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Surface Science 450 (2000) 1–11

surface science

www.elsevier.nl/locate/susc

A LEED comparison of structural stabilities of the three high-symmetry surfaces of Al–Pd–Mn bulk quasicrystals

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Received 28 May 1999; accepted for publication 11 November 1999

Abstract

It is shown that low-energy electron diffraction (LEED) patterns of the three high-symmetry surfaces (fivefold, threefold and twofold) of icosahedral Al–Pd–Mn are all compatible with quasicrystallinity, under specific conditions of preparation. This conclusion results from comparing symmetries of experimental surface LEED patterns with bulk X-ray diffraction data which are converted to the conditions of the LEED experiment. This conclusion is also based upon an analysis of relative diffraction spot spacings in LEED. Hence, none of the three surfaces exhibits a massive lateral reconstruction, i.e. massive deviation from quasicrystallinity. The LEED pattern of the fivefold surface is distinct from the LEED pattern of the pseudo-tenfold surface of an orthorhombic approximant. We believe that this rules out the possibility that the fivefold surface of the icosahedral quasicrystal reconstructs to an approximant with tenfold or pseudo-10-fold symmetry. The twofold and threefold surfaces facet more readily, indicating qualitatively that they are less stable than the fivefold surface. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Alloys; Aluminum; Low energy electron diffraction (LEED); Metallic surfaces

1. Introduction

Quasicrystals, discovered in 1982 by Shechtman [1,2], are typically binary and ternary metallic alloys, often containing 60–70 at.% aluminum. They present unique structural features [3–6], coupled with unusual combinations of physical properties [7,8]. Some of the interesting properties of quasicrystals, such as low friction and low adhesion, involve surface phenomena. This motivates fundamental studies of structure, composition, and chemical reactivity of their surfaces.

Many quasicrystalline phases are icosahedral and, as such, exhibit three high-symmetry axes: fivefold, threefold, and twofold. These axes are perpendicular to the three possible high-symmetry

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PII: S0039-6028(99)01183-8

surfaces. The relative stabilities of these three surface types has long been of interest in the quasicrystal community [9], motivated by the simple observation that small grains of some icosahedral alloys exhibit beautiful facets. Triacontahedra and dodecahedra, as well as more complex structures, have been observed, depending on alloy type [10]. (Perfect dodecahedra expose 12 fivefold facets, whereas triacontahedra expose 30 twofold facets, and icosahedra expose 20 threefold facets. All are compatible with icosahedral symmetry; more complex structures can be created from superpositions of these.)

The quasicrystal of the present study, Al–Pd–Mn, is also icosahedral. In this intermetallic, grains as well as voids can exhibit faceted shapes. Fivefold faces are most common, although twofold and threefold faces are also observed [10–13]. It is usually suggested that the fivefold surface is most stable for this icosahedral quasicrystal.

In this paper, we use low-energy electron diffraction (LEED) to compare structural aspects of clean, high-symmetry surfaces of the Al–Pd–Mn quasicrystal. It is well known that clean *crystalline* materials can have different surface stabilities depending upon surface symmetry. These different stabilities are often distinguished by the tendency to reconstruct [14]. (Reconstruction is a strong lateral perturbation from the bulk-terminated atomic positions.) A general rule of thumb is that the least dense surfaces are most prone to reconstruct [14]. Faceting is also an indication of surface instability – in fact, some crystalline surface reconstructions can be regarded as microfaceting [15]. Both reconstruction and faceting can be detected by LEED. The present work is meant to test whether these phenomena, so well known for crystalline surfaces, may occur at quasicrystalline surfaces as well.

2. Experimental details

The icosahedral Al–Pd–Mn samples were grown via the Bridgman technique [16]. The grains were oriented to the selected zone axes within 0.25° using Laue X-ray diffraction. The nominal composition (i.e. the initial liquid composition used in growth) of each icosahedral sample is $Al_{72}Pd_{19.5}Mn_{8.5}$. Prior to experiments, scanning Auger and electron microscopies showed the samples to be single-phase to within 1% by volume.

