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Structure and oxidation at quasicrystal surfaces

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Abstract

We have investigated the atomic and electronic structure, chemical composition, and oxidation characteristics of the surfaces of icosahedral, Al-rich quasicrystals, using a variety of surface-sensitive techniques (LEED, XPS, STM, AES). We have systematically investigated the way that these traits vary with preparation conditions (e.g. sputtering and then annealing to various temperatures, vs. fracture), with surface symmetry (e.g. 2f vs. 3f vs. 5f surfaces), and with bulk composition (e.g. i-Al–Pd–Mn vs. i-Al–Cu–Fe). We have also compared our results for the quasicrystals with results for crystalline approximants and other related crystalline phases. Our main conclusions are that, under specific conditions of sputter-annealing, the bulk atomic and electronic structures of the clean quasicrystal propagate to the surface. Also, the oxidation chemistry is dominated by that of the primary constituent, aluminum.

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In 1994, I was in search of a major new research direction for my group. My friend and colleague, Alan Goldman, had been a leader in the field of quasicrystals since near its inception. Alan suggested that surfaces of quasicrystals would be a rich—and ripe—topic of research. He was right.

About 5 years earlier, a group led by Jean Marie Dubois at the CNRS in Nancy, France, had begun to report that quasicrystals exhibit intriguing surface properties, in air [1–7]. Among the properties reported by this group were low coefficients of friction, low propensity for wetting by polar liquids, and excellent oxidation resistance. These properties impelled us to investigate *why* the materials exhibit unusual surface properties, using the diverse and powerful tools of modern surface science.

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We were forced to begin by asking a very fundamental question, namely, what is the nature of the surface? The excellent oxidation resistance had led to speculation that the materials were very inert chemically, and a theory had rationalized chemical passivity based upon the bulk electronic structure [8]. There was speculation that even the air-exposed samples were clean. Therefore, we turned our attention to the nature of the surfaces exposed to oxygen, and to air.

Our very first work consisted of classic surface science-type experiments, using LEED and AES [9]. We chose to work with i-Al–Pd–Mn because high-quality samples were available to us from Tom Lograsso and Drew Delaney at the Ames Laboratory; also, this seemed to be the most thoroughly-characterized alloy in the field of quasicrystals. We found that a sample introduced into UHV from air was contaminated heavily with carbon and oxygen, as any other metal would be, and so we cleaned it by sputtering and annealing. We then exposed it to oxygen. The AES data showed that the quasicrystal surface readily adsorbs oxygen. Furthermore, the LEED pattern of the clean surface is extinguished as oxygen adsorbs, and the AES lineshape of Al changes from that of metallic Al to oxidized Al. Also, the change in AES line shape lags significantly behind the extinction of the LEED pattern during oxygen exposure, suggesting that oxidation is preceded by a disordered chemisorbed state. All of these features were quite comparable to the behavior of clean Al reported in the literature, suggesting that this Al-rich quasicrystal oxidizes much like pure Al.

We then performed an extensive series of XPS experiments, in which we used the intensities and positions of the photoemission lines to estimate the average depth of the oxide, to calculate the change in surface metallic composition accompanying oxidation, and to identify the elements that underwent oxidation [10–17]. Samples were oxidized at various temperatures, and in various environments—from UHV to air to liquid. In all cases, we characterized the ‘final state’ of the surface, not the kinetics of the processes. The quasicrystals were compared with samples of the pure constituent elements, and also with chemically-similar crystalline alloys. Comparisons were also made within a single quasicrystalline composition but across different surface orientations and microstructures. Initially, the quasicrystal we studied was i-Al–Pd–Mn, but later we performed similar work with i-Al–Cu–Fe, and i-Al–Cu–Cr–Fe. Consistently, the data supported the conclusion that the Al-rich quasicrystals self-passivate much like pure Al. The quasicrystals form a skin of pure, or nearly-pure, aluminum oxide which is about 5 Å thick after exposure to oxygen in UHV, and 20–30 Å thick in air. High relative humidity in air can lead to deeper oxides. The oxide protects the elements other than Al from oxidation. Hence, the speculation we had encountered initially—speculation that the quasicrystals were remarkably inert—was unfounded. The ones we tested derived their chemical inertness from their high Al content, not from their aperiodic structure. There have been some indications, since then, that quasicrystals may be distinctive in other ways [12,18–20], such as the kinetics of oxidation, and so oxidation is a subject that is still worthy of further consideration.

