pd-Mn and conclusions are drawn.

2. Experimental Description.

Samples were grown, characterized, and prepared as discussed in previous papers.[23, 24] The two samples used in STM were adjacent slices from the same single grain, whose composition was determined via inductively coupled plasma-atomic emission spectroscopy (ICP-AES) to be $Al_{61.5}Cu_{24.8}Fe_{13.7}$. The composition of the sample used in LEED was determined similarly to be $Al_{63.4}Cu_{24.0}Fe_{12.6}$. In both the STM and LEED experiments, we cleaned the sample in ultrahigh vacuum with cycles of ion etching and annealing. In the STM experiments, we used He ions, whereas in the LEED experiments, we used Ar ions. [13] Etching with Ar is known to shift the surface composition far away from the icosahedral region of the phase diagram in the Al-rich quasicrystals. [5, 11, 13, 14, 25-29] Helium was chosen in the STM experiments (done more recently than the LEED experiments) to reduce preferential etching of Al.[30]

A fresh sample, introduced from air, was typically cleaned by sputtering for 30 minutes, followed by 30 minutes of annealing, starting at 450 K and stepping up by 50 K when significant carbon and oxygen were no longer detected by AES at a given temperature. The sample was heated to a maximum temperature of 875 K.

STM and LEED experiments were performed in three separate ultrahigh vacuum chambers. The two STM chambers were each equipped with an Omicron STM, instrumentation for Auger electron spectroscopy (AES), a mass spectrometer, ion sputtering gun, sample heating capability, and a manifold for introduction of selected pure gases by backfilling. A typical base pressure during STM measurements was 2 to 6 x 10^{-11} Torr. The STM samples were each about 3x4 mm^2 in area, and 1.5 mm thick. Before each STM measurement, the sample was sputtered for 30 minutes with He (1.0 KeV beam voltage, 8-10 μA from sample to ground with no bias), annealed at the stated temperature for one to two hours, and cooled down to room temperature. The typical tunneling current for the STM measurements was 0.3-0.5 nA, and the tunneling voltage was 1.0 V.

In the course of measuring the step heights with STM, we used two different scanners. Comparison revealed that it was important to calibrate the piezoelectrics accurately. We used Ag(100) as the standard, with known atomic step heights of 2.04 Å. Without this in-house calibration, errors up to 40% would have resulted.

The LEED chamber and measurements have been described previously.[13, 21]

3. Experimental STM Data.

After annealing at temperatures lower than 825 K, STM reveals a rough morphology with cluster-like protrusions. These protrusions have different sizes, varying from 1 nm to 2.5 nm in diameter (Fig. 1a). Terraces start to appear at about 825 K, though still dotted by clusters (Fig. 1b). At higher annealing temperatures (850 – 875 K), a step-terrace morphology predominates (Fig. 1c, 1d). This cluster-to-terrace sequence is similar to the progression of structures that we, and others, have reported already for 5f[7, 31, 32] and 3f [33] surfaces of i-Al-Pd-Mn. Commonly, the well-annealed surfaces exhibit apparent screw dislocations, as shown by the black arrow in Fig. 1e, and by the white arrow in Fig. 1f. It is also common that the large terraces contain broad but shallow pentagonal pits (black arrows in Fig. 1f). These two features--the screw dislocations, and the pentagonal pits--are distinctive, since we never observe screw dislocations and pentagonal pits on the 5f Al-Pd-Mn surfaces.

The fine structure on the terraces after high temperature annealing is shown in Fig. 1g-h. It consists of many flower-like features that are approximately 18 Å in diameter, (most obvious in Fig. 1h) and of small black holes arranged in Fibonacci pentagrids (most obvious in Fig. 1g). The flowers are presumably the same as the "daisies" noted earlier by Becker, et al..[3] The origin of the fine structure on this surface will be discussed elsewhere. The corrugation in Fig. 1g is about 0.5 Å peak-to-peak. (Statistical analysis gives 0.25Å for the root mean square, and 0.18Å as the arithmetic mean.) The main point is that the corrugation on the terraces is much smaller than the step heights, and hence does not interfere significantly in the following analysis.

