Nonicosahedral Equilibrium Overlayers of Icosahedral Quasicrystals

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We demonstrate that icosahedral Al-Pd-Mn quasicrystals can have nonicosahedrally ordered thermodynamic equilibrium overlayers. The formation of orthorhombic or decagonal equilibrium surface structures is determined by the phase equilibrium of the ternary alloy at given composition and temperature as well as by the surface acting as nucleation site. Nonequilibrium steady-state orthorhombic and hexagonal structures can also be derived with the same methodology when taking preferential evaporation into account. The results describe consistently all presently observed surface structures.

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One of the scientifically most intriguing questions in the field of nonperiodic solids is the thermodynamic stability of their surfaces. The stability of the surfaces is closely connected to the formation mechanism and a major factor in the growth of nonperiodic solids. Therefore, surfaces of quasicrystals, i.e., solids with a well defined but nonperiodic crystallography, were intensively investigated in the last decade. However, against all expectations, not only one surface structure but rather a large number of different surface structures were observed, e.g., on icosahedral Al-Pd-Mn quasicrystals [1–14]. These different surface structures differ even in their basic symmetry, which ranges from cubic via orthorhombic and decagonal to icosahedral. To date it is unclear if these surface structures are equilibrium surfaces or not. In fact, for all observed nonicosahedral structures it is typically assumed that they were obtained kinetically due to preferential sputtering, preferential desorption, and/or segregation during the cleaning procedures [5,7,9,12]. In contrast, the icosahedrally ordered surface structure is implicitly considered to be the equilibrium surface of an icosahedral quasicrystal, although no experimental proof has ever been published. So far only the facets of grown-in voids were identified as equilibrium surfaces, but except their composition, nothing is known about the atomic structure [11,15]. As a consequence, at present the structure of the equilibrium surface(s) of icosahedral quasicrystals is not known.

In this Letter we determine the thermodynamically stable structures at surfaces of icosahedral Al-Pd-Mn quasicrystals, using extended annealing experiments and a precision determination of the relevant parts of the ternary Al-Pd-Mn phase diagram. On this basis we distinguish between equilibrium and kinetically reached steady-state surface structures and extract their formation mechanisms. We show that in all cases the driving force for the formation of crystallographically different overlayers is the motion of the system toward its phase equilibrium, modulated by preferential evaporation, if present. These results allow us to demonstrate that both nonicosahedral (orthorhombic and decagonal) and icosahedral structures can exist in thermodynamic equilibrium at the surfaces, depending on the initial composition of the icosahedral quasicrystal.

The first step toward identifying equilibrium surface structures of an intermetallic compound is the determination of the corresponding ternary Al-Pd-Mn phase diagram. For this determination we investigated a large set of icosahedral single quasicrystals grown by Czochralski technique and polycrystalline alloys produced by levitation induction melting in a water-cooled copper crucible under Ar atmosphere. The Czochralski-grown quasicrystals were long-term annealed at 873 and 923 K (up to 2445 h) in quartz ampoules evacuated to about 10^{-5} mbar. The polycrystalline samples were annealed at temperatures between 983 and 1153 K for up to 570 h in an Ar-flow furnace in order to avoid preferential evaporation. The time of annealing was sufficient to reach the phase equilibrium in each case as confirmed by detailed scanning electron microscopy (SEM) investigations.

The so-prepared samples were polished and investigated in their unetched state by SEM with an energy-dispersive x-ray (EDX) composition analysis. From this we extracted the chemical composition ranges of the different phases formed in the annealed samples. In addition, the compositions of all single-phase samples were determined by inductively coupled plasma optical emission spectroscopy (ICPOES). These ICPOES-based composition values were used to calibrate the sensitivity factors of the EDX analysis. For the identification of the phases, we used x-ray diffraction and transmission electron microscopy diffraction.

