Surface structure of Al-Pd-Mn quasicrystals: Existence of supersaturated bulk vacancy concentrations

Ph. Ebert,[1] M. Yurechko,[1] F. Kluge,[1] T. Cai,[2] B. Grushko,[1] P. A. Thiel,[2] and K. Urban[1]
[1]*Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany*
[2]*Department of Chemistry and Ames Laboratory, Iowa State University, Ames, Iowa 50011*
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We identified the presence and chemical nature of bulk vacancies in Al-Pd-Mn quasicrystals by measuring the structure and composition of two- and fivefold cleavage surfaces of different *preannealed* quasicrystals subjected to postcleavage heat treatments using scanning electron microscopy and Auger electron spectroscopy. A strong dependence of the surface structure from the preannealing is observed and explained by varying concentrations of bulk vacancies. The analysis of the data shows that as-grown Al-Pd-Mn quasicrystals contain Al, Pd, and Mn vacancies in supersaturated but near stoichiometric concentrations, while long-term preannealed samples contain a much lower vacancy concentration, with a tendency to have excess Al vacancies. We found that Al and Mn vacancies are more mobile at lower temperatures than Pd vacancies, and that the diffusion of Mn vacancies is directly coupled to the mobility of Al vacancies. The results demonstrate that the evolution of the surface structure is primarily affected by bulk vacancies migrating toward the surface during heat treatments and provide a new methodology to characterize the vacancies in intermetallic alloys.

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I. INTRODUCTION

The properties of quasicrystals, such as heat conduction or electron transport, are to a large degree affected by the presence of disorder and structural defects.[1–7] Most investigations of defects in quasicrystals focused on line or planar defects,[8,9] which give rise to clear contrasts in transmission-electron microscope images, or on phason strain fields, whose signatures can be observed by neutron- and x-ray scattering experiments.[10] Point defects, such as vacancies, turned out to be much more difficult to identify and characterize, because positron annihilation measurements[11–13] could not distinguish between missing atoms, i.e., real vacancies, and the densely distributed vacancylike sites arising from open spaces in, e.g., the perfect Al-Pd-Mn quasicrystal structure.[11,12] The high concentration of open spaces in the perfect icosahedral structure makes all positrons annihilate in such open spaces, which have long positron lifetimes and thus appear as vacancylike sites. As a consequence the positron annihilation signals are saturated and no decomposition of the lifetime spectra is possible. The latter is, however, the prerequisite for identifying unambiguously the physical origin of the positrons' increased lifetime,[14] i.e., distinguishing between structural open spaces and real vacancies in the icosahedral Al-Pd-Mn quasicrystal.

An apparently totally different aspect of Al-Pd-Mn quasicrystals is the pronounced variation of their surface structures. Depending on the particular sample and preparation technique, the surfaces of quasicrystals were found to roughen macroscopically or remain atomically smooth, and form clusterlike structures or clean atomic layered morphologies. In addition, large changes in surface composition were found. These effects exist on surfaces prepared by sputter and annealing cycles[15–19] as well as by cleavage and subsequent annealing.[20–22] To date the physical origins of these effects have been attributed to preferential sputtering, preferential evaporation under Langmuir conditions, chemical inhomogeneities, and segregation. However, it has recently been shown that evaporation starts only above 900 K,[23] i.e., a temperature much higher than that needed for the abovementioned changes of the surface structure and composition. Furthermore, the preferential sputtering does not occur on cleaved surfaces. Thus there must be additional physical mechanism(s) affecting in a more fundamental manner the evolution of the surface structure.

In this paper we combine the two aspects of quasicrystals, the presence of point defects and the structure of their surfaces, by investigating the evolution of the surface structure and composition for a variety of *preannealed* Al-Pd-Mn quasicrystals. By changing the vacancy concentration in the quasicrystals through preannealing, we show that the presence of bulk vacancies directly affects the surface structure and composition. The results obtained are twofold: On the one hand, the experiments performed allow to identify and characterize the presence and chemical nature of bulk vacancies in Al-Pd-Mn quasicrystals. We find that a supersaturation of quenched-in vacancies exists in as-grown Al-Pd-Mn quasicrystals. On the other hand, our experiments allow us to determine the physical mechanisms affecting the surface structure of Al-Pd-Mn quasicrystals. We find that the surface structure is primarily governed by vacancies in the underlying bulk, which migrated during heat treatments toward the surface acting as sink. Since the vacancy concentration sensitively depends on the growth and annealing conditions of every individual sample, the widely varying surface structures can be understood on the basis of just one simple physical effect, migration of vacancies toward the surface. On top of this, secondary effects, such as preferential sputtering and preferential evaporation, affect the details of the structure. On the basis of these results, we find that quasicrystals with rather small thermal vacancy concentrations are best for reaching high quality surface structures for detailed surface characterization experiments.