Consistent with the known equilibrium ternary phase diagram [17], the ξ'-Al–Pd–Mn sample was grown via a self-flux technique [18] from a melt of composition $Al_{80.50}Pd_{17.25}Mn_{2.25}$ [19]. Crystals prepared by this technique exhibit a multifaceted, rod-like morphology, with the pseudo-tenfold axis oriented along the length of the rods. They typically have dimensions of up to 2 cm along this axis. Transmission electron microscopy (TEM) and X-ray diffraction were used to verify the crystal structure of the as-grown samples, and TEM was used to check for crystalline imperfection, especially phason strain [20]. Selected area diffraction patterns were obtained for the three diad axes, [100], [010] and [001]. Lattice images were also obtained from some zones, principally the [010]. The flux-grown samples showed few phason defects. The lattice parameters determined from electron diffraction were 2.34, 1.65 and 1.24 nm for *a*, *b* and *c*, respectively, consistent with previously published values [21]. The high energy electron diffraction patterns were consistent with the *Pnma* space group expected for the ξ' phase [21].

The ξ' crystal used here was oriented by Laue to within $\pm 0.2°$ of the pseudo-tenfold axis, and polished. Its surface was irregularly shaped, approximately 5 mm × 3 mm in size. Because of flux inclusions (and eutectic solidification), regions of Al-rich phases were detected by scanning electron microscopy and energy-dispersive spectroscopy, coexisting with the ξ' phase, especially in the center of the sample. In spite of this inhomogeneity, the LEED pattern was uniform across the sample. This indicates that LEED does not sense the regions of Al-rich phase, except perhaps as a contribution to the background intensity.

Most LEED experiments were performed with Varian retarding grid optics, with an instrumental limit of about 150 Å in real space [22]. The ultrahigh vacuum (UHV) chamber [23] had a typical base pressure of 3×10^{-11} Torr. The sample was cleaned with cycles of Ar ion bombardment and annealing, to a maximum of 900 K. Elsewhere, we

provide other details of our standard surface preparation techniques and instrumentation [22,24]. Some LEED data in this paper were acquired in a separate chamber equipped with Omicron SPA-LEED optics for high-resolution LEED. There, the nominal instrumental limit was about 1200 Å, and the chamber base pressure was $3–4 \times 10^{-11}$ Torr.

3. Experimental results and interpretations

For all three icosahedral surfaces, the observed LEED patterns can be divided into three categories. We call these cubic, faceted, and quasicrystalline like.

The first type of pattern results after sputtering at room temperature, and usually requires annealing in the range 500–700 K. These patterns (with one exception) can be assigned to crystalline overlayers of the cubic B2 structure [22,25]. They are characterized by broad spots, corresponding to real-space domains of size 40–80 Å, and high backgrounds. These patterns have been discussed extensively elsewhere [22].

The second type of LEED pattern, the faceted one, typically appears after annealing in the temperature range 800–900 K. It often coexists with the quasicrystalline-like pattern, although the two are not distributed uniformly over the surface. This non-uniformity suggests that the facets may form preferentially at chemical or structural defects. The signature of faceting in LEED is the non-convergence of spots toward the center of the LEED optics as beam voltage increases, using normal incidence [26,27]. In our LEED experiments, no faceting is observed for fivefold surfaces when heated to temperatures up to 900 K. Facets are observed, however, for twofold [28] and threefold surfaces after annealing at these temperatures. The facets on the twofold surface are perpendicular to the threefold and fivefold zone axes. The facets on the threefold surface are perpendicular to fivefold axes, and to an unidentified axis. Our data cannot distinguish between facets as depressions or protrusions.

This paper concerns mainly the third type of LEED pattern, the quasicrystalline like. Such patterns are obtained by annealing to temperatures in the range 700–900 K, and are shown in the top three frames of Fig. 1. These patterns are characterized by very sharp, dense LEED spots. The widths of the spots correspond to a real-space dimension greater than 150 Å [22], and the widths are instrument-limited in the low-resolution experiments. A high-resolution LEED study of the fivefold surface shows that the average domain size is about 900 Å (again, close to the resolution limit of the instrument). The data from the high- and low-resolution experiments are compared in Fig. 2, for similar conditions of sample preparation. The existence of large terraces, with average lengths in the range of hundreds of Å, is also supported by data from scanning probe microscopies. Such data are available for the fivefold surface of Al–Pd–Mn [29], and for the threefold surface of Al–Pd–Mn [30,31]. Large terraces, with average lengths in the range of about 400 Å are also supported by X-ray diffraction data for the fivefold surface [32,33].