During this time, our colleagues Dan Sordet and his group had been investigating the stability of quasicrystalline, gas-atomized powders at elevated tempera-

tures in air [21]. They had found that the powders convert from the quasicrystalline phase to a crystalline phase at much lower temperatures than one would expect from the bulk phase equilibria. Our oxidation work proved helpful in interpreting their result, as follows: oxidation is accompanied by surface segregation of aluminum (to form the nearly-pure aluminum oxide). This depletes the bulk of aluminum. In a macroscopic sample, this depletion is negligible, but in a small particle, the depletion can be significant. The depletion of Al in the particle's core is sufficient to destabilize the quasicrystalline phase (which has a narrow region of phase stability). Because the particle is at elevated temperature, its core can rearrange to the favored phase, in this case a cubic B2 phase. Hence, an understanding of the surface oxidation chemistry helped to clarify the stability of powders at elevated temperatures.

In parallel with our oxidation work, we turned our attention to the nature of the clean surface. When we started, in 1994, the only UHV work in the literature was that published by the Bell Labs group [22–25], but the papers by Schaub et al. [26–29] were just appearing and the paper by Ebert et al. [30] would appear shortly thereafter. The skepticism that greeted the Schaub work, plus the conclusions in the Ebert paper, made us realize that a major issue existed, namely, whether or not a clean surface could be both flat and quasicrystalline (as had been suggested by Schaub et al.) The controversy really arose from the interpretation of the importance of clusters in stabilizing the bulk structure of quasicrystals. One group of scientists felt that clusters, such as the pseudo-Mackay icosahedron, were configurations that stabilized the aperiodic structure and that could account for many physical properties of quasicrystals. This group felt that a flat surface, such as reported by Schaub et al., could not be bulk-terminated because a flat surface would necessarily cut through some of the clusters. They argued that a flat surface would be unstable, and therefore would reconstruct, i.e. that it *could not* be bulk-terminated.

We began by mapping out conditions that yielded good LEED patterns, such as those shown in Fig. 1a–c. Such patterns had been reported already by two groups [27–29,31], but conditions had not been optimized systematically. We found [32–34] the best patterns after ion bombardment, followed by anneals of one-half to several hours at temperatures in the range 800–900 K. (These annealing times were—and still are—unusually long in light of the conditions typically required to prepare ‘good’ surfaces of crystalline elements.) The common wisdom of surface science held that a good LEED pattern could only be obtained from a surface containing terraces with widths on the order of at least a few tens of Å. Therefore, the existence of the LEED patterns indicated that the surface contained flat terraces. While the patterns in Fig. 1a–c were obtained with low-resolution optics, a later experiment with high-resolution optics [35] showed that the diffraction spots were intrinsically very sharp. In this measurement, shown in Fig. 1d, the widths of the diffraction spots corresponded to *average* terrace widths of 870 Å—very broad indeed, by the standard of single-crystal metals.