II. EXPERIMENT

The principle of our experiments is based on the preparation of quasicrystals with controlled vacancy concentrations by subjecting them to a suitable preannealing, unlike the samples used in previous surface structure investigations. Samples from these preannealed quasicrystals are then cleaved to obtain a well-defined and known starting point as well as a clean surface and to avoid changes of the defects by the thermal treatments during the cleaning procedure. Then we heat treat the cleaved surfaces and monitor the evolution of the surface structure and composition by scanning electron microscopy (SEM) and Auger electron spectroscopy (AES).

For our experiments we used seven different Al-Pd-Mn single quasicrystals grown by the Czochalski method along the fivefold and twofold directions. We investigated a part of the quasicrystals in their *as-grown* state. Other samples were subjected to either a short-term preannealing for 65 h at 820 °C or a long-term preannealing for 2445 h at 800 °C. For the long-term preannealing the samples were in evacuated quartz ampullae, in which the equilibrium vapor pressure is built up during annealing. Since the equilibrium vapor pressure is not instantaneously built up, the short-term annealing was done in an Ar flow furnace. This allows to limit the evaporation. The average composition of the quasicrystals has been measured by inductively coupled plasma optical emission spectroscopy (ICPOES) to be $Al_{70.5}Pd_{21.0}Mn_{8.5}$. The preannealing procedures did not change the chemical composition or phase of the samples. All samples were single quasicrystals. The cooling rates after annealing and after the Czochralski growth were estimated to be about 20–50 K/min.

For the experiments we cut by spark erosion in each sample with dimensions of typically $3\times3\times7\,mm^3$ two cleavage slots perpendicular to the long axis of the samples, which was either parallel to the fivefold or twofold axis. After transferring the samples into the vacuum chamber they were outgassed in ultrahigh vacuum for several hours at temperatures ranging from 350 °C to 550 °C before cleavage. The samples were cleaved using a double wedge technique at pressures between 0.3×10^{-8} and 1×10^{-8} Pa at room temperature. After cleavage the samples were subjected to three to five consecutive heating cycles of 1 h duration with increasing temperature. The heating was achieved by indirect radiation or electron-beam heating of the whole sample holder from the back side. During the postcleavage heat treatment up to 300 °C the pressure remained at about 1×10^{-8} Pa. With increasing temperature the maximum pressure gradually increased and remained usually in the low 10^{-7}-Pa range. After heat treatment the pressure quickly reached the low 10^{-8}-(or even high 10^{-9}-) Pa range. After cleavage and after each heat treatment the surface composition and structure were monitored by AES, SEM, and light-optical microscopy. After the final measurement the samples were investigated *ex situ* by a high-resolution scanning electron microscope to monitor the surface morphology with the highest possible resolution. The AES data were acquired as described in Ref. 21 with a primary electron-beam energy of 3.00 keV and a beam current of 0.8–7 μA. The compositions of the near surface region (probed layer about 1–2-nm thick at the used conditions) were deduced from the differentiated Auger spectra as described in Ref. 24 using the peak-to-peak heights of the Pd MNN (330 eV), Mn LMM (589 eV), and Al KLL (1396 eV) peaks. The sensitivity factors were calibrated using the spectra obtained at room temperature directly after cleavage and the chemical composition determined from the ICPOES measurements. For each sample the system was recalibrated. Each data point is based on four to ten Auger electron spectra measured at different locations on the surface. The error bars indicate the standard deviation and thus provide a measure of the variations within the samples' surface. The temperatures were measured below 350 °C using a phosphorescence-decay-based absolute measurement technique manufactured by Luxtron and above 350 °C by an infrared pyrometer.[21]

III. RESULTS

Directly after cleavage all Al-Pd-Mn cleavage surfaces exhibit in SEM images large flat areas with metallic optical reflectivity and no measurable roughness independent of the preannealing before cleavage and independent of the surface orientation (two- vs fivefold). At nanometer-scale scanning-tunneling microscopy images reveal a cluster-subcluster structure with a roughness of about 2 nm.[25] In addition, the fracture of the as-grown samples exposed small grown-in voids. As-grown samples contain voids with typical dimensions of up to 10 μm and concentrations of up to 10^3 cm^{-2}. In contrast, 2445-h preannealed samples exhibit mostly very large voids with dimensions of 100–300 μm in diameter. These large voids nucleated preferentially at the outer surfaces of the samples, at small-angle grain boundaries, or cracks in the material, but also less frequently in defect-free material. We considered in the following investigation only the samples with no detectable grain boundaries or other defects.