A second way to analyze the LEED patterns is to examine the arrangements of the diffraction spots, and whether this arrangement is consistent with expectations for the bulk-terminated structure. For a crystalline material, it is straightforward to predict the arrangement for a low-index surface, and to compare this prediction with experiment. However, the prediction and comparison are not so trivial for a quasicrystalline material. The approach we use is to convert an X-ray diffraction pattern taken along the appropriate zone axis with the conditions of the LEED experiment. To calculate the patterns we employed the bulk X-ray structure factors measured by Boudard et al. for the icosahedral phase of Al–Pd–Mn [34], and used these to assign a relative intensity to rods of scattering parallel to the surface normal. The predictions based on X-ray data are shown in the bottom panels of Fig. 1.

First, consider the gross symmetries of the patterns. The surface cut perpendicular to the twofold axis displays a LEED pattern (Fig. 1a) with twofold, rectangular symmetry, consistent with the projection from X-ray scattering shown in Fig. 1d. An interesting observation here is that the LEED pattern from the twofold surface differs considerably from the higher energy diffraction patterns,

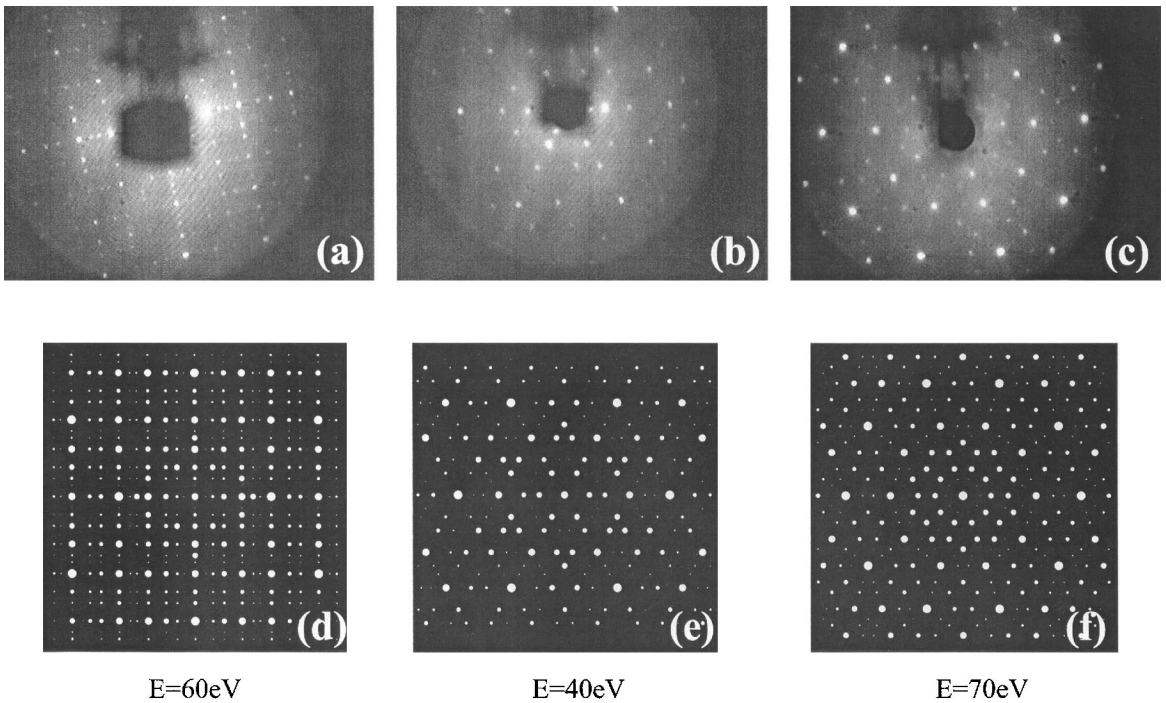

Fig. 1. Measured and calculated LEED patterns of quasicrystalline-like surfaces: (a) LEED pattern of Al–Pd–Mn twofold surface obtained by annealing at 900 K for 4 h, $E=60$ eV; (b) LEED pattern of Al–Pd–Mn threefold surface obtained by annealing at 700 K for 1 h, $E=40$ eV; (c) LEED pattern of Al–Pd–Mn fivefold surface obtained by annealing at 800 K for 2 h, $E=70$ eV; the calculated LEED patterns for (d) twofold surface; (e) threefold surface; (f) fivefold surface.