The obtainment of a good LEED pattern put one in mind of the possibility of carrying out a dynamical scattering analysis of the surface structure. Several times in the past, we had collaborated with various theory groups to determine structures of complex crystalline surfaces—we had performed the experiments, while they had

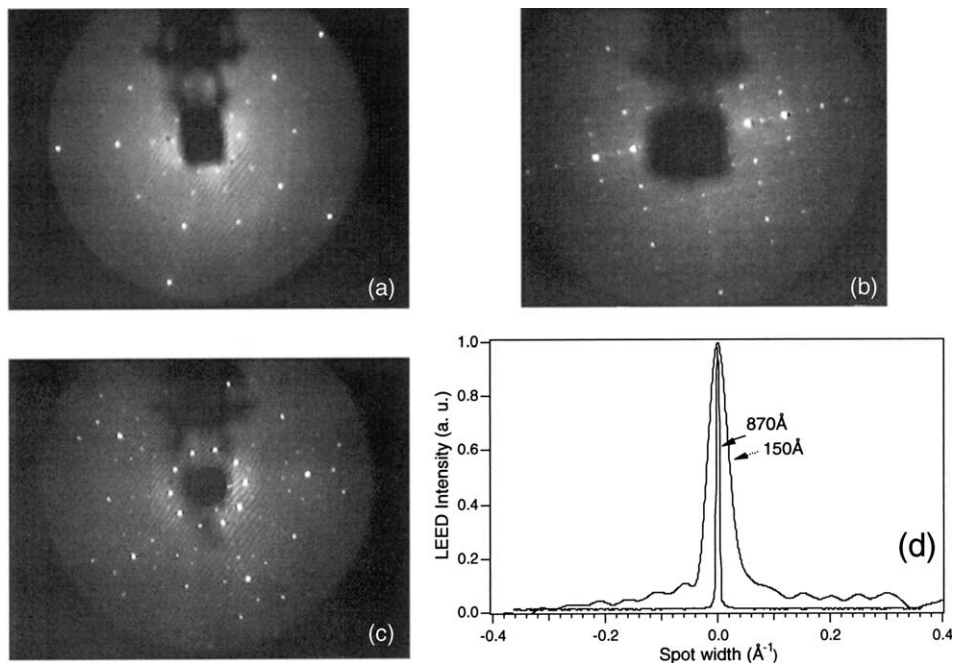


Fig. 1. (a)–(c) LEED patterns of the high-symmetry surfaces of i-Al–Pd–Mn: (a) 5f surface at 50 eV, after annealing to 750 K; (b) 2f at 50 eV, after annealing to 900 K and (c) 5f at 50 eV, after annealing to 850 K. From Ref. [34]. Copyright 1998 by World Scientific Publishing Co. (d) Diffraction spot profiles of the 5f surface. The numbers indicate the spatial lengths that correspond to the spot half-widths, which are 150 Å with conventional LEED optics and 870 Å with high-resolution optics. Reproduced from Ref. [35]. Copyright 2000 by the American Physical Society.

carried out the modelling [36–38]. At this point, I approached one of the experts in that type of theory, Michel Van Hove, to see if he might be interested in performing such an analysis on quasicrystals. He was, and he engaged a postdoc, Martin Gierer [39,40], for the project.

The challenge, of course, arose from the fact that the dynamical scattering analysis had to be done for a non-periodic structure. In fact, in an icosahedral quasicrystal, no two atomic planes are identical; no two scatterers have an identical environment. In order to deal with this complexity, Van Hove and Gierer [39,40] devised a number of new approximations, painstakingly checking the validity of each. The standard of comparison for each approximation was an exact scattering calculation carried out on a section of a three dimensional quasicrystal, extracted from a bulk model. Perhaps the most crucial approximation was the average neighborhood approximation, in which each scatterer was assigned an average environment. A limited number of different average environments was identified and employed in the calculation. In addition, the average *T*-matrix approximation was used. This approximation, which assigned an average chemical identity to each scatterer, had been previously tested and accepted in other metallic alloys.