Although all surfaces from the differently preannealed samples exhibit the same properties directly after cleavage, significant differences occur after the cleaved surfaces were subjected to postcleavage heat treatments in ultrahigh vacuum. Figure 1 shows the chemical compositions determined from the Auger electron spectra acquired on the cleaved surfaces as a function of the temperature of the postcleavage heat treatment for the three types of preannealed samples investigated. Filled and open symbols show the compositions of the five- and twofold Al-Pd-Mn surfaces, respectively. In order to avoid any influences of oxygen on our composition measurements, we only considered samples with negligible oxygen contaminations. The following results were obtained:

(i) Based on measurements of the fivefold cleavage surface of as-grown Al-Pd-Mn,[21] we made additional experiments for the twofold surfaces. Figure 1(a) shows that as-grown materials exhibit for both the two- and fivefold surfaces large changes in composition. The changes are primarily a decrease in the Al concentration (coupled to an increase of the Pd concentration and a decrease of the Mn concentration) at

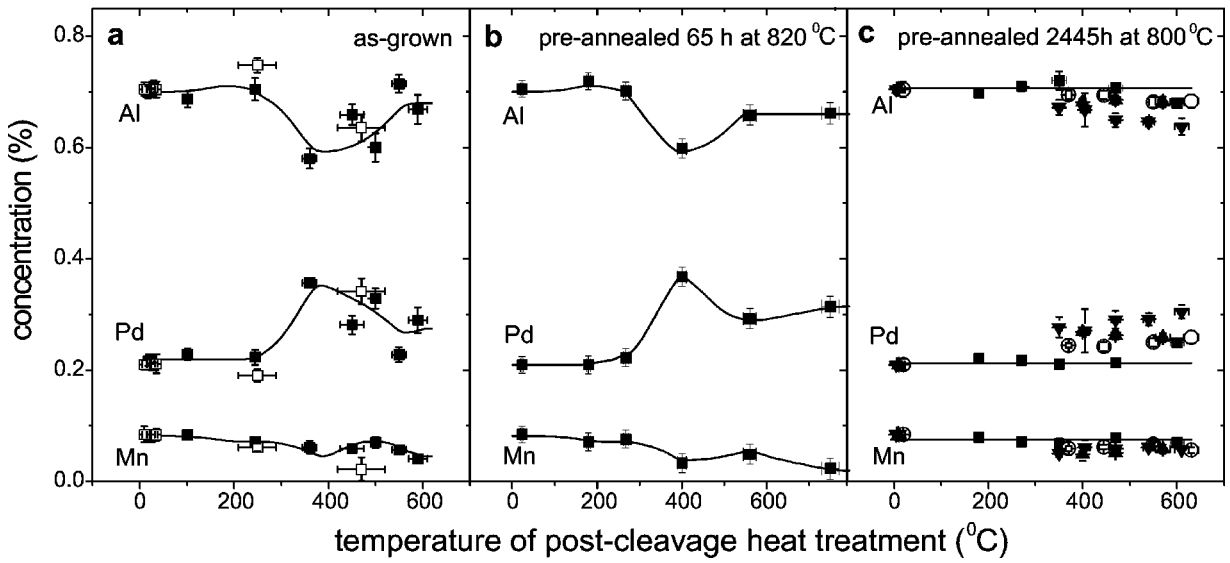

FIG. 1. Compositions of the two- and fivefold cleavage surfaces determined from Auger electron spectra as a function of the postcleavage heat treatment for different types of preannealed Al-Pd-Mn quasicrystals. Open and filled symbols show the data for the two- and fivefold surfaces, respectively. Shown are the compositions of the cleavage surfaces of (a) five- (Ref. 21) and twofold as-grown, (b) fivefold 65-h at 820 °C preannealed, and (c) two- and fivefold 2445-h at 800 °C preannealed Al-Pd-Mn quasicrystal samples.

about 350 °C, as well as a decrease of the Pd concentration (coupled with an increase of the Al and Mn concentrations) at 500 °C–600 °C. The new results corroborate previous observations[21] and in addition show that the two surface orientations exhibit the same evolution in the surface composition.

(ii) Essentially no differences can be found in the behavior of as-grown [Fig. 1(a)] and short-term preannealed (65 h at 820 °C) Al-Pd-Mn [Fig. 1(b)].