We also analyzed the step heights carefully. Determination of individual step heights was problematic, for two reasons. First was the sloping background evident in Fig. 2, which could not be corrected satisfactorily by planing the entire image—either due to STM drift, or to a meandering, large-scale curvature of the surface. Second was the fact that the step height determined from a single line profile varied significantly, depending upon the exact point where the profile cut across the step. Hence, we devised a procedure to obtain a statistical average of heights measured along a continuous step, within localized regions of the image. For background correction, we used standard Omicron software to plane the original image. For individual step heights, we used the

Omicron software to construct histograms of pixel intensities in the immediate vicinity of each step. These histograms showed the frequency of z-values versus z within the local area bridging two neighboring terraces. This resulted in a histogram with two peaks, one corresponding to the lower terrace and the other to the upper terrace. We took the separation of the peaks as the step height across the two terraces. A typical histogram for a single step height measurement spanned roughly 300 nm^2. An example of one such histogram is shown in Fig. 3, and corresponds to the pixel height distribution encompassed within the rectangular box of Fig. 1c.

We avoided steps originating obviously from screw dislocations in the analysis of the step height distributions. Steps originating from screw dislocations predominantly displayed heights of 2.5 Å.

The entire set of values of step heights is illustrated in the distribution of Fig. 4. We see three step heights: 2.5 Å, 4.0 Å and 6.2-6.6 Å. These values form consecutive ratios of 1.6 and 1.55-1.65, i.e. close to the golden mean, τ=1.618. The step height of 2.5 Å is found much less frequently than the other two values. For instance, in Fig. 4, we have 30 steps with height of 6.2 Å, compared to 5 with a height of 2.4 Å.

Line profiles across series of terraces display sequences of step heights such as those illustrated in Fig. 2. Steps are labeled as low (L) and high (H), corresponding to heights of about 4 Å and 6 Å, respectively. If the surface were perfectly bulk-terminated, one would expect to see a Fibonacci sequence of L and H steps, in which sequences such as L-L-L would be forbidden.[34] The fact that we observe the forbidden L-L-L sequences indicates that the surface cannot be perfectly bulk-terminated; instead, it appears that layers--or, more likely, groups of layers--are stacked imperfectly.

The observation of a relatively high density of screw dislocations on this surface (on the order of 3 dislocations per 200 Å x 200 Å) is also consistent with imperfections in the layer stacking sequence. In a regular periodic lattice, as one spirals around a screw dislocation, all layers line up properly again after each turn, preserving a simple sequence of equal step heights. But in a quasicrystal, because of the non-periodic spacings between layers, most layers do not line up correctly when spiraling around a screw dislocation, leading to mismatches and thus stacking errors. For example, if one propagates a step of height L around a screw dislocation (as in spiral growth), and if that step height is maintained, it will create a sequence of heights L-L-L-…, adding one height L at each turn. This simple example, if continued, leads to a periodic sequence.

The exact relationship between screw dislocations and the non-Fibonacci step height sequences is not clear at this stage. Among other things, such a relationship must explain how the screw dislocations generate 2.5 Å step heights in their immediate vicinity, whereas the non-Fibonacci sequences include 4.0 and 6.2-6.6 Å steps (Fig. 2); for example, a 2.5 Å step may join another step and increase or decrease its height by 2.5 Å (Fig. 1e). It is nonetheless true that the screw dislocations and the non-Fibonacci step heights are both manifestations of imperfect quasicrystalline stacking, such as locally periodic stacking.

Periodic sequences of interlayer spacings have in fact been observed by high-resolution transmission electron microscopy (TEM) in defect areas of bulk i-Al-Cu-Fe samples. Similar periodic regions have been observed by TEM in the types of samples we use, and are associated with strain fields. Strain fields arise because the samples are first prepared via liquid-assisted growth, then hot-isostatically-pressed to reduce porosity, and finally annealed again to reduce strain from the pressing. Strain fields become particularly abundant after the hot isostatic-pressing step, as shown by comparing the TEM images of Fig. 5a and 5b. Fig. 5a is a TEM image of an as-grown sample, whereas Fig. 5b shows a sample immediately after pressing. The strain fields are reduced considerably, although not eliminated, after the final annealing. Fig. 5c is a TEM image after the final treatment, showing a region that is locally perfect. We speculate that remnant strain fields from the hot-pressing procedure may play a role in the imperfections at our surfaces.