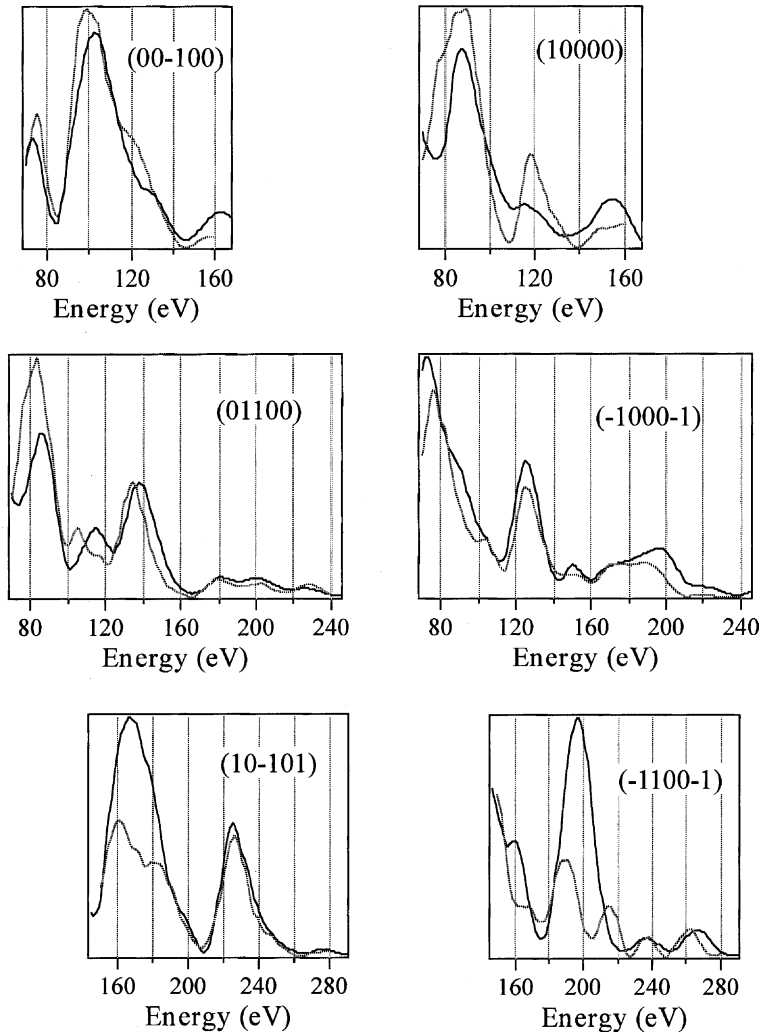


Fig. 2. Comparison of theory with experiment for the I - V curves of the main diffraction spots of the 5f surface of i-Al-Pd-Mn. Experimental data are averaged over all symmetry-equivalent beams. Reproduced from Ref. [39]. Copyright 1997 by the American Physical Society.

We therefore measured the LEED intensity-voltage (I - V) curves. We established that they were quite robust, varying only slightly with conditions of sample preparation [39], and not at all during oxygen adsorption [9]. Our data are shown in Fig. 2 for the fivefold surface of i-Al-Pd-Mn. Having established the formalism for the LEED I - V calculations, Van Hove and Gierer used our data to search for a surface structure that would provide a good match between the theoretical and measured I - V curves. They did this by using a three-dimensional volume of a quasicrystal generated from the bulk model of Boudard et al. [41], and placing a scatterer at each

atomic location. They then proceeded to peel off atomic planes, calculating the I – V curves for each newly-exposed surface. (It should be noted that we did not use the published model of Boudard et al., [41] but rather a refined version that was kindly provided to us by one of the coauthors, Marc de Boissieu.)

The result can be judged by a quantity called the R -factor. This is a measure of the fit between experiment and theory, with lower R -factors corresponding to better fits. An R -factor of about 0.3 or below is generally considered an acceptable result in surface analyses. Various exposed planes yielded minima in the R -factors. Upon closer examination, Gierer and Van Hove saw that these planes were self-similar. They consisted of 90–100% Al, the remainder being Mn. Furthermore, another plane was very close (0.5 Å) below, consisting of about 50% Al and 50% Pd. Focussing on these preferred terminations, they then undertook to optimize the R -factor by allowing relaxation and segregation. The best fit in the end [39,40] indicated a 25% contraction; (relative to the bulk spacing) between the top two planes, but no other modification. The top-layer contraction, and the Al-rich nature of the surface, were confirmed in a subsequent XRD study by Capitan et al. [42] and also in the LEIS-based work of Jenks and Bastasz [43,44], reviewed elsewhere in this volume.

