Evidence for a Cluster-Based Structure of AlPdMn Single Quasicrystals

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For the first time quasicrystal surfaces produced by *in situ* cleavage in ultrahigh vacuum have been investigated by scanning tunneling microscopy. Twofold and fivefold surfaces of icosahedral AlPdMn single quasicrystals have been studied. The surfaces were found to be rough. Their structure is determined by cluster aggregates formed on the basis of an elementary cluster whose contrast behavior and diameter of about 1 nm point to the Mackay-type cluster. Crack propagation occurs along zones of lower strength between clusters. This supports the cluster approach to quasicrystal structure. [S0031-9007(96)01557-8]

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The structural basis of a quasicrystal is a lattice which exhibits orientational but not translational order [1,2]. Neutron and x-ray *diffraction* experiments [3–5] have led to structure models containing as a basic element large atom clusters, whose particular noncrystallographic symmetry is assumed to play a decisive part in the formation of the quasicrystal lattice. In icosahedral AlLiCu [4] the elementary cluster is related to a Bergman polyhedron of about 100 atoms, whereas in AlCuFe [3] and AlPdMn [5] icosahedral quasicrystals it is derived from the Mackay icosahedron with 55 atoms [6]. For the decagonal AlNiCo quasicrystal, columnar clusters forming pentagonal antiprismatic channels were identified by x-ray scattering experiments [7]. The structure of quasicrystals has been studied *in real space* by high-resolution transmission electron microscopy and by scanning tunneling microscopy (STM). Since high-resolution electron microscopy is based on the imaging of atom columns, a study of nonperiodic structures encounters particular difficulties. Nevertheless, the wheel-shaped features of tenfold symmetry occurring in lattice images taken along the fivefold axes of icosahedral and the tenfold axis of decagonal quasicrystals were attributed to projections of the mentioned elementary clusters [8,9]. In an STM study on decagonal AlCuCo atomic resolution was obtained on tenfold surfaces [10]. The observed atom arrangements were used to construct a model based on pentagonal columnar clusters [11]. In a recent study on icosahedral AlPdMn quasicrystals by STM atomic resolution could not be obtained [12,13]. However, the two-dimensional autocorrelation function of the images exhibited typical quasicrystal symmetries.

In the present work the STM approach is resumed avoiding a particular problem of the previous investigations. This problem arises from the fact that atomically clean surfaces are required. In the earlier work, the samples were prepared outside the microscope under ambient conditions. After transfer into the microscope vacuum, they had to be subjected to repeated cycles of ion bombardment and high-temperature annealing in order to remove the oxide coating. This is a well-tried technique for semiconductor surfaces. However, in its application to metallic alloys problems may arise from surface segregation, as indeed observed in Ref. [13], and from surface phase transformations. The latter may be induced by a change in stoichiometry due to selective evaporation or sputtering. Furthermore, quasicrystalline phase are chemically ordered phases whose equilibrium structure at a surface need not be the same as in the bulk.

In the present work the surfaces were prepared at room temperature by *in situ* cleavage inside the ultrahigh vacuum chamber of the tunneling microscope. This technique avoids all the mentioned risks of artifacts. In fact, the observations made possible this way provide us with new insight into the structure of the surfaces of icosahedral quasicrystals: Large atom clusters are found to play a decisive role. On the other hand, the structure of the surface reflects the physics of cleavage, i.e., of crack propagation. This allows us to draw conclusions on the micromechanical properties of quasicrystals.

The investigations were performed with samples cut from large (5 cm long, 1 cm diam) Czochralski grown single quasicrystals of composition $Al_{70.5}Pd_{21}Mn_{8.5}$. The details of quasicrystal preparation have been described elsewhere [14]. The samples were cleaved perpendicular to twofold and fivefold axes in ultrahigh vacuum (5×10^{-9} Pa), transferred to the tunneling microscope without breaking the vacuum, and investigated in constant current mode.

Particular care was taken to avoid "multiple tip" effects. These are especially critical when rough surfaces of unknown structure and scale are studied. In this case a possible atomic-scale roughness of the tip may give rise to image artifacts, which are not easy to recognize as such. Therefore we tested our images for stability upon changing the scanning direction and, prior to the measurements, the tips' imaging conditions were tested on semiconductor surfaces. There the lateral resolution was better than 0.2 nm. After the STM study, the samples were investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM).

As indicated by SEM and AFM, the cleavage yielded large apparently flat planes separated by thin rough

areas (similar to macroscopic cleavage steps on crystalline samples). The "miscleavage" angle was less than $\pm 5°$. Within these large flat areas no features could be resolved by SEM and AFM except a slight waviness with an amplitude of about 5 nm over a lateral scale of several micrometers.