(iii) As shown in the discussion section, Al-Pd-Mn quasicrystals should fully reach their equilibrium after 65 h at 820 °C according to the measured diffusion values. Since no effect of annealing occurred after 65 h we performed a long-term preannealing of 2445 h. As shown in Fig. 1(c) the behavior of the surface compositions of the 2445-h preannealed material differs considerably from that of as-grown material. The main effect is that the changes in composition are much smaller than for as-grown or 65-h annealed samples. In addition, at a close look one can see that if any notable changes occur they are only discernable at temperatures above 400 °C. These second-order effects consist of a slight *monotonic* decrease of the Al concentration coupled with a corresponding monotonic increase of the Pd concentration with increasing temperature. Note that with increasing temperature the composition is not driven back to the initial bulk composition, in contrast to the behavior of as-grown samples [compare Figs. 1(c) and 1(a)]. The magnitude of the second-order changes in composition varies from sample to sample and is investigated in more detail below.

(iv) For 2445-h preannealed Al-Pd-Mn quasicrystals no differences between the two- and fivefold surfaces can be detected. Both surface orientations show the same evolution of the chemical composition.

In addition to the changes in surface composition, we observed structural changes of the morphology of the initially flat surfaces exhibiting a metallic reflectivity. The changes in the morphology are directly correlated with the preannealing of the Al-Pd-Mn quasicrystals:

(i) Surfaces of as-grown samples become optically matt during postcleavage annealing at temperatures of about 350 °C and higher. The matt appearance is due to the development of a very pronounced roughness, as visible in SEM images [Fig. 2(a)].

(ii) Surfaces of 65-h preannealed material become optically matt during postcleavage heat treatments in a very similar manner as those of the as-grown quasicrystals. The same type of roughness as in case of as-grown samples is developed.

(iii) In contrast, cleavage surfaces of 2445-h preannealed samples undergo no visible change and keep their metallic optical reflectivity during postcleavage heat treatments. The surface remains smooth at the optical level. Again no differences between the two- and fivefold cleavage surfaces can be found.

Furthermore, Fig. 1(c) shows that although in first order the composition changes of the cleavage surfaces of the

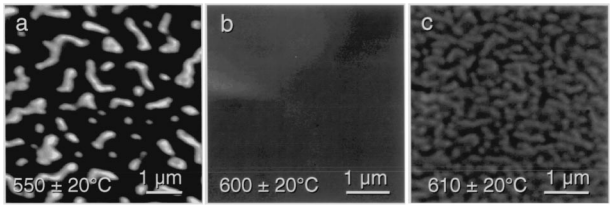

FIG. 2. Scanning electron microscopy images of cleavage surfaces of (a) as-grown, and (b) and (c) 2445 h at 800 °C preannealed samples subjected to postcleavage heat treatments at (a) 550 ± 20 °C, (b) 600 ± 20 °C, and (c) 610 ± 20 °C. The 2445-h preannealed samples exhibited a surface structure ranging between no roughness at all and a very subtle roughness, which is much smaller than that of as-grown samples shown in (a). The two extreme cases are shown in (b) and (c), respectively.

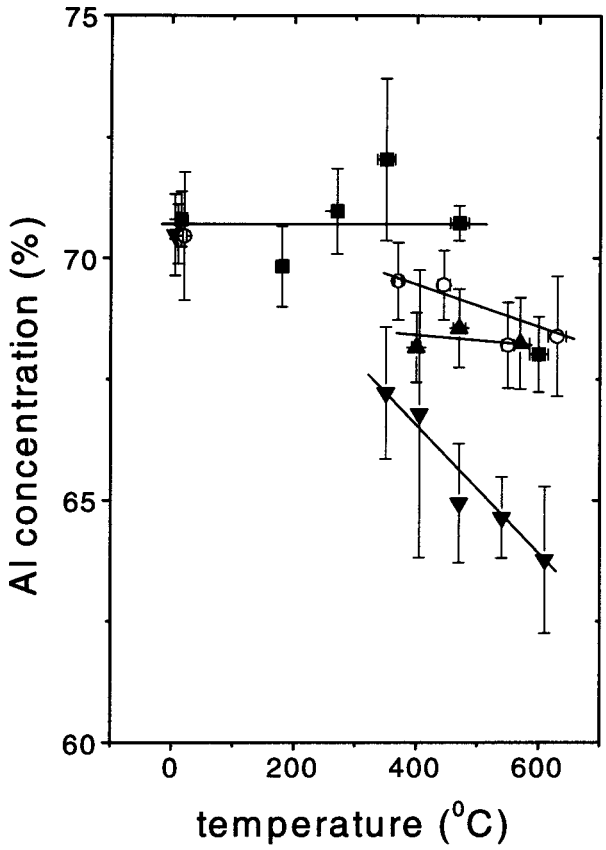

FIG. 3. Al concentration for four different samples preannealed 2445 h at 800 °C as a function of the temperature during postcleavage heat treatment. The different symbols correspond to different quasicrystals. The scanning electron microscopy images in Figs. 2(b) and 2(c) correspond to the uppermost and lowermost data sets, respectively. The more roughness in SEM images increases, the lower the Al concentration after postcleavage heat treatment.