This result was very gratifying, for two reasons. First, it could be understood in terms of principles known to govern surfaces of simpler metals. That is, the preferred terminations were rich in Al, which is the constituent with the lowest surface energy. Also, the two planes at the surface are so closely spaced that they could be considered as a single rumpled surface layer. The density of this rumpled layer is very high—approaching that of the close-packed face of Al. These two factors—high density, and high concentration of the element with lowest surface energy—would be expected to stabilize these layers, relative to other possible terminations.

Second, the preferred terminations were not separated by a single distance. Rather, they were separated by two distances of 4.0 and 6.6 Å. This corresponded exactly to the two step heights that had been reported by Schaub et al. [26–28].

This first LEED I – V analysis was done with the 5f surface of i-Al–Pd–Mn [39,40]. Later, we carried out a similar analysis, and obtained a very similar result, for the 5f surface of i-Al–Cu–Fe [45]. For this second alloy, we complemented the LEED study with our own STM study of the step height distribution, again confirming that the two results were mutually consistent. The histogram of step heights is shown in Fig. 3. We also attempted a structure analysis of the 2f and 3f surfaces of i-Al–Pd–Mn, but were unable to obtain a satisfactory R -factor in either case, despite extensive efforts on the part of Martin Gierer. The structures of the non-5f surfaces deserve further work.

Did the LEED I – V result help to address the issue of bulk termination? The 25% contraction between the top two planes certainly indicated a deviation from the bulk arrangement *perpendicular* to the surface plane. However, the LEED I – V result had to be interpreted cautiously regarding atomic arrangements *within* the surface plane. Because of the nature of electron scattering in LEED, plus the approximations used in the calculations, the structure analysis was far more sensitive to planar densities and interplanar separations than to lateral atomic arrangements. The fact that a

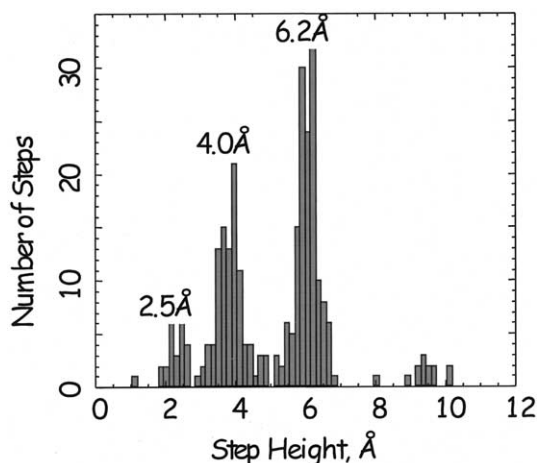


Fig. 3. Histogram of step heights on 5f i-Al–Cu–Fe. Reproduced from Ref. [45]. Copyright 2001 Elsevier.

successful result had been obtained starting from a bulk structure model was supportive of lateral bulk termination, but certainly not conclusive. Other types of experiments had to be done.

The LEED data could be used in other ways toward this end. One way was to analyze the relative values of parallel momentum transfer, represented by the relative diffraction spot spacings. Doing this for the 5f, 2f, and 3f surfaces of i-Al–Pd–Mn [35], and for the 5f surface of i-Al–Cu–Fe [33], we found that the spacings were consistently aperiodic, and were related (as expected for a laterally-terminated quasicrystal) by the golden mean, τ . Another way was to measure LEED patterns of surfaces of other bulk phases, with compositions similar to the quasicrystal. The reasoning was that if the quasicrystalline surface reconstructed, it might reconstruct to one of these other phases and data from the two samples would overlap. To this end, we measured [35] LEED patterns of an approximant to i-Al–Pd–Mn, the so-called ξ' -phase. It has a pseudo-10f axis that we deemed to be a reasonable candidate for mimicking the 5f axis of the quasicrystal. Its LEED pattern, however, exhibited 10f symmetry, clearly distinct from the 5f symmetry of the quasicrystalline surfaces. Thus, the LEED data built a firmer and firmer case for lateral bulk-termination in the quasicrystalline surfaces.