Figure 1 shows STM images of the surface of a sample cleaved perpendicular to a twofold axis. The surfaces exhibit a rough structure. In Fig. 1(a) grains can be recognized with diameters between 2.5 and 5 nm forming lumps with typical diameters of about 15 nm. The contrast of the grains is compatible with that of a sphere or a spherical segment. Together these lumps form a very irregular hill and valley structure. At higher magnification [Fig. 1(b)] a substructure can be recognized in the grains of Fig. 1(a), which consists of grains of an even smaller diameter. At still higher magnification [Fig. 1(c)] this subgrain structure can be shown to consist of elements of 0.6 to 1 nm diam. Their contrast is again pseudospherical since we cannot distinguish between the spheres and spherical segments.

Figure 2 shows, for the fivefold surface, qualitatively the same results as those obtained on the twofold surface. However, the contrast is slightly weaker.

We studied the contrast behavior of the pseudospherical elements of Figs. 1(c) and 2(c). We could not resolve any further details on them. On the other hand, a study of the image variations in different local environments upon charging the tip to sample voltage or the scanning direction did not give rise to any doubts that the tip was still producing atomic resolution. From this we conclude that the contrast arises from an atom cluster exhibiting a smooth spatial distribution of the electronic density of states.

The grey-scale contrast does not yield a direct measure of the surface corrugation. Figure 3 shows the trace of the vertical z position of the tunneling tip along the diagonal (lower left to upper right corner) of Fig. 1(a). Employing a voltage calibration of the scanning piezo on stepped semiconductor-crystal surfaces a total corrugation amplitude (deepest depression to highest elevation) of 2 nm was determined. The average vertical roughness is in the order of 1 to 1.5 nm.

In Fig. 1(c) the twofold, threefold, and fivefold directions are indicated. Figure 4(a) shows the two-dimensional autocorrelation function calculated from pictures of the Fig. 1(c) type after removing the low-frequency contributions by high-pass filtering. We find a twofold symmetry. The x-ray Laue-diffraction pattern in Fig. 4(b) demonstrates that the symmetry axes of the autocorrelation function are parallel to the twofold directions of the quasicrystal lattice. The two most frequency projected cluster separations are 0.8 and 1.2 nm. In the fivefold case the cluster size distribution deduced from Fig. 2 is broader compared to that on the twofold surface, and we could not observe a clear symmetry of the autocorrelation patterns in this case.

The major result of our study of cleaved, untreated surfaces of AlPdMn single quasicrystals is that the structure is rough. The surface morphology is determined by clusters of various sizes, which, in turn, are formed by the aggregation of a smaller elementary cluster of about 0.8 to 1 nm diam. It is obvious to relate the elementary cluster to a fundamental structural entity of the quasicrystal. In the structure model derived from scattering experiments on AlPdMn by Boudard *et al.* [5] the basis structural element is the so-called pseudo Mackay cluster of 51 atoms. It consists of a central core derived from a dodecahedron, an intermediate shell consisting of an icosahedron, and an external shell which is an icosidodecahedron. Its diameter of 0.9 nm is in good agreement with the size of the fundamental cluster observed in our experiments. Indeed we do not expect, upon scanning an agglomerated structure of spherical elements of the same size, that only the "real" cluster diameter is observed. Effectively smaller diameters are expected when scanning inclined surfaces and in cases where only a fraction of the cluster volume stands out from the heap.

Janot and de Boissieu [15,16] have suggested to relate the stability and the properties of the AlPdMn quasicrystal, in particular, its very high electrical resistivity, to a packing of the pseudo Mackay clusters which combine to form a self-similar hierarchy of aggregates each a factor of τ^3 larger in diameter than the previous size class [$\tau = 1/2(1 + \sqrt{5})$ is the golden mean]. A specific

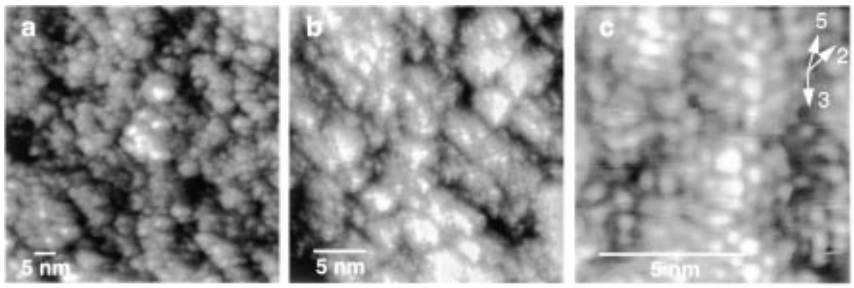

FIG. 1. STM constant current images of the occupied density of states of an AlPdMn icosahedral single quasicrystal cleaved along a *twofold* plane. With increasing magnification smaller clusters appear. Arrows indicate the direction of a fivefold, twofold, and threefold axis. The images were obtained at a tunneling current of 1 nA at voltages of -250 (a), -300 (b), and -200 mV (c).