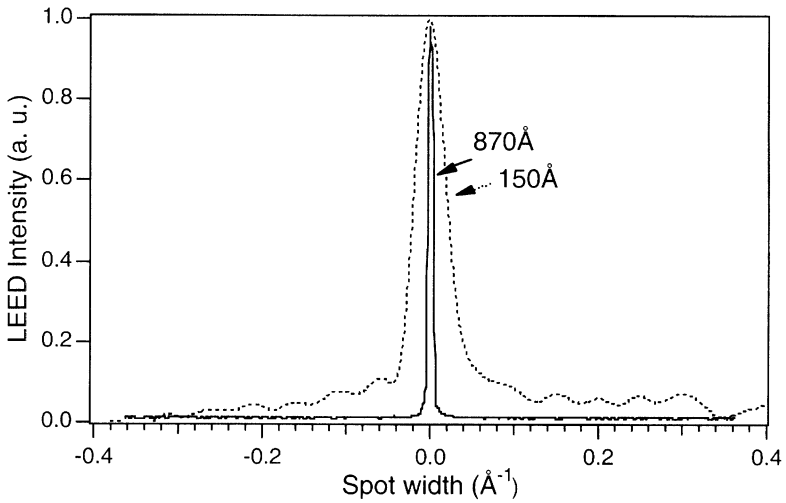

Fig. 2. Comparison of high- and low-resolution LEED spot profiles on the i-Al–Pd–Mn fivefold surface, at an incident beam energy of 85 eV. In both experiments, the sample was ion sputtered for 15 min and annealed before the measurement. The annealing parameters were 800 K for 2 h and 750 K for 0.5 h, in the high- and low-resolution experiments, respectively. The real-space dimension that corresponds to the spot width is indicated.

obtained in conjunction with transmission electron microscopy (TEM), along the twofold axis. The differences arise from both the lower energy (and hence larger curvature of the Ewald sphere) for the LEED measurements, and from the fact that 2D scattering is characterized by rods rather than points of intensity. In fact, the LEED pattern measured from the twofold surface is misleadingly similar to the TEM pattern of the "pseudo-twofold" orientation [28]. Hence, it is important to convert carefully the conditions of one diffraction experiment to the other.

The symmetries of the LEED patterns of the other two surfaces are also consistent with expectation, as seen by comparing the top and bottom panels of Fig. 1. At the electron energies chosen for Fig. 1, the threefold surface (Fig. 1b) seems nearly sixfold, and the fivefold surface (Fig. 1c) seems tenfold. However, at other energies these symmetries are reduced clearly to threefold and fivefold, respectively. Patterns at other energies are shown in Fig. 3a–c for the threefold surface, and in Fig. 4a–c (and elsewhere [22–24,35–39]) for the fivefold surface. Again, note that the differences in symmetry between the LEED and X-ray diffraction patterns (threefold versus sixfold, and fivefold versus tenfold) are due to differences in the scattering conditions.

Predictions of relative spot intensities also compare well with experiment under the conditions of Fig. 1, which is somewhat surprising, given that LEED intensities are highly sensitive to multiple scattering whereas X-ray data are not. Presumably, at the energies chosen for Fig. 1, kinematic scattering happens to dominate in LEED, making the comparison appear optimal. At other energies, the relative intensities change dramatically, as one would expect. See, for instance, Fig. 3. A more rigorous comparison between calculated and experimental data might be made if the experimental data could be energy averaged. This was not feasible in our work, however, because different spots were visible over much different energy ranges.

A final point of information which can be extracted from the LEED data is the spot spacing, both absolute and relative. The spot spacings are shown in Table 1. The parameter k_j is the magnitude of the component of the scattering vector which is parallel to the surface, in Å^{-1}. Each index j denotes a set of intense diffraction spots which are equidistant from the specular beam. First,