Other groups were doing XPD [46–49] and SEI [50–54] experiments, showing that the local atomic environments at quasicrystalline surfaces were consistent with expectations for bulk truncations. However, there had been no STM work on an icosahedral surface since that of Schaub et al. With sample preparation conditions now well-established, it seemed essential to employ this powerful real-space technique.

Our first STM data revealed fine structure on the terrace of 5f i-Al–Pd–Mn. The Fourier transform and autocorrelation function revealed that the patterns of light

and dark were, in fact, well-ordered and consistent with 5f symmetry. The auto-correlation revealed characteristic spacings between self-similar features. The distribution of spacings coincided very well with the spacings between pseudo-Mackay icosahedra tangent to the surface plane. Hence, we interpreted the image in terms of an electronic surface structure in which the atomic clusters determined the electron density contours. Later experiments, both by us and by other groups, showed that much better spatial resolution could be achieved, in which individual atoms could be resolved. An example is shown in Fig. 4a. The lateral structure—and the distribution of spacings between self-similar features—would both be expected to scale laterally as τ^3 . Hence, our first data probably represented poor resolution more than atomic clusters.

Nonetheless, the fact that individual features in STM images can be mapped 1:1 onto bulk-terminated structural models provides perhaps the most convincing evi-

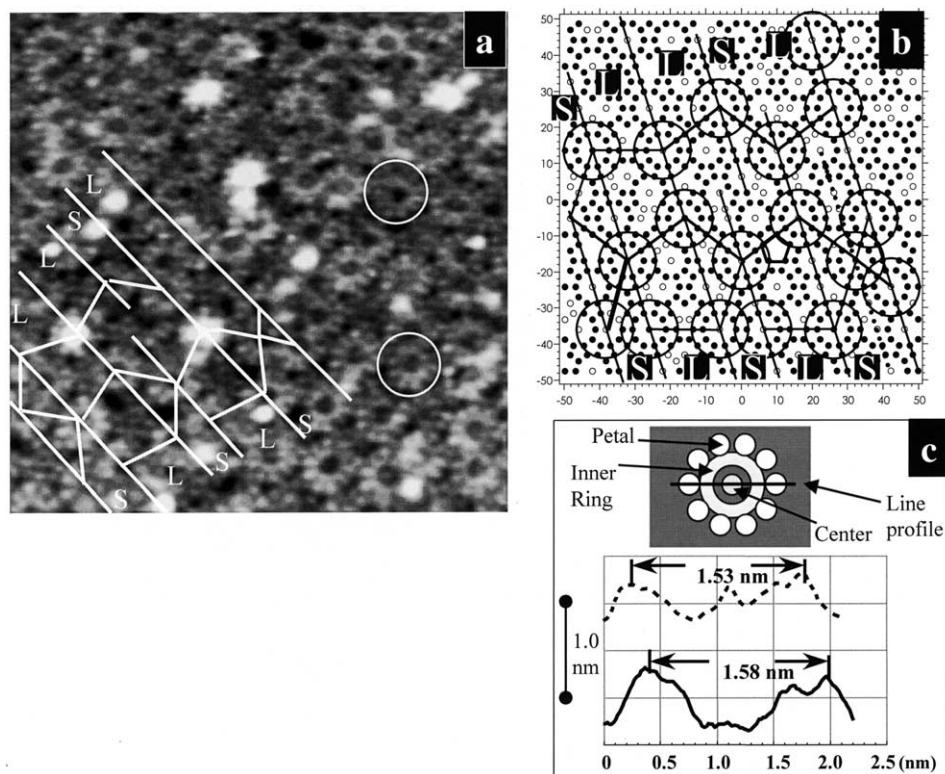


Fig. 4. Fine structure on the terraces of 5f i-Al-Cu-Fe, from Ref. [69]. Copyright 2002 Elsevier. (a) STM image. Circles show the flowers. Lines connect centers of flowers on one region of the terrace; (b) atomic arrangement in a favored type of termination, based on the LEED $I-V$ analysis. Lines connect centers of flowers and reveal the same extended structure shown in the experimental image and (c) schematic of the atomic structure of the flowers.