4. Sketch of dynamical LEED theory for quasicrystalline surfaces

In spite of their non-periodicity, quasicrystals often produce LEED patterns with a set of well-defined spots, as shown in Fig. 6. The LEED patterns can be even sharper and clearer than for normal crystals; quasicrystals are thus structurally very different from amorphous materials. The sharp LEED pattern is evidence that quasicrystals are a class of ordered materials with particular long-range order and orientation symmetries; in fact they can be described with self-similar models (i.e. as structures that can be scaled up by constant factors to yield similar structures at different length scales). It has been proven in many studies that the Fourier transform of a quasicrystal structure is well ordered in reciprocal space, although again not periodic.[34] In LEED, the Fourier transform corresponds to single scattering theory. Just as with periodic crystals, multiple scattering does not change the LEED pattern in reciprocal lattice, but modifies the LEED spot intensities. The LEED IV curves for these patterns have the same qualitative appearance as for a normal crystal, and are illustrated in Fig. 7 and Fig. 8, where diffraction spot intensity is plotted as a function of momentum transfer parallel to the surface, $\Delta k_{||}$.

As a starting point for the structural LEED analysis, we need a source of bulk atomic coordinates with icosahedral symmetry. Quasicrystals are most conveniently represented as a periodic bcc lattice in 6 dimensions. The "atoms" in that lattice are replaced by atomic hypersurfaces. Tricontahedral atomic hypersurfaces, instead of the usual spherical ones, are used in our models for Al-Cu-Fe and Al-Pd-Mn, in order to yield reasonable bond lengths. [35] The three-dimensional structure is generated as a particular projection from that six-dimensional bcc lattice into a 3-dimensional space, and the two-dimensional surface is obtained by terminating the three-dimensional lattice. The bulk structure of Al-Cu-Fe is determined by x-ray and neutron diffraction, which fix the atomic hypersurfaces. Once the 3-dimensional bulk structure of Al-Cu-Fe is determined, a 5f surface is obtained by rotating the bulk structure so that the surface plane is perpendicular to the 5f axis.

The resulting atomic structure along the surface normal shows well-defined and separated atomic planes, with one, two or three chemical types of atoms in each plane. (We shall use the term "plane" for sets of coplanar atoms and "layer" for more general sets of atoms, including groups of atomic "planes", as in "composite layers"). The interplanar spacings vary systematically according to Fibonacci sequences and the Golden mean. As a result of the non-periodicity, each plane is different. If we assume that the surface terminates along such atomic planes, there is, strictly speaking, an infinite number of inequivalent terminations. Within each atomic plane, although there is no repeating unit cell, one finds repeating local 5f rings throughout the plane. The atomic density of different planes varies strongly in the range from 100 to 800 atoms in an area of 100 Å x 100 Å. The smallest size of the local rings varies with the atomic density. These planes are found to belong to subsets of planes with very similar compositions, atomic densities and geometry. Thus, the infinite variety of planes actually has a relatively small number of distinct types of structure, and we shall exploit this property.

The major difficulty in the LEED analysis of quasicrystals comes from multiple scattering. In a single scattering LEED theory, which assumes that all electrons are scattered only once before they leave the surface, the outgoing wave amplitude from an atom depends only on the chemical identity and the position of the atom. In dynamical LEED, however, the outgoing wave amplitude from an atom is composed not only of that directly scattered wave, but also of waves that have undergone other scattering events within the surface. The latter events depend not only on the chemical identity and position of the scatterer, but also on the environment of the scatterer. In principle, the environment of every atom is different from that of every other atom, measured on an infinitely large scale. Therefore, the total wave amplitude of outgoing electrons from any given atom is different from that from all other atoms. In this sense, there are an infinite number of different atoms that have to be taken account in a dynamical LEED analysis of quasicrystals. This is fundamentally different from the dynamical LEED theory of periodic crystals, in which the number of different atoms is finite, due to the repeating unit cells.