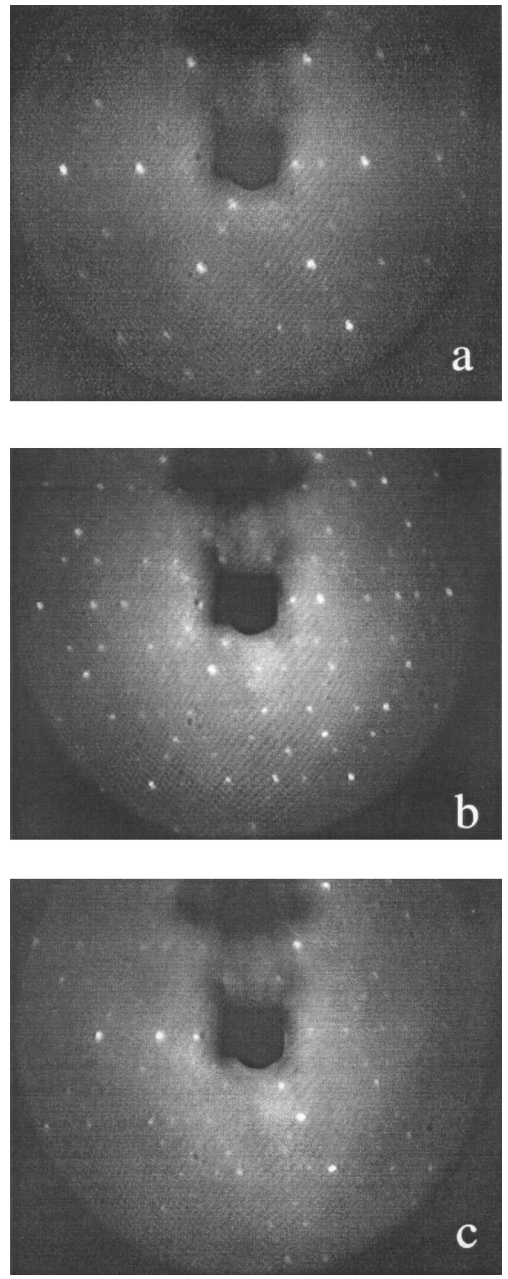

Fig. 3. LEED patterns of quasicrystalline-like threefold surface measured at: (a) 30 eV; (b) 65 eV; (c) 110 eV.