2445-h preannealed quasicrystals are negligible or much smaller than those found for as-grown and 65-h preannealed samples, there is a second-order effect detectable, whose magnitude depends on the exact sample investigated. In order to clarify this issue Fig. 3 shows the changes in Al surface concentration with different symbols referring to the different 2445-h preannealed quasicrystal samples investigated. In addition to the chemical and light optical microscopy information, we studied the morphology of the cleavage surface of each 2445-h preannealed sample with high-resolution SEM after the postcleavage heat treatments. Two examples of high-resolution SEM images are shown in Figs. 2(b) and 2(c), corresponding to the 2445-h preannealed sample with the smallest and biggest change in Al concentration (in Fig. 3), respectively. We observed that the larger the magnitude of decrease of the Al surface concentration, the more pronounced was the roughness observed in SEM images. Samples exhibiting no detectable roughness on the scale of high-resolution SEM also showed no changes in composition [Fig. 2(b) and squares in Fig. 3]. In contrast, samples with roughness [Fig. 2(c)] exhibited changes in composition. Note, however, that even the biggest surface roughness was barely detectable by SEM and was much smaller than that observed on any of the as-grown or 65-h preannealed samples. The fact that the surface roughness of the 2445-h preannealed samples is much smaller in magnitude for all samples than for the as-grown samples is also corroborated by the observation that the surfaces of as-grown samples become optically matt, while the surfaces of *all* the 2445-h preannealed samples keep their metallic optical reflectivity. Thus the surface composition and roughness changes of the 2445-h preannealed samples in Figs. 1(c) and in 3(c), respectively, are indeed second-order effects.

Finally, we also investigated a number of samples, which were either exhibiting a residual oxygen contamination, cleaved in air, and then directly transferred into the vacuum system, or subjected to an oxygen partial pressure of about 1×10^{-8} Pa. In all cases no roughness developed and the Al concentration increased during postcleavage heat treatment independent of the preannealing performed. Two- and fivefold surfaces show the same behavior. In order to avoid this effect of oxygen, we only focus in the following on the oxygen-free surfaces, where possible additional chemical effects can be neglected.

IV. DISCUSSION

The experimental data shows that the surface roughness is directly coupled in a quantitative relation to the changes in composition and that the key parameter governing the behavior is the preannealing. At first we therefore address the effect of preannealing on the Al-Pd-Mn quasicrystals. As-grown quasicrystals contain a void and vacancy concentration determined by the kinetics during the Czochralski growth and the cooling after growth. All previous investigations as well as our own data show that the void concentration is rather high in as-grown Al-Pd-Mn. The voids formed by aggregation of individual vacancies (real atomic vacancies, not structural vacancylike sites) and grow by Oswald ripening in Al-Pd-Mn quasicrystals.[26] In analogy, the fact that the voids in as-grown are much smaller than those in long-term preannealed quasicrystals leads us to conclude that during long-term preannealing vacancies aggregate in large voids and these voids can in addition grow by Oswald ripening in agreement with Ref. 26. These mechanisms have as a consequence a reduction of the void and vacancy concentration and an increase of the few remaining voids in size. Thus the preannealing drives the quasicrystal toward its equilibrium vacancy concentration in the remaining material (while the structural vacancylike sites remain unaffected, because they are part of the defect-free Al-Pd-Mn atomic structure). The different types of samples investigated therefore differ by their vacancy concentration, with the as-grown material having the vacancy concentration quenched-in from the growth temperature, whereas the 2445-h preannealed quasicrystals are close to the equilibrium vacancy concentration at 800 °C. The latter seems to be lower, because preannealing at 800 °C leads in our samples to an aggregation of vacancies in large voids and not to a dissolution of voids in the material. On this basis we now discuss the changes in structure and composition of the cleaved surfaces during postcleavage heat treatments.

Changes in structure and composition of surfaces exposed in ultrahigh vacuum are the signatures of surfaces trying to minimize the energy of the surface-bulk system. In our particular case of Langmuir conditions imposed by the vacuum, only diffusion and evaporation may contribute. Recent evaporation experiments showed, however, that no evaporation is detectable up to about 600 °C from surfaces of Al-Pd-Mn quasicrystals.[23] Starting at temperatures of about 627 °C the first traces of Mn appear and above about 727 °C Al evaporation occurs. Thus at lower temperatures, in particular, at temperatures as low as 350 °C, evaporation is negligible. Therefore, we have to consider diffusion and the different types of samples, i.e., the vacancy concentration, in order to explain our results.