As a result, certain approximations have to be made in a realistic dynamical LEED analysis of quasicrystals. In this paper, we apply efficient approximations that were tested in a previous LEED analysis of an i-Al-Pd-Mn surface;[21] these are sketched in the following. The basic idea is that the local environments of atoms tend to have only a few basic structural arrangements, as described above. Due to the limited mean free path of propagating electrons within the surface, the LEED IV curves are determined primarily by the scattering within such local environments. The different approximations depend on how we treat the similar local environments in a quasicrystal lattice.

More specifically, the approximations in our theory take into account that the atoms are explicitly arranged in atomic planes parallel to the 5f surface in a bulk terminated quasicrystal. The atoms within a given atomic plane are typically evenly distributed in space. The atomic density measured per unit area is uniform within a plane, but fluctuates from plane to plane, in the range 0.01-0.13 atoms/Å^2. The "effective" atomic scattering properties (including all multiple scattering events) are more alike within an atomic plane than between different atomic planes, as the average scattering properties of atoms in an atomic plane depend largely on the composition and the atomic density of that plane. Therefore, as an approximation, we assume that all atoms within a certain atomic plane are equivalent, but different from atoms in other planes.

This approximation, in the single scattering theory, implies that the scattering properties of an atom are averaged over chemical identities. It leads to the average t-matrix approximation (ATA),[36] [37] [38] according to which the scattering matrices t of the individual atoms within one plane are replaced by an averaged scattering t-matrix:

$$\langle t\rangle = c_{Al}t_{Al} + c_{Cu}t_{Cu} + c_{Fe}t_{Fe},$$

where C_i are the relative concentrations within the plane.

Next, as an approximation in the multiple scattering LEED theory, the variable environments of the atoms in a particular plane are replaced by a fixed, simplified average geometry, referred to as "average neighborhood approximation" (ANA). More specifically, the final wave amplitude from an atom, with all multiple scattering events considered, is replaced by an averaged wave amplitude over all atoms in the plane. The ATA is applied before the wave amplitude is averaged. For more details, see Ref. [21].

With these approximations, we can perform the calculation with a relatively small number of atoms, equivalent to the number of atomic planes, with different plane-dependent scattering properties. If we take atomic planes as deep as 10 Å into account, we obtain about 12 planes, i.e. 12 atoms with different scattering properties. The incident beam is damped into the surface due to inelastic scattering events, so that the contributions of deeper atoms do not influence the IV curves significantly. The calculation of the averaged propagator matrix $\langle G\rangle$ which describes electron propagation within and between closely-spaced planes, is performed by averaging in an area of 100 Å x 100 Å. The averaged wave amplitude depends strongly on the atomic density of the plane. For a plane with high atomic density, the averaged amplitude is affected by multiple scattering events within the plane more than that between planes. Inversely, for a plane with low atomic density, it is affected more by the multiple scattering events between atomic planes than by that within the plane.

The ANA, in which all atoms in a particular atomic plane have the same averaged effective scattering properties, can be improved in several respects. First, it is possible to use the ANA without the ATA. In this case, a single coplanar atomic plane is divided into several mono-atomic planes such that each has only one chemical species. All atoms in one mono-atomic plane are then assumed to have the same scattered wave amplitude. The computation time increases because one has to deal with more mono-atomic planes, i.e. more atoms in the calculation. It has been demonstrated for Al-Pd-Mn that most IV curves are little affected by the use of the ATA: thus one can safely apply ATA and gain computational time. The ANA may be further improved if one divides an atomic plane into several subplanes in which the atoms in each subplane have exactly the same local environment within and out of the plane. For example, one can assume that the local environments of two atoms are similar only if the nearest-neighbor distances and the number of nearest-neighbors are equal. All the atoms are thus sorted into a few classes of atoms, each with the same local neighborhoods. Notice that the number of different atoms increases sharply if the size of the local neighborhood increases. In the LEED calculation for Al-Pd-Mn 5f surfaces, it was shown that the IV curves are also very similar under this approximation. This at least shows that the ANA is reliable for the 5f quasicrystal surfaces. However, the approximation was found to be less successful for the surfaces of Al-Pd-Mn with lower symmetry, such as the two- and three-fold surfaces. [39]