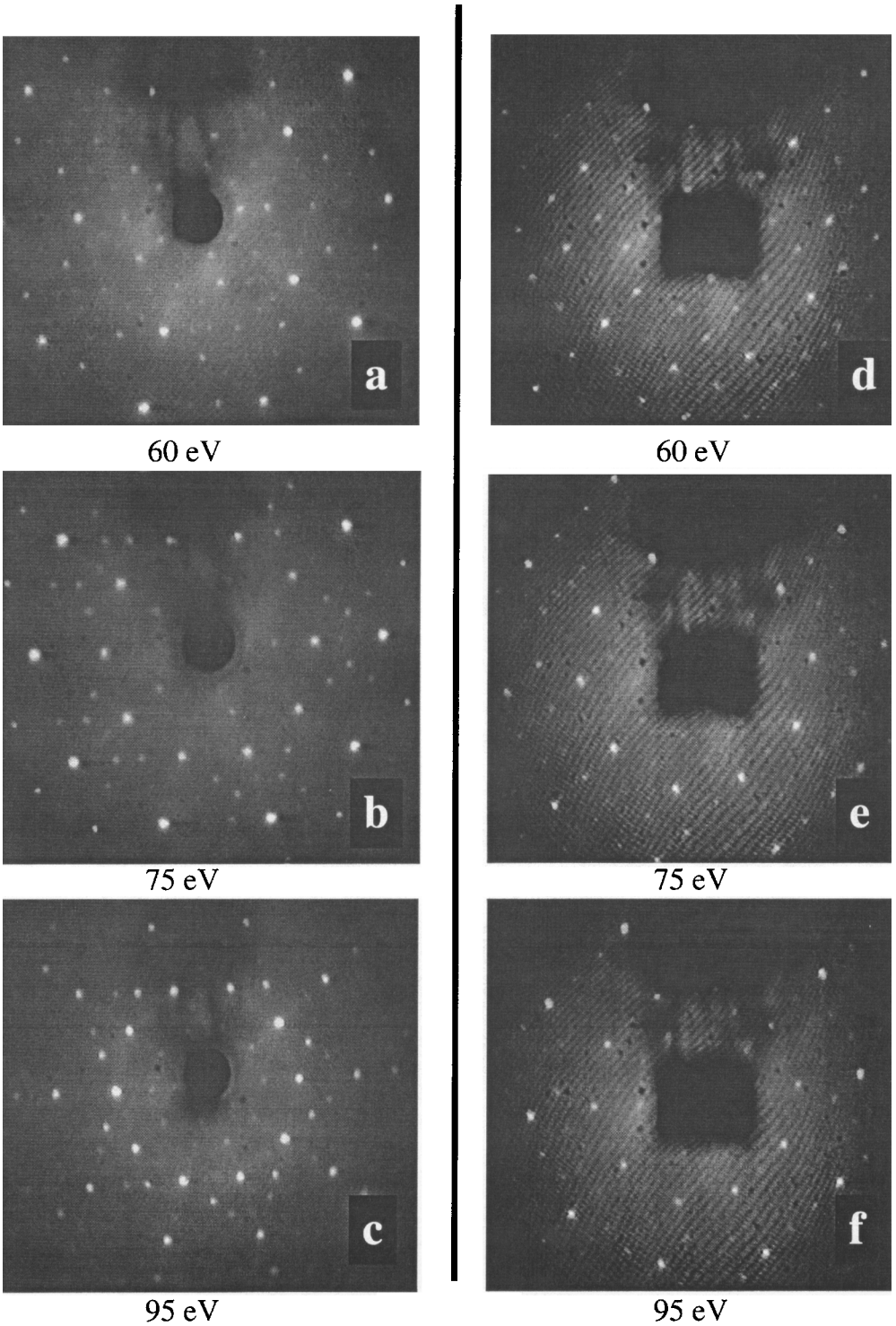

Fig. 4. LEED patterns of quasicrystalline-like fivefold surface measured at: (a) 60 eV, (b) 75 eV, and (c) 95 eV. LEED patterns of the pseudo-tenfold face of the ξ'-phase of Al–Pd–Mn, measured at (d) 60 eV, (e) 75 eV, and (f) 95 eV.

Table 1
Spot spacings, and ratios of spot spacings, for the three high-symmetry surfaces. The ideal ratios are determined from the X-ray scattering data illustrated in the bottom panels of Fig. 1. The values of k_j at each individual energy were obtained by averaging over all equivalent spots that were accessible at that energy. (Some spots were always blocked by the sample manipulator.) Uncertainties are given as ± 1 standard deviation, i.e. they delimit a 67% confidence interval

Al–Pd–Mn twofold:				
	$j=0$	$j=1$	$j=2$	$j=3$
No. of measurements at different energies		5	10	6
k_j	–	1.029 ± 0.010	1.663 ± 0.028	2.716 ± 0.021
Bulk value		0.948		
k_j/k_1	–	1	1.616 ± 0.043	$(1.624 \pm 0.014)^2$
Ideal ratio	–	1	$1.618 = \tau$	$1.618^2 = \tau^2$
Al–Pd–Mn threefold:				
	$j=0$	$j=1$	$j=2$	$j=3$
No. of measurements at different energies	3	8	8	4
k_j	0.699 ± 0.012	1.123 ± 0.014	1.826 ± 0.018	2.992 ± 0.028
Bulk value	0.677			
k_j/k_0	1	1.607 ± 0.048	$(1.616 \pm 0.022)^2$	$(1.624 \pm 0.014)^3$
Ideal ratio	1	$1.618 = \tau$	$1.618^2 = \tau^2$	$1.618^3 = \tau^3$
Al–Pd–Mn fivefold:				
	$j=0$	$j=1$	$j=2$	$j=3$
No. of measurements at different energies	5	4	13	9
k_j	0.669 ± 0.006	1.080 ± 0.012	1.752 ± 0.029	2.867 ± 0.031
Bulk value	0.616			
k_j/k_0	1	1.617 ± 0.032	$(1.619 \pm 0.021)^2$	$(1.624 \pm 0.012)^3$
Ideal ratio	1	$1.618 = \tau$	$1.618^2 = \tau^2$	$1.618^3 = \tau^3$

consider the absolute values of k_j. It can be seen that the measured values are consistently larger than those predicted from bulk data, the deviation being in the range 3–8%. This corresponds to the (quasi)lattice constant of the surface being smaller than that of the bulk by the same percentage. Note that LEED is not a good technique generally for measuring absolute lattice constants, because systematic errors arise if the sample is not exactly at the focal point of the LEED optics. A similar reduction of k, relative to the bulk value, was found in a LEED study of another icosahedral alloy in our laboratory [40], and also in the LEED and STM work of Schaub et al. [35–37,41]. However, a fortuitous coincidence of systematic errors (including a slight miscalibration of piezoelectrics used in STM) cannot be ruled out – and is, in fact, suggested by a recent STM study of the fivefold surface in our own laboratory [42].

Ratios of distances should be affected less than absolute distances by such a possible error. Table 1 also shows such ratios for the major spots. A similar analysis has been implemented by Schaub et al. for the fivefold surface [35]. The ideal ratios in Table 1 are again taken from the calculations (e.g. Fig. 1d–f). It can be seen that the ideal ratios should equal the golden mean, τ ($\tau = 1.618$), raised to integral powers. For instance, for the threefold and fivefold surfaces,

$$\frac{k_j}{k_0} = \tau^j.$$

Table 1 shows that the measured ratios equal the predicted ones, within experimental uncertainty, for all three surfaces.