From the observations of different phases and their compositions in the samples, we extracted (i) the single-phase regions, (ii) the vertices of the tie triangles from three-phase regions, and (iii) the boundary compositions in two-phase regions at chosen temperatures. This allowed us to construct isothermal cuts in the vicinity of the icosahedral Al-Pd-Mn quasicrystalline phase. Figure 1 shows such a data set at 983 ± 10 K. One can see that the icosahedral phase is in equilibrium with the orthorhombic H, decagonal D, hexagonal δ, and another orthorhombic ϵ [16,17] phases. The labels for the different phases unfortunately

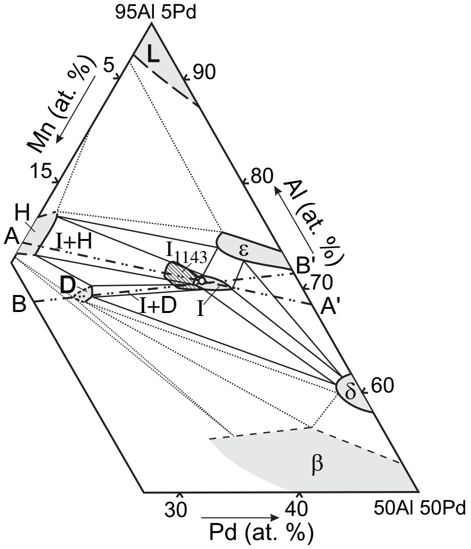

FIG. 1. Isothermal section of the ternary Al-Pd-Mn phase diagram at 983 ± 10 K in the vicinity of the icosahedral phase. H, D, I, ϵ, β, and δ label the different phases present (see text). L stands for liquid melt. The crosshatched region labeled I_{1143} corresponds to the stable phase area of the icosahedral phase at 1143 K. Solid lines represent borders quantitatively determined on basis of the measured vertices of the tie triangles from three-phase regions and/or boundary compositions in two-phase regions. Dashed and dotted lines should guide the eye and are approximate. Along the dot-dashed lines A-A' and B-B' polythermal (vertical) cross sections were determined (Fig. 2).

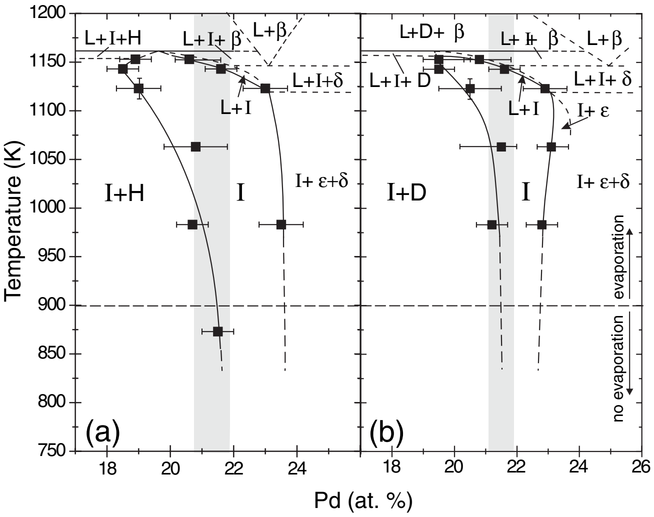

FIG. 2. Polythermal cross sections along the lines (a) A-A' and (b) B-B' in Fig. 1 in the vicinity of the icosahedral phase area. The data points were derived from a series of isothermal sections of the phase diagram. On the Pd-poor sides of the cross sections the icosahedral I phase is in equilibrium with the (a) orthorhombic H and (b) decagonal D phase. The solid lines should guide the eye to highlight the position of the boundary of the icosahedral single-phase area. Dotted lines were included on the basis of Ref. [19] for information only. The shaded vertical bars highlight the measured composition range of as-grown Al-Pd-Mn single quasicrystals.

differ within the literature. The phase labeled H here following Refs. [16,17] is very likely associated with two phases labeled T and R in Ref. [18], because of the overlapping compositional ranges and the same orthorhombic crystallography. In addition, there are indications [16] that the H phase is an extension of the high-temperature binary orthorhombic $Al_{11}Mn_4$-HT phase [19]. Furthermore, the phase labeled ϵ in Refs. [16,17] is also called the ξ'-Al-Pd-Mn approximant [20]. At closer look the phase has a number of structural variants closely related to each other and not just one single structure as initially thought [21]. For the present work these inconsistencies in labeling throughout the literature are, however, not significant for the physical mechanisms involved.