5. LEED structural analysis

Some of the experimental LEED IV curves are shown in Fig. 7 and Fig. 8. Normal incidence is established by optimizing the agreement between curves for different, but symmetry-equivalent, diffraction spots, as shown in Fig. 7. Each curve shown in Fig. 8 is a symmetry-averaged composite, normalized to approximately the same value. Different curves represent different sample treatments. We varied sample treatments in order to check the robustness of the IV data. In all, we reproduced the complete set of IV curves 9 times. We conclude that the IV curves are not sensitive to sample preparation conditions, within the range of sputtering conditions (15-30 minutes with Ar^+) and annealing conditions (1-2 hours at 800-850 K) tested. This is similar to our previous findings for 5f i-Al-Pd-Mn, where the experimental IV curves were also found to be very robust.

In the LEED analysis of the 5f Al-Cu-Fe surface, we first explored individual bulk terminations, with possible relaxations of the top few interplanar spacings. Later we also considered combinations of terminations. For the calculation, we used relativistic phase shifts of Al, Cu and Fe, which have also been used in the LEED analysis of the (110) surface of crystalline β-$Al_{1-x}(CuFe)_x$ with a similar composition. [40] Thermal effects were included through the usual Debye-Waller factor. The Pendry R- factor was used for comparison between theory and experiment.

We thus started by analyzing a large set of individual terminations of the 5f Al-Cu-Fe surfaces, namely those that exist within a rectangular box with surface dimensions of 100 Å x 100 Å and a depth of 50 Å. Those terminations run through all the atomic planes along the surface normal in the entire depth of the box. For each termination, the top 12 atomic planes are chosen as a composite layer for LEED calculation. At first, in a rough search, we only allowed the relaxation of the topmost interplanar spacing using a grid search, i.e. the R-factor was calculated on a grid of points in the range from -0.3 to 0.3 Å.

The resulting R-factors for all the terminations that we examined are plotted in Fig. 9. It is seen that the R-factor varies from about 0.5 to 0.9 for different terminations. The R-factor drops if more planes are allowed to relax, but it is found that the change in R-factors is much smaller than the fluctuations between R-factors for different terminations. So the R-factors shown in Fig. 9 are reliable as a basis for further analysis. It is also interesting to find that the different terminations yield very similar optimized structural parameters.

Next, we focused on the most promising surface terminations as given by the R-factors shown in Fig. 9. We interpret the "better" terminations of Fig. 9 to be all present on the real surface, forming an array of terraces separated by steps of variable height.

The favored step heights can be understood in terms of groups of closely-spaced planes. Even though there is no periodic repetition in the quasicrystalline bulk structure, certain groups of planes occur frequently (even if not identically). We recognize three main sets of grouped planes, each group containing 3, 5 or 9 atomic planes (they can be identified in Fig. 9, while the 5- and 9-plane cases are also illustrated in Figure 10; note that there sometimes exist additional planes of very low atomic density between these planes, resulting in 11-plane groups, for instance). Within each group, the distance between successive atomic planes is smaller than 0.78 Å. The different groups are mutually separated by at least a distance of 1.5-1.6 Å. The two large groups with 5 and 9 planes share some common features. Each group has an approximate central symmetry around the middle plane. Both outer surfaces of such a group have two planes separated by only 0.48 Å; these planes have the highest combined atomic density.

It is found that the surface tends to form between these grouped planes, i.e. by splitting through the relatively large spacings of 1.5-1.6 Å, and thus exposing the closely-spaced pairs of planes. Since the outermost plane within these pairs has a high aluminum concentration and the other an Al:Cu ratio of about 50:50, these pairs are enriched in aluminum compared to the bulk average. Their combined surface atomic density is close to that of the densely-packed Al(111) crystalline surface. The step heights between terraces with such terminations are obtained by measuring the distances between two kinds of terminations, which are 3.99 Å for 5-plane steps (Fig. 10 shows one such step) and 6.47 Å for 9-plane steps; 3-plane steps give 2.40 Å heights. (Spacing relaxations, if identical for the terminations involved, do not change these distances).

