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Structure of the tenfold *d*-Al-Ni-Co quasicrystal surface

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The structure of the tenfold surface of decagonal Al-Ni-Co was studied using low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM). The surface region is a relaxed truncated bulk structure, having the same composition as the bulk. The outermost layer spacing is contracted by 10% relative to the bulk interlayer spacing, while the next layer spacing is expanded by 5%. A small degree of intralayer rumpling was observed within each layer. There is a one-to-one correspondence between protrusions observed in the STM images and a subset of atoms in the model structure, indicating that in-plane reconstruction is minimal.

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The surfaces of quasicrystals hold tremendous interest due to their potential for creating new forms of matter having exotic and useful electronic and structural properties.[1–3] Quasicrystalline order in bulk metal alloys can cause large changes to their electronic properties, for instance, producing a pseudogap at the Fermi level in what would otherwise be a normal metallic alloy.[4,5] Quasicrystallinity can also produce changes in the surface electronic structure, as shown for the 10-fold face of d-$Al_{72}Ni_{15}Co_{13}$.[2] As the behavior produced by aperiodicity at surfaces continues to be investigated, overlayers and films having quasiperiodic structures offer even greater potential for new phenomena. Thin films having quasicrystalline order can be grown on quasicrystal surfaces,[6] which also act as templates for the growth of quasiperiodic arrays of nanocrystallites.[7,8] The ability to extend these discoveries to the design of structures with new properties depends on having accurate structure models of quasicrystal surfaces.

Previous structural studies of fivefold surfaces of icosahedral quasicrystalline aluminum alloys have demonstrated that they are bulklike, with long-range quasiperiodic order.[9–12] Recently, low-energy electron diffraction (LEED), scanning tunneling microscopy (STM), He-atom diffraction and ion scattering spectroscopy were used to establish that the fivefold surface of Al-Pd-Mn consists mainly of Al atoms, and that its structure is essentially a truncation of the bulk structure.[9,13,14] However, the surfaces of icosahedral quasicrystals comprise many terraces, each of which is different, and a complete atomistic structural characterization of such a surface is a very complex task indeed.

The characterization of tenfold decagonal surfaces should be simpler because their structures are periodic perpendicular to the surface, and therefore only a few terminations are possible. The first structural study of a quasicrystal surface was of decagonal $Al_{65}Co_{20}Cu_{15}$.[15] That structure was suggested to be a bulk termination, based on a tiling approach to the STM images. Two other STM studies of decagonal Al-Ni-Co have reported various structural features of the surface,[11,16] but the atomic structure of the surface was not determined. In this paper, we propose an atomic structure for the d-Al-Ni-Co tenfold surface based on the combination of dynamical LEED and high-resolution STM measurements.

The $Al_{73}Ni_{10}Co_{17}$ quasicrystal used in this study was grown at Ames Laboratory using the melt decantation method.[17] According to the phase diagram for Al-Ni-Co,[18] this composition lies in the basic Co-rich phase. The sample, a 2-mm-thick disk, was prepared in ultrahigh vacuum by many cycles of Ar+ ion bombardment (0.5 keV ions) alternated with annealing for six to eight hours at temperatures up to 1060 K, measured by a K-type thermocouple and an optical pyrometer. The LEED pattern was then observed to have well-defined spots and the impurity level was below Auger detectability. The symmetry of the LEED pattern is tenfold, due to the presence of two equivalent surface terminations rotated by 36°.[19] The LEED intensities were measured using a rear-view LEED system, with the electron beam at normal incidence to the surface, which was held at $T=60$ K. The STM measurements were carried out in an Omicron room temperature STM-1. The LEED and STM data were acquired using methods described previously.[20,21]

The LEED calculations were performed using the LEED program of Moritz,[22] which was modified for quasicrystalline structures.[14] The agreement between the calculated and experimental spectra was tested using the Pendry R factor.[23] The absence of a repeating unit cell parallel to the quasicrystal surface means that the number of atoms with different scattering properties is infinite. Therefore, some approximations have been applied to make the calculation tractable. These approximations[14] are the average neighbor approximation (ANA), the diagonal dominance approximation, and the average T-matrix approximation (ATA).