In short, the LEED patterns observed after annealing in the range 700–900 K are consistent with expectations for the bulk quasicrystal, for all three surfaces.

Note that the data could also be compatible with a high-order approximant. Spot spacings and intensities in an approximant can be very similar to those in the parent quasicrystal [6]. In order to

acknowledge this possibility, we term these LEED patterns quasicrystalline like.

It has been suggested that an orthorhombic approximant might form on the surface of the icosahedral quasicrystal [43]. In order to test this possibility, we have prepared a pseudo-tenfold surface of the ξ′ orthorhombic approximant [21]. The bulk composition of this approximant is about 4 at.% lower in Mn than the icosahedral alloy [21]. X-ray photoelectron spectroscopic analysis suggests that its surface is even lower in Mn than its bulk [44]. Its LEED pattern, after annealing at 700 K, is shown at representative energies in Fig. 4d–f. At most energies, as in Fig. 4f, this pattern shows tenfold symmetry, in contrast to Fig. 4a–c. At other energies, periodicity is apparent, as in Fig. 4d. Thus, the pseudo-tenfold face of the approximant is clearly distinguishable from the fivefold face of the icosahedral material.

4. Discussion

Based upon LEED, the three quasicrystalline-like surfaces exhibit two characteristics. First, the LEED patterns are consistent with expectations from bulk quasicrystalline structure. Second, a common set of conditions are required for the formation of these patterns – long anneals in the temperature range 700–900 K. These similarities are somewhat surprising, given that high-symmetry surfaces of a clean crystalline material often show more variation, particularly in their tendency to undergo lateral rearrangement (reconstruction) [14]. In many cases, a reconstruction is understood as a rearrangement of the least-dense planes into a semblance of close packing, and is marked by development of extra LEED spots at positions incompatible with the bulk-terminated structure. We do not see this, indicating that the quasicrystalline surfaces do not undergo a massive lateral rearrangement.

We cannot rule out the possibility is that there is an arrangement of atoms at the surface different from the bulk, but fortuitously giving a LEED pattern with the observed symmetry and spot spacings – if, for instance, all of the Al atoms in the surface were replaced by Pd atoms and vice versa, or if certain atomic planes were simply absent. While these are indeed possibilities, we regard *large* changes in composition (>10 at.%) as remote, given that the bulk quasicrystalline phase is stable only over a very narrow range of compositions. Furthermore, *large* changes in composition at the topmost surface layers are incompatible with LEIS [45] and X-ray scattering data [32], combined with the LEED-based structure determination [39,45] for the fivefold surface. In terms of the planar distributions of atoms, large deviations (such as missing planes) again would probably have precluded a successful structure determination [39,45] at least for the fivefold surface. However, there is good evidence from the electron- and X-ray-based structure determinations that the fivefold quasicrystalline-like surface exhibits a contraction of the first interlayer spacing [32,39,45]. Such a relaxation would not affect the LEED spot spacings or arrangements, because it would not necessarily change the *lateral* surface structure.

Another possibility is the existence of more subtle surface rearrangements, such as reconstruction to a high-order (large unit cell) approximant. In electron diffraction, approximants can be very difficult to distinguish from quasicrystals [6,46]. To be compatible with the fivefold LEED symmetry of the fivefold icosahedral surface, a pentagonal approximant has been suggested [8], even though there is no pentagonal approximant known (yet) in the bulk Al–Pd–Mn system [17]. The suggestion is made by analogy with the related alloy, Al–Cu–Fe, where two pentagonal approximants are known [46]. The lack of a known pentagonal approximant makes experimental comparison impossible at this time.

The fivefold surface does appear to exhibit a small deviation from the bulk Mn composition, which is deficient by several atomic per cent [32,45]. Based upon this composition, an orthorhombic approximant that exists in the bulk phase diagram [17] has been suggested [43]. However, the data for the pseudo-tenfold face of the orthorhombic ξ' approximant, shown in Fig. 4d–f, are clearly distinguishable from the fivefold face of the icosahedral intermetallic. (The ξ' phase is closely related to the ξ phase, which was originally sug-

gested [43].) We believe that this demonstrates that an approximant with tenfold or pseudo-tenfold symmetry does not form at the surface of the fivefold icosahedral quasicrystal [44].