One of the key properties of the ternary Al-Pd-Mn system investigated here is that the icosahedral single-phase region shifts in composition with temperature [compare the single-phase areas at 983 ± 10 (labeled I) and 1143 ± 10 K (crosshatched region labeled I_{1143} in Fig. 1)]. The composition shift can be illustrated best in the polythermal (vertical) cross sections (Fig. 2) constructed along the lines A-A' and B-B' (see Fig. 1) in the vicinity of the icosahedral phase. Several features can be seen: (i) The icosahedral phase is formed through a peritectic reaction at 1161 K [17] at a composition of about $Al_{70.4}Pd_{19.5}Mn_{10.1}$. (ii) On the Pd-poor side, the icosahedral phase is in equilibrium with the orthorhombic H [Fig. 2(a)] and/or decagonal D [Fig. 2(b)] phase. (iii) Finally, the composition range of the icosahedral phase shifts to the Pd-rich side and narrows below 1120 K with decreasing temperature.

At this stage we have to consider the effect of the shape of the liquidus and solidus surfaces as well as the noncongruent melting behavior on growth of Al-Pd-Mn single quasicrystals. When a melt with an initial composition of $Al_{72.4}Pd_{20.5}Mn_{7.1}$ as used for our material [22] is slowly cooled down to about 1153 K in Czochralski growth, the melt starts to crystallize not with its initial composition, but rather with the significantly shifted composition of the solidus surface at 1153 K (close to $Al_{70.5}Pd_{21}Mn_{8.5}$). With further lowering of the temperature the composition shifts along the solidus surface toward a Pd-richer composition. As a consequence, the Pd (Mn) concentration of as-grown icosahedral Al-Pd-Mn single quasicrystals increases (decreases) from the seed to the tail end by up to 1 at. %, while the Al concentration remains essentially unchanged. The resulting wide extension of composition of as-grown quasicrystals (indicated by the shaded bar in Fig. 2) was extracted from composition measurements of 49 different Czochralski-grown samples.

The composition shift has, however, a critical implication. Below 1000 K the composition range of as-grown single quasicrystals [shaded bars in Figs. 2(a) and 2(b)] is increasingly outside of the icosahedral single-phase area.

Annealing at lower temperatures can thus lead to the formation of precipitates even for initially single-phase material. The particular case presented in Fig. 3(a) shows an initially single-phase icosahedral single quasicrystal with a composition of $Al_{70.9}Pd_{21.1}Mn_{8.0}$ (marked by a circle on the A-A' line in Fig. 1, which lies at 873 K in the two-phase H-I region. During annealing at 873 K the orthorhombic H phase with a composition of $Al_{77.5}Pd_{5.8}Mn_{16.7}$ (darker contrast than icosahedral phase) nucleated. In analogy, dark platelets of the decagonal D phase with a typical composition of $Al_{70.6}Pd_{13.2}Mn_{16.2}$ form for samples with slightly lower Al concentrations [Fig. 3(c)]. The decagonal precipitates mostly form platelets oriented parallel to the fivefold directions of the surrounding icosahedral matrix [23]. The precipitates nucleate preferentially at internal interfaces, such as voids formed by condensation of vacancies during annealing [24] [Fig. 3(a)] or grain boundaries [Figs. 3(b) and 3(c)]. In single quasicrystals, almost all precipitates nucleate at the outer surfaces [see inset of Fig. 3(a)], due to the lack of nucleation sites in single grain material. In analogy, for Al-Pd-Mn quasicrystals with compositions in a three-phase region at low temperatures, decagonal D and orthorhombic H precipitates may form simultaneously.