The next stage in our LEED analysis mixes different terminations. In a full LEED analysis of quasicrystals, one can explicitly take into account the coexistence of terraces with different types of terminations. Since they are all assumed to contribute to the LEED IV curves, one needs to mix their contributions. Assuming that the area of each terrace is large compared to the coherence width of the electron beam (which is justified by the STM observations in Section 3), then only the reflected intensities from different terraces need to be mixed, as opposed to reflected amplitudes. As shown both in the LEED analysis and in the STM data (Sec. 3), the frequencies of the three kinds of terminations are different. To reduce the number of fit parameters, we take into account that the terminations in 5-plane groups appear to have the better R-factors, and mix only this kind of termination. Since they have essentially the same structure perpendicular to the surface, the number of fit-parameters can be reduced to a few, representing the number of interplanar spacings that one wishes to fit.

We thus mixed the 6 terminations that yielded the best R-factors (indicated by the short arrows in Fig. 9) and gave them equal weights. We also allowed relaxation of the top 5 interplanar spacings. This was done by the linear LEED approximation.[41] In this very efficient approach, the wave fields are calculated for one reference and several trial structures. Then the Powell optimization scheme is applied to optimize the structure. The linear LEED approximation is valid for this material if the deviations between reference and trial structures are smaller than about 0.2 Å (which was always the case in our analysis).

As a result, the R-factor could be reduced to 0.39, which we take as our optimum fit. The comparison between the experimental and theoretical IV curves for this best-fit structure is shown in Fig. 11, and the structure itself in Fig. 12 (again, this represents an average best-fit structure for the 5-plane terminations). The topmost interplanar spacing contracts from the bulk value by 0.10±0.08 Å, going from 0.48 Å to 0.38Å, while the second interplanar spacing expands, the third interplanar spacing contracts and the deeper spacings are close to bulk values, cf. Fig. 12. Since the third plane has a low atomic density, the error bar for the second and third interplanar spacings is large (comparable to the changes from the bulk values).

We assumed the bulk composition for each layer, since the earlier work with Al-Pd-Mn showed little sensitivity of LEED to these compositions.[21] Thus, on average, the bulk composition of the outermost atomic plane is 90% Al and 10% Fe atoms, while the second atomic plane contains 45% Al, 45% Cu and 10% Fe atoms. The average lateral density of the two top planes taken together is 0.14 atoms/Å^2, a value very close to that of a single plane of Al(111), 0.141 atoms/Å^2. This indicates a very densely packed surface double-layer. We notice that the optimized structure for a single termination is exactly the same as that for mixed terminations. This again indicates that the selected terminations are very similar in structure.

From Fig. 9 it is to be noted that some 9- and 3-plane terminations give R-factors that are not much worse than those for 5-plane terminations. While the LEED analysis cannot be used to state that these terminations are also present on the surface or with what relative abundance, at least the LEED analysis is consistent with the presence of some 9- and 3-plane terminations on the surface: the LEED results are therefore also compatible with the STM data, which indicate the presence of several step heights.

Finally, we note that other authors have suggested that three step heights may be a normal situation on 5fold surfaces of icosahedral quasicrystals. Fradkin [42, 43] has shown that three step heights are to be expected on supercooled quasicrystalline samples along the fivefold axis. The relative population of these three step heights depends upon the extent of supercooling, i.e. the extent of deviation from equilibrium. At the exact points where one population disappears, the ratio of the other two populations should be $\tau = 1.61$…. In Fig. 4, the 2.4 Å population is very small, and in the context of the Fradkin model, one might think that it is on the verge of disappearing. The ratio of the three populations is about 9%:37%:54%, i.e. the two largest populations are in the ratio of about 1.5. While this value is not exactly τ, it is close enough to be qualitatively in accord with the hypothesis of Fradkin.[42, 43]

Another prediction has been made recently by Gratias, et al., [44] who, on the basis of the specific structural model for i-Al-Cu-Fe, forecast that steps should adopt three values of heights with predictable frequencies. These heights (frequencies) are, relative to the longest step, L: L (31%); L/τ (51%); and L/τ^2 (19%), i.e. the two largest populations should be in the ratio of 1.65. Again, we see that our experimental value of 1.5 is only slightly lower than expected. Also, our experimental values of the step heights (2.5, 4.0, and 6.2-6.6 Å) follow the predicted ratio of L, L/τ, and L/τ^2 exactly.