The bulk decagonal Al-Ni-Co quasicrystal has been the subject of many structure studies,[24–34] and the basic structure consists of a stack of identical or nearly identical fivefold symmetric planes, each related to its neighboring planes by a $\pi/5$ rotation, thus producing a structure having $ABAB$ stacking and a tenfold screw axis. The initial coordinates used for the atoms of one quasicrystal layer in this study are adapted

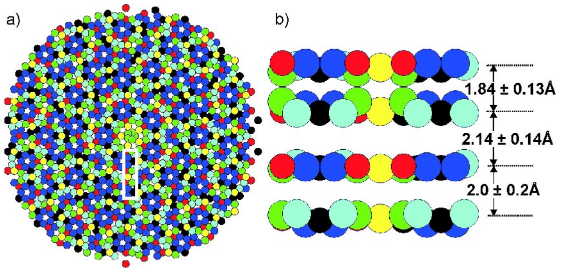

FIG. 1. (Color online) (a) One layer of the quasicrystal slab, having a diameter of about 90 Å. The different shades of gray (or color) correspond to the sublayer groups listed in Table I. The atoms are, in order of grayscale darkness (darkest first) and color: TM-2 (black), Al-2 (blue), TM-1 (red), Al-1 (green), Al-3 (cyan), and Al-4 (yellow). (b) Side view [viewing white box in (a) from the left] showing the surface relaxations and rumpling for the top four layers. The rumpling is exaggerated for clarity—its maximum amplitude is 0.1 Å.

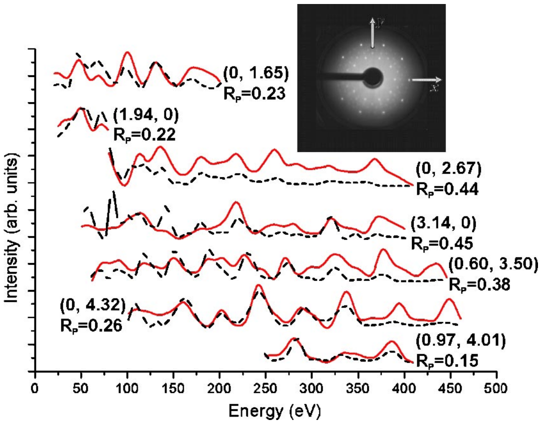

FIG. 2. (Color online) LEED $I(E)$ spectra. The solid curves are the experimental data and the dashed curves are calculated spectra. The inset shows the LEED pattern at 72 eV. The beam indices correspond to the (x,y) axes shown in the inset. The total energy range of the dataset is 1760 eV.

from those determined by the x-ray diffraction study of Steurer *et al.*[25] for the basic Ni-rich phase of Al-Ni-Co. The top view of one layer of atoms is shown in Fig. 1(a). The structure of the Co-rich phase studied in this paper is not exactly the same as the Ni-rich phase studied in the x-ray diffraction studies. However, it still provides a good starting point for this surface structure determination because the main difference between the two structures is believed to mainly reside in differences in the layer stacking and/or intralayer rumpling,[25] both of which are adjustable parameters in this study. The composition is also an adjustable parameter, although because LEED is insensitive to the difference between Ni and Co, only Al and transition metal (TM) atoms are distinguished.

In the LEED calculation, each quasicrystal layer is separated into six different groups of atoms (sublayers), as shown in Table I. Since most of the atoms in the coordinate set reside on vertices of the rhombic Penrose tiling with an edge length of 2.43 Å, the dominant NN distance is 2.43 Å. This is, in general, too short for an Al-Al bond, and to reduce the number of unfavorable Al-Al bonds, the occupancy of all atoms is set to 0.90 (apart from the atoms in the Al-1 group, which have an occupancy of 0.50) using ATA at the beginning of the analysis. The quasicrystal slab was built by stacking the layers described above in an *ABAB* sequence, where the layers *A* and *B* are related by a 36° rotation. In these calculations, a slab had a thickness of about 14 Å (eight layers) and a radius of about 45 Å.