In order to apply the above results on the question of the quasicrystals' equilibrium surface structure, we first have to recall the surface preparation methods. Mostly, the surfaces are cleaned by cycles of bombardment with noble gas ions followed by annealing to remove the damage left by sputtering [25] At this stage we bear in mind that a surface is only an equilibrium surface if the whole vapor-surface-bulk system is in equilibrium, i.e., if the appropriate thermodynamic potential of the whole system is minimized. The equilibrium with the bulk is mediated by diffusion of all components of the alloy. At the typical annealing temperatures in the range of 820 to 920 K [1–7,13,14] this is assured. For the equilibrium with the vapor, we have to consider the vapor pressures of the components, of which Mn has the highest one. Unfortunately, the vapor pressure is only known for pure metallic Mn, which may have significantly different values for the vapor pressure as compared to a quasicrystal with large covalent contributions to the bonding. Since the vapor pressures are closely connected to desorption, we turn to desorption measurements on Al-Pd-Mn quasicrystals [5]. These measurements showed that up to about 900 K no evaporation is detectable. Between about 900 and 1000 K only Mn desorbs and above about 1000 K Mn and Al desorbs. Thus three different temperature regions need to be distinguished in the discussion: (i) annealing below the evaporation onset, where the surfaces are in thermal equilibrium due to the negligible vapor pressures, (ii) annealing with only Mn evaporation, and (iii) annealing with Mn and Al desorption. In the latter two temperature ranges, only steady-state surface structures can be expected.

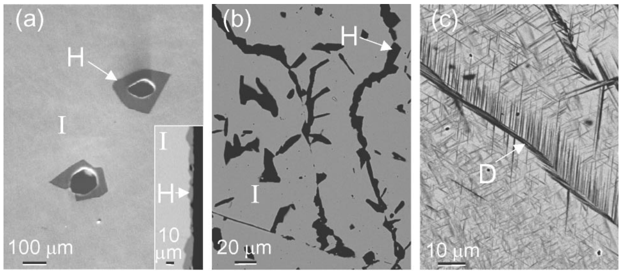

FIG. 3. SEM images in secondary electron mode showing (a) an initially single-phase $Al_{70.9}Pd_{21.1}Mn_{8.0}$ single quasicrystal annealed at 873 K for 1055 h. During annealing the orthorhombic H phase with dark contrast is formed around voids condensed from the vacancies, if present, or (inset) at outer surfaces ($Al_{70.2}Pd_{21.5}Mn_{8.3}$ annealed at 923 K for 2428 h). (b) and (c) show polycrystalline $Al_{71.4}Pd_{18.4}Mn_{10.2}$ and $Al_{70.1}Pd_{20.2}Mn_{9.7}$ samples annealed at 923 K for 265 h and 1063 K for 570 h, respectively. Both the orthorhombic H and the decagonal D phase nucleate preferentially at grain boundaries (which are now decorated by dark precipitates).

(i) With no evaporation, the system surface-bulk can reach its equilibrium through diffusion. Furthermore, when annealing quasicrystals at low temperatures (~820–920 K) we have to recall that a significant fraction of the quasicrystals will have compositions, which will be in a two- or three-phase region (depending on the initial composition of the melt and thus of the quasicrystal) instead of being in the single-phase area of the icosahedral phase (see Fig. 2). As a result, orthorhombic H and/or the decagonal D phase precipitates form. Since internal surfaces in voids and outer surfaces are preferential nucleation sites, the precipitates will primarily form overlayers on the icosahedral Al-Pd-Mn substrate. This is in agreement with the experimental observations of orthorhombic [12,14] and decagonal [13] surface structures after annealing.