The pronounced difference in surface composition and structure of as-grown and 2445-h preannealed Al-Pd-Mn quasicrystal samples (which only differ in their concentration of vacancies) points to the importance of vacancies in the evolution of the surface and the understanding of the diffusion between the surface and the underlying near surface bulk. The heat treatment of the freshly cleaved samples induces above a certain temperature diffusion of vacancies. If vacancies are present in the near surface layer these vacancies will reach the surface and be trapped at the surface during postcleavage heat treatment, in analogy to the long-term preannealing procedure of the whole sample in a quartz ampulla explained above. This vacancy diffusion process will affect the surface composition and structure: For example, a sample containing only Al vacancies will have a net Al flow from the surface to the bulk once vacancy migration is possible. Thus at the surface the Al concentration is reduced as soon as the vacancies reach the surface by migration. Furthermore, if different species of vacancies are present, one has to take into account that these different types of vacancies may have different onset temperatures for diffusion, due to different diffusion barrier heights. In such a case the presence of different species of vacancies affects the surface composition even if the vacancies occur in stoichiometric concentrations. Thus the composition at the surface reflects the relative concentrations of Al, Mn, and Pd vacancies reaching the surface at a given time and temperature. The vacancies reaching the surface aggregate and form holes or overlapping holes at higher concentrations, leading to rough surface morphology as long as surface diffusion cannot equilibrate the whole surface. Thus the degree of roughness is a signature of the concentration of vacancies, which migrated to the surface, and consequently of the concentration of vacancies in the bulk.

This explanation allows us to deduce information about vacancies from the combined composition data and roughness observations. First, the *absence* of roughness on 2445-h preannealed samples after postcleavage heat treatment indicates a low concentration of bulk vacancies. This conclusion is in agreement with the observation of large voids formed by aggregation of vacancies during annealing and thus the reduced vacancy concentration in the remaining material. In contrast, the observation of very rough surfaces of as-grown samples after postcleavage heat treatment points to a high concentration of vacancies in the bulk of as-grown samples. On basis of this result we can deduce that as-grown material must exhibit a supersaturation of vacancies. These can be annealed out to reach the much lower equilibrium vacancy concentration.

Secondly, we recall that the changes in composition carry information about the chemical nature and onset temperatures for diffusion of vacancies. In Fig. 1(c) we observed only minor changes in composition of the surface during postcleavage heat treatment for the 2445-h preannealed samples. This is a further indication of a low concentration of bulk vacancies. On the other hand, the large variation of composition of the surfaces of as-grown samples during postcleavage heat treatment indicates again a significant vacancy concentration in the bulk and a large flow of vacancies toward the surface. Three effects are distinguishable: (i) The most prominent effect observed is the pronounced decrease of the Al concentration at 350 °C, which is coupled to a strong increase of surface roughness. If Al vacancies present in the bulk reach by migration the surface (acting as sink) the concentration of Al at the surface is reduced. Thus the pronounced decrease of the Al concentration at the surface indicates that Al vacancies are able to migrate above 350 °C. (ii) In the same temperature range the Mn concentration drops by 50%, i.e., even stronger than the Al concentration. This points to a even higher diffusivity of Mn vacancies, which is, however, directly coupled to the Al. The coupling is conceivable, because Mn cannot diffuse without changing onto the Al sublattice of the Al-Pd-Mn quasicrystal, while Al can diffuse solely on the Al sublattice, which represents a connected net of nearest-neighbor sites. Thus a Mn vacancy is only mobile if Al vacancies are mobile. This conclusion is independent of the details of the migration path, which can be very complicated in a complex intermetallic alloy. (iii) Finally, the Pd concentration decreases in the range of 500 °C–600 °C by about 30%, suggesting an out-diffusion of Pd vacancies. At this higher temperature diffusion of Pd vacancies via Al lattice sites is not limited by the Al mobility. The slower Pd diffusivity as compared to Mn is in agreement with diffusion data.[3,27,28] From (i) to (iii) we thus conclude that Mn, Al, and Pd vacancies are present in the as-grown quasicrystals.

The fact that the surface regains a composition close to the initial bulk composition at 550 °C–600 °C indicates that at those temperatures the relative flows of the different vacancies toward the surface are close to the stoichiometry of the initial sample. This suggests that the vacancies occur in a near stoichiometric distribution in the bulk (neglecting the effect of different diffusion constants). Once the flow of vacancies from the bulk toward the surface is sufficiently small, surface diffusion would smoothen the surface. First traces of this effect occur, however, only above 550 °C–600 °C, suggesting that only for very high temperatures the flow of bulk vacancies toward the surface gets small enough such that the rate of surface diffusion can smoothen the roughening of the surface induced by the flow of bulk vacancies reaching the surface.