dence that the surfaces are laterally bulk-terminated. An example is the mapping shown in Fig. 4a–b, for i-Al–Cu–Fe; others are described in papers by McGrath et al., and by Barbier and Gratias, in this volume. The 10-petal flowers circled in Fig. 4a correspond to 10-fold rings of atoms, as shown in Fig. 4c, which exist at the dense, Al-rich terminations predicted by the LEED- I - V analysis.

It should be noted that the reconstruction of a quasicrystal surface to an extremely large unit-cell approximant, or to a surface that is slightly off-stoichiometry, can probably never be excluded. None of the experiments described above (nor to follow) will ever provide absolutely irrefutable evidence that the surface structure is the same as that of the bulk, atom-for-atom—since one would have to show this to be true over an infinitely large area. However, at some point the preponderance of evidence must be accepted in order that the field can move forward.

Not only the study of quasicrystals, but also the study of related intermetallics is a rich topic. Although we originally began to examine them as part of our effort to distinguish whether surface phases were quasicrystalline or crystalline, we soon realized that the surfaces of complex intermetallics are quite interesting—and unexplored—in their own right. In this vein, we studied the surfaces of i-Al–Pd–Mn and i-Al–Cu–Fe quasicrystals that had been converted to the cubic phase within the near-surface region [33,55,56], as well as the surface of a bulk sample of cubic Al–Pd–Mn [57], and the surface of a bulk orthorhombic Al–Pd–Mn approximant [35,58]. In the first case, we established the identity of the cubic (B2) overlayers based on several types of evidence, including an LEED I - V analysis and an LEED step height analysis. We found that the relation between the cubic overlayers and the quasicrystalline substrate could be understood from the related symmetries of cubic close-packed and icosahedral-packed materials. This approach explained not only the symmetries of the cubic surface terminations, but also the number and orientation of domains. In the second study, we examined the surface of a bulk sample of B2-Al–Pd–Mn [57], and discovered a complex set of LEED patterns that presumably represent a series of surface reconstructions. These had not been observed in the B2 overlayer grown atop the quasicrystal. Perhaps these reconstructions do not exist in the latter case, or perhaps they are present but undetectable. Either explanation could be rationalized on the basis of a small domain size in the grown cubic overlayer, relative to the domain size on the surface of the bulk sample. In the third case [58], we found that the surface structures on the ξ' -Al–Pd–Mn approximant can be explained as bulk terminations, although—surprisingly—two types of terminations existed on two different samples grown via different techniques (self-flux vs. Bridgman). Transmission electron microscopy revealed different degrees of bulk disorder in these samples, which presumably led to the difference in surface terminations [58]. Seeing that bulk growth conditions could exert such a strong effect on surface structure, it began to seem rather remarkable that such a strong consensus had emerged regarding the surfaces of bulk quasicrystals.

We also investigated the electronic surface structure via XPS. In 1996, we first reported [59] that the $3d_{5/2}$ line of Mn is strikingly narrow when the surface is prepared to yield the quasicrystalline phase. This led us to study and compare this spectral feature in quasicrystals, approximants, and even elemental bulk Mn [59,60].