TABLE I. Separation of quasicrystal planes into subplanes.

Group	Coordination	NN distance (Å)	No. atoms	% atoms
TM-1[a]	3	2.43	110	12
TM-2[a]	4 or 5	2.43	140	15
Al-1	1	2.24	165	17
Al-2	2	2.43	300	32
Al-3	3	2.43	145	15
Al-4	4 or 5	2.43	85	9

[a] Although indistinguishable in LEED, TM-1 can be identified with Co and TM-2 with Ni, after the EXAFS study which identified their coordinations (Ref. 34).

In the LEED analysis, only the relaxations of different atom groups perpendicular to the surface were considered, i.e., interlayer relaxations and intralayer rumpling are allowed, but lateral shifts of atoms are not. This produces 26 free geometrical parameters, giving an energy range of 68 eV per parameter. After optimization of the structure to achieve the lowest *R* factor, the average interlayer spacings were found to be $d_{12}=1.84\pm0.13$ Å, $d_{23}=2.14\pm0.14$ Å, $d_{34}=2.0\pm0.2$ Å, $d_{45}=2.1\pm0.2$ Å, and $d_{56}=d_{67}=d_{78}=2.0\pm0.2$ Å. When compared to the bulk spacing (2.04 Å) the spacings of the first two layers are contracted by 10% and expanded by 5%, respectively, while the remaining interlayer spacings are close to the bulk value. Figure 1(b) shows a schematic drawing of the layer structure and the intralayer rumpling, which has a magnitude of 0.1–0.2 Å. Although the chemical compositions were allowed to change when applying the ATA approximation, the best fit structure has the same composition as the bulk layers. The Pendry *r* factor for the best-fit structure is 0.32. Figure 2 shows the experimental and calculated intensity spectra.

The magnitude of the observed relaxation is similar to those observed in relatively open metal surfaces. The atom density of one layer of the structure determined here is $0.123\ \text{Å}^{-2}$ while that for a comparable alloy surface NiAl(110) is $0.170\ \text{Å}^{-2}$. The contraction of the top layer spacing on metal surfaces is generally understood to be a response to the charge smoothing present at metallic surfaces.[35] This relaxation is therefore consistent with a metallic surface, in agreement with the delocalized charge density deduced from photoemission studies of this surface.[2] The observed layer rumplings are similar to those observed in the bulk structure by x-ray diffraction[25] and supported by total energy calculations.[30,31] The main feature of the observed rumpling is that the atoms that are part of the deca-

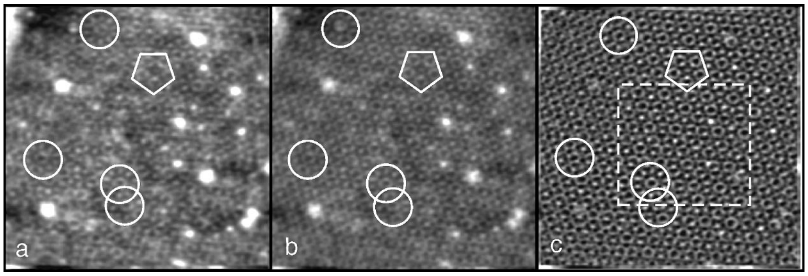

FIG. 3. (a) STM image from Al-Ni-Co. Tunneling conditions are: sample bias −1.00 V, current 1 nA. (b) Same as (a) after Fourier filtering. (c) Same as (b) after an unsharp mask filter is applied. The circles and pentagons assist in identification of features in the image after the processing. The dashed square indicates the area shown in Fig. 4.

prismatic columnar clusters, made up of TM1, Al2, and Al3, tend to be located toward the surface (away from the bulk) relative to the other atoms.