Repeated sputtering of such quasicrystals, will remove the H and/or D phase overlayers. If annealed, the H and/or D phase overlayers will form again, until the composition of the substrate is moved back to the single-phase area of the icosahedral phase. Then no more overlayers form. This effect is in fact observed during the preparation of clean surfaces [1]. Thus at low temperatures, H, D, and I phases are the thermodynamic equilibrium structures at surfaces of the icosahedral Al-Pd-Mn quasicrystal. (ii) Annealing at temperatures where only Mn desorbs enriches the surface in Al and Pd. This shifts the composition toward the Mn-poor side into the two-phase region, where the icosahedral phase is in equilibrium with the orthorhombic ϵ phase. As a result orthorhombic ϵ-phase overlayers form on the initially phase pure icosahedral surface. In this case, the sample continuously loses Mn by evaporation and thus the ϵ-phase overlayer represents only a steady-state but not an equilibrium configuration. (iii) Annealing at temperatures where both Al and Mn evaporate enriches the surface with Pd. Thus the phase equilibrium of the Al-Pd-

Mn ternary system shifts to the Pd-rich side and hexagonal δ-phase overlayers can form on the icosahedral substrate. In analogy to (ii), this surface structure is not an equilibrium configuration. The above conclusions are corroborated by the experimental observation upon annealing at 1023 K of a new, yet still inhomogeneously distributed, phase at the surface, leading to an average composition of $Al_{65.8}Pd_{32.4}Mn_{1.8}$ [26]. This composition suggests a mixture of the icosahedral and δ phases at the surface, in line with our explanation.

At this stage, we emphasize that an initial composition of the melt prepared for the growth of the quasicrystal is effectively governing the surface structure of the quasicrystals. For example, melts with a slightly higher Al concentration lead to quasicrystals with compositions on the Pd-rich side considering the liquidus and solidus surfaces [19]. As a result, those quasicrystals have at low temperatures compositions in the single-phase area of the icosahedral phase and will not form nonicosahedral overlayers. Such materials would be best to investigate the icosahedral surface structure.

Finally, the surface atoms can undergo a relaxation as they experience other forces as compared to bulk atoms due to the missing half-space. However, except a slight reduction of the interlayer distances [27], no surface reconstruction was observed so far for any of the complex intermetallic alloys (quasicrystals and approximants). The atoms seem to keep almost exactly their bulk positions [2,6,28] and it was even possible extract the bulk structure from surface measurements. Therefore, the phase diagram seems not to be modified significantly by surface reconstructions and the symmetry of the surface atoms remains unchanged.

In conclusion, we illustrated that icosahedral Al-Pd-Mn quasicrystals have both icosahedral surface structures and nonicosahedral (orthorhombic H and/or decagonal D phase) overlayers in thermodynamic equilibrium of the vapor–surface–Al-Pd-Mn system. The nature of the structure that is formed is governed by the phase equilibrium at the annealing temperature used for surface preparation and the composition of the solidified Al-Pd-Mn quasicrystal (and thus of the melt) as well as by the preferential nucleation at surfaces. Only in a very narrow composition range or using kinetic pathways do icosahedrally ordered surfaces exist. Nonequilibrium steady-state surface structures present at higher annealing temperatures can also be derived with the same methodology, when taking a nonstoichiometric evaporation into account. With only Mn evaporation orthorhombic ϵ-phase overlayers should form, whereas at higher temperatures, with Mn and Al evaporation, hexagonal δ-phase overlayers will be observable. The results describe consistently all presently observed surface structures. The mechanisms described here for a quasicrystal can be extended to predict the surface structure of many of the periodic complex intermetallic alloys currently investigated, since a large fraction of them exhibit analogous properties. Thus crystallographically different overlayers may represent also thermodynamic equilibrium structures at the surfaces of many intermetallic alloys, depending on their exact composition and temperature.

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