All comparisons showed that the Mn line is narrowest in the quasicrystal, and can be a useful fingerprint of this phase. By fitting the photoemission line, Jenks et al. concluded that its narrowness is the result both of an intrinsically small width (lifetime effect), and a suppression of the high-energy tail associated with electron–hole pair excitations near E_F . This conclusion was supported by our later analysis, although the numerical parameters involved in the line-fitting were corrected in the later work [60]. We also found that the analogous Fe line is anomalously narrow in the quasicrystalline surface phase of i-Al–Cu–Fe [60]. We attributed the narrowness ultimately to the pseudogap of the bulk electronic structure, which is deepest in—but not restricted to—the quasicrystal [60,61]. Comparable effects are observed in the corresponding Auger lines [60,61]. Finally, angle-resolved XPS showed that the pseudogap of the bulk is not retained up to a surface prepared by fracture, but can be restored by annealing, or by sputter annealing to sufficiently high temperatures. Based upon this, we suggested that the heat-treated surfaces are more stable than the surface obtained by fracturing at room temperature [60].

Accompanying these investigations, we collaborated with Andrew Gellman and his students [18,62,63] at Carnegie Mellon University to study friction at quasicrystalline surfaces in ultrahigh vacuum. They found that the coefficient of friction at the clean quasicrystalline surface was much lower than had been reported previously for clean metals such as Ni. It became even lower when the surface was oxidized. A comparison between the 5f surface of i-Al–Pd–Mn and the surface of a bulk B2 Al–Pd–Mn phase showed that the friction coefficient was two times higher on the clean cubic phase, than on the clean quasicrystal. When the surfaces were oxidized by exposure to O_2 or H_2O , the friction coefficients decreased by roughly a factor of two for both materials but the friction coefficient for the approximant remained roughly twice that of the quasicrystal. A question remains: Is the friction coefficient of the quasicrystal—at least in UHV—simply attributable to its hardness? The trend between the quasicrystal and the cubic phase is, in fact, paralleled by the trend in hardness. We continue to investigate this question.

Throughout this project, we were fortunate to work with talented colleagues in Ames who grew excellent samples. Even with the best of samples, however, we learned that phase impurities can exist or precipitate at the surfaces [32,34]. To detect and minimize these phases in as-grown quasicrystals, SAM and SEM were extremely valuable—and able to detect levels of impurities that went unnoticed by X-ray diffraction or TEM. An example is shown in Fig. 5. STM also revealed regions of secondary phases at the surface of one particular 5f Al–Pd–Mn surface, after different heat treatments [58]. One of these phases could be identified as the known T-phase, but the other did not correspond to a known bulk phase, to our knowledge. This articulates the possibility that phases exist at surfaces of quasicrystals which cannot exist in the bulk. It is well-known that strain can induce surface-specific phases in thin alloy films [64,65], so it is perhaps not surprising that such phases can exist at surfaces of bulk alloys as well.

In 2001, we began studying thin films of metals on surfaces of quasicrystals [66–68]. That topic is not reviewed here, but will be reviewed elsewhere [71], since it would simply be too voluminous for the present manuscript.

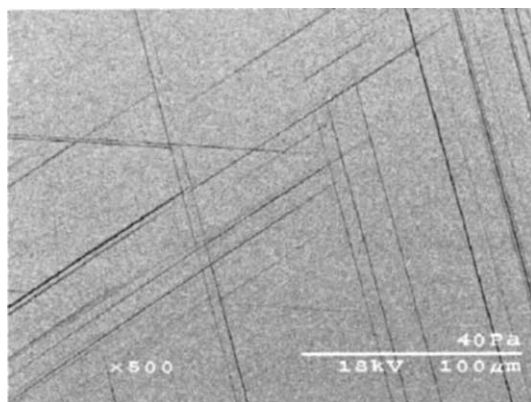


Fig. 5. SEM of a sample of i-Al–Pd–Mn, cut so the surface is normal to the 5f axis. The straight lines reveal a second phase. There was no evidence of this phase in the Laue pattern. The straight lines make 72° angles, and are probably Widmanstätten plates. Reproduced from Ref. [70]. Copyright 2002 Elsevier.

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