Because the sensitivity of LEED to lateral atom positions is limited, high-resolution STM experiments were performed to investigate in-plane structure. STM images were acquired from large flat terraces with dimensions on the order of 1000 Å. A 180 Å × 180 Å scan of a single terrace is shown in Fig. 3(a). It shows protrusions of atomic dimensions and the pentagonal and decagonal groupings of these features [some are outlined in Fig. 3(a)] are similar to those reported previously.[11] The presence of larger white protrusions, which have also been observed in previous studies of this surface[11,16] and appear at sites having local pentagonal symmetry.[11] As there is no trace of contamination on the surface, they apparently consist of bulk material too strongly bonded at these sites to diffuse to step edges during the annealing process.

To facilitate the comparison of these STM data to the structure determined using LEED, the images were first processed using a Fourier filter which involves enhancement of the strongest Fourier components of the image, followed by an inverse transformation. The result is shown in Fig. 3(b), with the outlined areas corresponding to the same decagonal and pentagonal features highlighted in Fig. 3(a). The final step in the image processing is to apply an unsharp mask filter to the data of Fig. 3(b), which enhances contrast and partially removes the large protrusions [Fig. 3(c)].

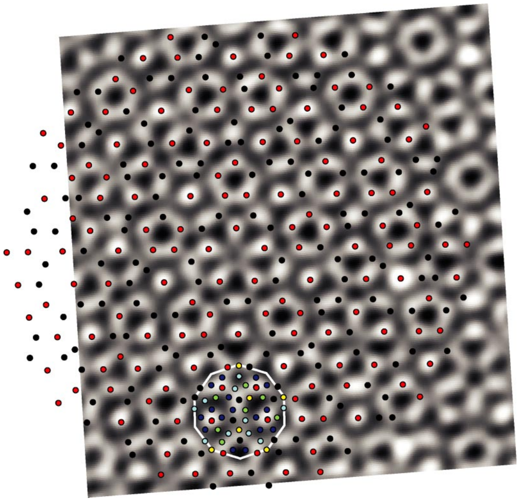

FIG. 4. (Color online) Superposition of the atom positions from the LEED result onto the STM image. The shading (color) of atoms is the same as that shown in Fig. 1. The protrusions corresponding to TM-1 atoms are generally brighter, consistent with them being closer to the surface. The decagon denotes the quasi-unit-cell identified in bulk structure studies (Refs. 36, 37).

The STM data were compared to the LEED structure by superposition of the top layer of the LEED structure model and the STM data. A 75 Å × 75 Å patch of the STM data [dashed box in Fig. 3(c)] was chosen and a match was sought between the protrusions and the atomic model. Because the number of protrusions in the STM image is significantly smaller than the number of atoms present in the single layer of the LEED model, subsets of atoms in the layer were tried. A very good match was found for the transition metals, shown in Fig. 4, although other matches may be possible. The closeness of the match indicates that lateral distortions in the surface structure are likely to be minimal.

The general features of the structure determined here are similar to those found for icosahedral quasicrystal surfaces, e.g., the basic surface structure is similar to the bulk, with a degree of relaxation consistent with a non-close-packed metal surface. One difference is that the top layers of both *i*-Al-Pd-Mn (Ref. 14) and *i*-Al-Cu-Fe (Ref. 12) were found to be Al-rich, whereas both the LEED and STM data presented here are most consistent with a surface structure that has essentially the same composition as the bulk. The higher Al content at the surfaces of the icosahedral quasicrystals is believed to be related to the relatively low surface energy of Al.[12,14] It is likely that the surface of Al-Ni-Co will have a higher surface energy than the icosahedral surfaces discussed above, and this is likely to affect film growth by making the surface more prone to adsorbate-induced reconstruction, but otherwise it may also be more ‘‘wettable.’’

In conclusion, we have used the complementary techniques of LEED and STM to establish the structure of the tenfold surface of *d*-AlNiCo. A unique and important feature of this study is that the positions and types (Al or TM) of all surface atoms have been identified. Unlike the icosahedral surfaces, the decagonal surface structure is wholly determined because there is effectively only one type of termination (two terminations related to each other by a rotation symmetry). This result provides a definite model for the surface structure, which can be used in the interpretation of other studies of this surface, as a basis for the interpretation of adsorption and growth on this surface, and for first principles calculations of surface geometric, electronic, and dynamical properties.

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