Thus far we concentrated only on the differences between the 2445-h preannealed and the as-grown samples. However, as pointed out in Fig. 3 there are as second-order effect dis-

cernable differences between the different 2445-h preannealed quasicrystals, which are directly related to a subtle surface roughness. Only the quasicrystal surfaces showing no roughness have a constant surface composition, whereas with increasing roughness the surface composition becomes Al poorer with increasing postcleavage heat treatment. Note that even at 600 °C, where for as-grown samples the surface composition is restored to values close to those of the bulk, the Al concentration still decreases for those 2445-h preannealed quasicrystals, which exhibited the subtle roughness. These observations can be explained as follows: Although 2445-h preannealed Al-Pd-Mn quasicrystals have a much lower concentration of vacancies than in the as-grown state, some quasicrystals still have Al vacancies, which did not agglomerate in sinks or were introduced by the preannealing. These remaining Al vacancies lead upon postcleavage heat treatment to a reduced Al surface concentration and a subtle roughness. The absence of a restoration of the surface composition to that of the bulk at 600 °C indicates that no Pd vacancies exist. If Pd vacancies exist in sufficient concentrations, the decrease of the Al concentration would not be monotonic, but rather change into an increase at 500 °C to 600 °C. Thus even over 100 days preannealed quasicrystal samples sometimes contain Al vacancies in excess. The presence of Al vacancies implies that the quasicrystals investigated are slightly on the Al poor side of the ideal structure at the annealing temperature of 800 °C. The absence of the decrease of the Pd concentration at 600 °C for 2445-h preannealed samples corroborates, in addition, that the decrease of the Pd concentration at 600 °C at the surfaces of as-grown samples is due to Pd vacancy out-diffusion.

The interpretation of the surface structure and composition changes as a function of the preannealing can be applied for both the five- and twofold surfaces. Our data show that the behavior is identical for both surface orientations. This indicates that the vacancy diffusion is not strongly orientation dependent. We are not aware of a systematic orientation-dependent tracer diffusion study in Al-Pd-Mn, but for decagonal Al-Ni-Co quasicrystals very small orientation-dependent effects were observed.[29]

At this stage we compare quantitatively our observations with published diffusion data for Al-Pd-Mn quasicrystals. The diffusion coefficient at 800 °C for Mn diffusion in Al-Pd-Mn is about 10^{-12} m^2/s (Refs. 27 and 28), as for most transition elements.[3,30,31] With use of the same arguments above, one can assume that this value is in the same range and is thus also representative of Al diffusion in Al-Pd-Mn. With the well-known bulk relation of the distance reached by diffusion $r=(6Dt)^{1/2}$ within a time interval t, one obtains for the 65-h annealing at 820 °C a distance of about 1.2 mm. This distance should be by far large enough for vacancies to reach sinks, because at void concentrations of 10^3 cm^{-2} the average distance between voids is only 0.3 mm. In addition, one should consider that we underestimate the effective diffusion length, because the diffusion data has been measured by tracer diffusion, which underestimates the effective diffusion coefficients due to correlation effects. Furthermore, in the classical picture of vacancy-mediated tracer diffusion the diffusion barrier measured is constituted by the energy needed for the formation of a vacancy and the activation energy for the motion of the atom. Thus the diffusion coefficients should be even higher than those published for vacancy diffusion, because the vacancies are present and thus the formation energy is not required. From this we conclude that, in principle, the 65-h preannealing should have been sufficient to reach the equilibrium vacancy concentration. Obviously this is not the case, because even after 2445-h preannealing we still have a small excess vacancy concentration in the material, leading to the second-order effect of a subtle roughness and small composition change. There is another indication that full equilibrium is not reached after 2445-h annealing. It has been shown that the large voids formed still do not have a spherical shape, but rather a variety of elongated and irregular shapes.[32] In equilibrium the voids should have a spherical shape only altered by the formation of low-energy facets. Thus equilibrium of the vacancy concentration is obviously reached much more slowly than tracer diffusion suggests. This effect can be understood, if one considers that the Al-Pd-Mn quasicrystal is a specifically ordered intermetallic alloy, which can only grow if the proper type of atom is at its proper place in the right moment. In analogy, vacancies can only aggregate if they are present with the stoichiometric composition within the same area. For example, if only Al vacancies were aggregating, the quasicrystal would be enriched in Pd and Mn up to the point where the quasicrystalline phase is no longer stable. Thus a small aggregate of only Al vacancies would feel a driving force to dissolve and thereby lower the energy. Only if the stoichiometric combination of vacancies meet locally, a void can be formed. This effect would reduce the nucleation rate of voids considerably and explain why a residual Al vacancy concentration is sometimes still present even in 2445-h preannealed quasicrystals.