6. Conclusions

We have analyzed the atomic-scale structure of the 5f surface of an Al-Cu-Fe quasicrystal by STM imaging and a special dynamical LEED analysis. Basically, the surface is bulk-terminated with presumably a bulk-like layer-dependent composition. Our analysis finds that the surface tends to form between different groups of closely-spaced planes, i.e. by splitting the quasicrystal through the larger interplanar spacings that separate those groups. In particular, we find that those grouped planes can be sorted into three sets, with 3, 5 and 9 planes, respectively. The interplanar spacings are the same for the same set of grouped planes. The 5-plane and 9-plane groups are similar in that the top pair of planes have the highest combined atomic density, about 0.14 atoms/$Å^2$--very close to that of the Al(111) surface--and are rich in Al.

The sets of 3, 5, and 9 planes correspond to step heights of 2.47, 3.99, and 6.47 Å, respectively. The step height frequencies seen in STM hence favor the 9-plane steps, then the 5- plane steps and finally the 3-plane steps (Fig. 4). LEED does not measure step heights directly: the R-factors favor 5-plane terminations, then 9- and 3-plane terminations. The LEED R-factors contain information both on the quality of fit of individual coexisting terminations, and on the frequency of occurrence of the different terminations; however, it is not clear how one could extract these two aspects separately from the data. Nonetheless, the fact that LEED and STM favor the same sets of step heights indicates that the two techniques are in overall agreement on the types of terminations present at the surface. The measured distribution is also roughly consistent with the predictions of Fradkin,[42, 43] and of Gratias, et al.[44]

The sequence of step heights in STM (Fig. 2) suggests that there are defects in layer stacking, relative to a perfect bulk quasicrystalline termination. LEED shows that groups of planes are separated by distances of 1.4-1.6 Å with no atoms in between, as illustrated in Fig. 10. We speculate that “mistakes” in the quasicrystalline lattice, normal to the surface, occur between these groups of planes. In other words, we hypothesize that quasicrystalline order is maintained well *within* favored groups of planes, where atoms interconnect densely throughout the structure, but less well *between* groups of planes. Perhaps these mistakes occur as the surface regrows after ion bombardment. Or perhaps they are engendered by defects in the bulk structure incorporated during sample preparation (Fig. 5). In either case, this hypothesis provides some understanding for the observation that there is stronger evidence for defects *perpendicular to* the surface than for defects *within, or very near to,* the surface plane.

Finally, it is interesting to compare the present results for 5f i-Al-Cu-Fe, and those reported previously for 5f i-Al-Pd-Mn. The main *difference* is that the i-Al-Cu-Fe surface contains screw dislocations and pentagonal pits, neither of which has been observed on i-Al-Pd-Mn, in our laboratory and under analogous conditions. Our general impression is that the i-Al-Cu-Fe surface contains more defects, perhaps a remnant of the hot-pressing step which is a part of sample preparation, as discussed in Section 3. On the other hand, there are several *similarities* between the two types of surfaces. Both have been analyzed successfully by dynamical LEED theory. Similar R-factors are obtained for both materials. The preferred terminations, atomic densities, and chemical compositions are similar. As a result, the surface in both cases is aluminum-rich. The implied step heights are also very comparable. And the outermost interplanar spacing is contracted on both materials by 0.1 Å, leaving deeper spacings bulk-like within the error bars. Further discussion of geometric aspects of these surface structures can be found in ref. [21], given that the two materials are structurally so similar.

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Figure Captions.

Fig. 1. Micrographs of the 5f Al-Cu-Fe surface, after different thermal treatments and at different magnifications. (a) T < 825 K, 30x30 nm^2 (b) T ≈ 825 K, 50x50 nm^2 (c) T > 825 K, 100x100 nm^2 (d) T > 825 K, 200x200 nm^2 (e) T > 825 K, 100 x 100 nm^2 . Black arrow shows the origin of a screw dislocation. (f) T > 825 K, 100x100 nm^2 . White arrow points to a screw dislocation; black arrows point to the pentagonal facets. (g) T ≈ 825 K, 50x50 nm^2. (h) T ≈ 825 K, 15x15 nm^2. The circle outlines a the flower.