Under the conditions of our experiments, the twofold and threefold surfaces are more prone to facet than is the fivefold surface. Faceting has been reported previously by Chevrier et al. for fivefold and twofold surfaces that were heated to unspecified temperatures in ultrahigh vacuum; the facets were imaged with STM as depressions, and were attributed to sublimation [29]. The temperatures and annealing times necessary to achieve facets were not specified. If the temperatures were much higher, then their results are not necessarily inconsistent with our own. At sufficiently high temperatures, all surfaces might be expected to facet as a result of evaporative mass loss, as noted by Chevrier et al. [29]. Facets have also been observed via STM on the twofold surface by Schaub et al., who found fivefold facets after heating close to the melting point, 1100 K [35–37,41].

Our observation that the fivefold surface is somewhat more stable is consistent with the general observation that dodecahedral shapes – which, by definition, expose only the fivefold planes – are most common in small grains of this alloy. However, the energetic differences between the three high-symmetry surfaces are not large enough to cause a massive surface reconstruction. We speculate that energetic differences between high-symmetry surfaces may be less significant in quasicrystals than in crystals, because variations in atomic densities and chemical compositions can be relatively small in the quasicrystals. Unlike a crystalline material, a quasicrystal has many possible types of bulk-like terminations. No two are identical in composition or structure. However, the terminations can be divided into groups that are self-similar, based upon the bulk structural analysis of Boudard and de Boissieu et al. [34,47]. Gierer et al. [39,45] found that the fivefold surface of i-Al–Pd–Mn is terminated by rumpled layers which are high in Al content, with a combined lateral atomic density nearly the same as that of the close-packed surface of Al. Recent X-ray scattering [32] and low-energy ion-scattering data [45] are consistent with this LEED result (although both suggest that the surface composition may be deficient in Mn, relative to the bulk). In this context, it is interesting that similar dense, rumpled, Al-rich terminations can be identified for the twofold and threefold surfaces [48]. For such terminations, the total lateral density of the rumpled layer varies by 21% (from 0.120 to 0.145) across the high-symmetry faces, the twofold being most dense and threefold being least dense. (This is consistent with results of a recent calculation of cohesion energies of surfaces of icosahedral structures by Kleman et al. [49].) The variation in surface density for the quasicrystal is significantly less than for an fcc crystal, where the density increases by 63% (from 0.0866 to 0.141 $Å^{-2}$ for Al) in going from bulk-terminated twofold to threefold surfaces. However, if density alone controlled the relative stabilities of quasicrystalline surfaces, the twofold surface would be most stable, or at least comparable to the fivefold surface. Hence, factors other than density – such as chemical composition (e.g. Al content), or presence of certain types of clusters – must *also* be involved in stabilizing quasicrystalline surfaces [42,50].

Our speculation about energetic differences between high-symmetry surfaces of quasicrystals must be tested experimentally to probe what type of similarities *do* exist between the high-symmetry surfaces. (A preliminary LEED structural analysis by Gierer et al. [51] supports the idea that the twofold surface of i-Al–Pd–Mn is a dense, rumpled, Al-rich layer, like the fivefold surface.) Our speculation must also be tested by examining alloys of various chemical compositions, to see whether massive reconstructions are ever observed.

In conclusion, we have shown that LEED patterns of the three high-symmetry surfaces of i-Al–Pd–Mn are all compatible with quasicrystallinity, under specific conditions of preparation. This conclusion is based upon a comparison between symmetries of experimental surface LEED patterns, and bulk diffraction data converted to the conditions of the LEED experiment. This conclusion is also based upon an analysis of relative diffraction spot spacings in LEED. Hence, none of the three surfaces exhibits a massive lateral reconstruction, i.e. massive deviation from quasicrystallinity. The LEED pattern of the fivefold surface is distinct

from the LEED pattern of the pseudo-tenfold surface of an orthorhombic approximant. We believe that this rules out the possibility that the fivefold surface of the icosahedral quasicrystal reconstructs to an approximant with tenfold or pseudo-tenfold symmetry. However, the general existence of approximants at the surface – possibly even approximants not present in the bulk phase diagram – remains a possibility. The twofold and threefold surfaces facet more readily, indicating qualitatively that they are less stable than the fivefold surface.

Acknowledgements

M. Quiquandon and J.M. Dubois provided valuable comments and suggestions. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contracts No. DE-AC03-76SF00098 and W-405-Eng-82.

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