Previously it has been reported that voids in as-grown Al-Pd-Mn quasicrystals affect the structure of the cleavage surface in their direct surrounding.[33] In particular, SEM images showed a zone with no roughness around voids after the surfaces were subjected to a postcleavage heat treatment of 400 °C–600 °C. The results reported here provide a quantitative foundation of the interpretation of Ref. 33. The vacancy concentration close to voids is reduced, because of the vacancies aggregated in the void. Thus, locally, vacancies cannot reach by migration the cleavage surface and induce the roughness. On basis of this interpretation, we estimated the vacancy concentration in as-grown Al-Pd-Mn quasicrystals. The zone with no roughness would correspond to the area out of which vacancies aggregated to form the void. One has, however, to take into account that the zone with reduced vacancy concentration is larger than the zone with no roughness, because the latter corresponds only to the area with *no* vacancies. A close look of the increase of roughness with increasing distance from the voids suggests that the zone with reduced vacancy concentration is about two-to-five-times larger than the zone with no surface roughness. On the basis of these considerations and the information from Ref. 33 that the zone with no roughness has a diameter of twice the diameter of the void, we can estimate with the relation $c_{\mathrm{vac}}=(d_{\mathrm{void}}/d_{\mathrm{vac\text{-}reduced\ zone}})^3$ that the vacancy con-

centration c_{vac} is on the order of 0.1%–1.5% in as-grown Al-Pd-Mn quasicrystals. These concentration values are in line with porosity levels of up to 4% found in Al-Pd-Mn quasicrystals.[34]

The presence of different types of vacancies with different diffusion constants in Al-Pd-Mn quasicrystals should also be considered when interpreting anomalous diffusion data such as those in Ref. 3. Changes in diffusion constants may also arise if the diffusion of an additional type of vacancy is enabled thermally, e.g., Al vacancies are mobile at low temperatures, whereas at higher temperatures Pd vacancies can migrate. Thus the knowledge of the types of vacancies present in materials used for diffusion experiments is crucial, in particular, in view of the fact that the heat treatment and growth conditions affect the vacancy concentrations.

Finally, the same effects observed here for cleaved surfaces apply also for sputter and annealed surfaces. A comparison of as-grown and long-term preannealed samples showed that the latter ones yielded the best surfaces in terms of flatness and degree of ordering.[35] Thus one can conclude that during sputtering and annealing the roughness is also primarily determined by vacancies migrating toward the surface. Therefore long-term preannealed Al-Pd-Mn quasicrystals are best for obtaining well-ordered surfaces.

V. CONCLUSION

We demonstrated that the presence, nature, and migration properties of vacancies in Al-Pd-Mn quasicrystals can be extracted from the changes in surface roughness and composition of cleavage surfaces subjected to postcleavage heat treatments measured by scanning electron microscopy and Auger electron spectroscopy. By investigating different *preannealed* Al-Pd-Mn quasicrystals, we found that the roughness and the changes in composition of the cleavage surfaces during postcleavage heat treatments increase with the vacancy concentration in the underlying bulk. From the observations we conclude that as-grown Al-Pd-Mn quasicrystals contain Al, Mn, and Pd vacancies in approximately stoichiometric but supersaturated concentrations, whereas quasicrystals long-term preannealed before cleavage contain a much lower vacancy concentration with a tendency for Al excess vacancies in a small concentration. The data further show that the mobility of Al and Mn vacancies is higher than that of Pd vacancies. Mn vacancy diffusion is coupled to Al vacancy diffusion. The results also show that the surface structure of Al-Pd-Mn quasicrystals is primarily affected by the bulk vacancies migrating toward the surface during heat treatments, something applicable not only to cleavage but also to sputtered and annealed surfaces. Since the vacancy concentration sensitively depends on the exact growth procedure in terms of temperature profiles and postgrowth treatment, each type of sample should be expected to contain a different vacancy concentration specific to the growth and preparation technique. This explains the rather large variety of surface structures observed previously after thermal treatments, and the difficulty in preparing perfect quasicrystal surfaces. Finally, it is noteworthy that similar measurements may allow a determination of the presence of vacancy defects in a large number of cleavable intermetallic alloys and thus help to understand the properties of materials on the atomic scale.

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