Fig. 2. Line profiles across consecutive terraces, from the data of Figs. 1c-d. The labels (i)-(iii) indicate the specific profiles in Figs. 1c-d. Steps are labelled as H, high (6.2-6.6 Å) or L, low (4.0 Å).

Fig. 3. Histogram illustrating the method of step height measurement. The histogram shows the distribution of pixel heights, in the area encompassed by the rectangle in Fig. 1c. The two maxima correspond to the upper and lower terraces, respectively. Their separation is the step height.

Fig. 4. Frequency of step heights. Steps originating at screw dislocations are not included in this distribution. The total number of observations is 278. The height 2.5A is the average of 23 data points, and the calculated standard deviation is 0.2Å. The height 4.0Å is the average of 99 data points, with 0.4Å standard deviation. The height 6.2Å is from 142 data points, with 0.3Å standard deviation.

Fig. 5. TEM images of i-Al-Cu-Fe samples after different treatments. (a) Along the 2f axis, as grown. (b) Along the 2f axis, after hot isostatic pressing. Arrows point to periodic regions in the lattice; one such region is enclosed in a box to show it clearly. The

bands of periodic lattice align along the 5f directions. (c) Along the 5f direction, after pressing and annealing to 800˚C. The inset shows a selected area diffraction pattern. The lack of streaking between diffraction spots, and the high degree of perfection in the TEM image, indicate the absence or very low density of "periodic" defect regions. Contrast variations across the images in (a) and (c) are due to variations in foil thickness; in (b), the contrast variation is due to this and also to the strain fields associated with the periodic regions.

Fig. 6. LEED pattern of the surface after annealing at 850 K for 1 hour. The incident beam energy is 70 eV.

Fig. 7. LEED IV curves from the 5f surface of Al-Cu-Fe, taken after preparing the surface by sputtering at 15 minutes and annealing at 800 K for 1 hour, then cooling to 120 K for data acquisition. Diffraction spot intensity is plotted as a function of momentum transfer parallel to the surface, $\Delta k_{||}$. Each box encloses four symmetry-equivalent curves. At normal incidence, the curves should be identical. The values of $\Delta k_{||}$, based upon x-ray diffraction data for the bulk, are: bottom two boxes-- 1.647 $Å^{-1}$; middle two boxes--2.665 $Å^{-1}$; top two boxes--4.312 $Å^{-1}$.

Fig. 8. LEED IV curves from the 5f surface of Al-Cu-Fe, showing the effect of different annealing temperatures on the IV curves. Diffraction spot intensity is plotted as a function of momentum transfer parallel to the surface, $\Delta k_{||}$. Within each box, the lower and upper curves were measured after annealing for one hour to 800 and 850 K, respectively, then cooling to 120 K for data acquisition.

Fig. 9. R-factors for different terminations of bulk icosahedral Al-Cu-Fe, depending on the surface height z of the termination. (For each atomic plane shown as a vertical bar, the surface consists of this plane and all planes with higher z values; planes with lower z values are cut away.) The terminations giving the best R-factors are marked by arrows. In the lower part, the atomic planes are shown, at their respective depths z, as bars with thickness proportional to the atomic density in each layer. The colors of the bars suggest the chemical composition of each layer, according to the color codes shown below the figure.

Fig. 10. Side view (parallel to the surface, which is at top) showing several atomic planes: the five upper ones form a 5-plane layer, the left part of which is cut away to suggest a step down to a 9-plane layer (the structure at the step edge is completely unknown). The colors identify chemical elements: Al red, Cu blue, and Fe green. The larger spacing between the thicker layers is believed to be the preferred place where a surface forms.

Fig. 11. Comparison of the IV curves measured experimentally (solid lines) and generated from the best structural model (dashed lines). The experimental curves were measured after annealing at 800 K for 1 hour. The values of $\Delta k_{||}$, based upon x-ray diffraction data for the bulk, are, for the bottom two boxes-- 1.647 $Å^{-1}$; middle two boxes--2.665 $Å^{-1}$; top two boxes--4.312 $Å^{-1}$.

Fig. 12. Most favored termination for the five-fold Al-Cu-Fe surface, from LEED. Individual atomic planes are shown as colored bars (color coded to suggest their

approximate chemical composition). The optimized and bulk interplanar spacings are shown (at right), as well as a possible step height (at left).