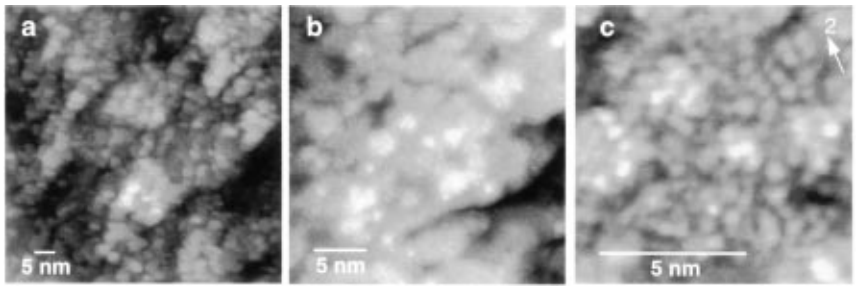

FIG. 2. STM constant current images of an AlPdMn icosahedral single quasicrystal cleaved along a *fivefold* plane. The contrast is slightly lower but the cluster size hierarchy is similar to that of Fig. 1. The arrow indicates a twofold axis. The images were obtained at a tunneling current of 1 nA at voltages of −600 (a), −300 (b), and −350 mV (c).

feature of this model is that the elementary clusters confine electrons in a deep spherical well potential and that the clusters are particularly stable if the number of quasifree electrons equal the total occupation number of the electron states. Electrons can tunnel from a given cluster to the neighboring ones. This is described as hopping within the cluster of the next size class, which in turn confines electrons in an inflated spherical well potential

This model provides a direct explanation for the observed STM contrast. In a first approximation, STM probes the local density of states at a certain distance from the surface [17,18]. The confined electron states in the deep well potential to which the elementary clusters owe their particular stability should not produce substantial atomic-scale corrugation outside the clusters. It is therefore not expected that the "atomic" structure of the elementary clusters can be resolved by STM. The fivefold planes are the most densely packed ones in the AlPdMn structure. Their weaker contrast indicates that they are, with respect to the electronic structure, flatter than the twofold planes.

The plastic mechanical properties of AlPdMn single quasicrystals have been studied in Refs. [14,19,20]. At room temperature the material exhibits only very limited ductility and breaks by brittle fracture. Because of the low temperature, the atomic structure is essentially frozen and thus the images of the cleavage planes can provide us with information on crack propagation.

In the Griffith model of mode I brittle fracture the critical stress σ_F for a crack of length c to expand spontaneously is given by

$$\sigma_F = \left(\frac{2\gamma E}{\pi c}\right)^{1/2},$$

where Young's modulus E is characteristic of the bond strength of the highly strained material at the crack tip. The energy created in the flanks of the crack is proportional to the surface energy γ. Both E and γ favor crack propagation in between the elementary clusters, which due to their low energy, form particularly rigid entities.

The τ^3 inflated clusters of Ref. [16] exhibit a concentric three-shell structure. The core and the outer shell consist of complete clusters while the clusters in the intermediate shell are truncated and overlap with their neighbors. Our observation of a size hierarchy of clusters can be interpreted as evidence for a mode of crack propagation by means of which transcluster fracture is avoided with respect to the basic clusters and, as far as this is permitted by the local stress situation, also for first-generation inflated aggregates (diameter ~5 nm). Any larger aggregates (the second-generation τ^3 inflated cluster has a diameter of 20 nm) cleave by crack propagation through the aggregate revealing the subcluster structure [Figs. 1(a) and 2(a)]. Crack propagation in a planar binary-tiling model has recently been investigated in a molecular-dynamics simulation [21]. It was found that a dislocation occurs at the crack tip whose

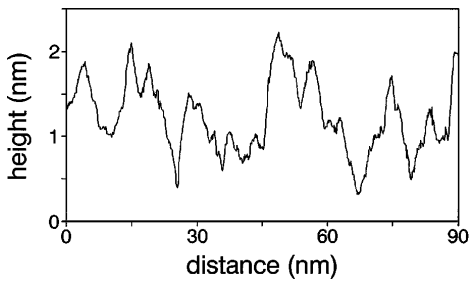

FIG. 3. Trace of the vertical z position of the tunneling tip along the diagonal (lower left to upper right corner) of Fig. 1(a).

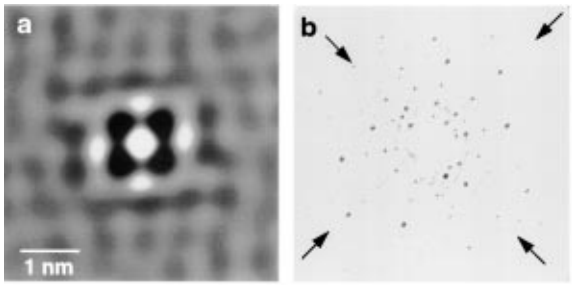

FIG. 4. Lateral autocorrelation function of the smallest cluster separations in pictures of the Fig. 1(c) type and an x-ray Laue diffraction pattern. The twofold symmetry axes are denoted by arrows.

phason-strain field induces an initial weakening of the structure along a line which later develops into the propagating crack. This line circumvents the atom clusters producing crack flanks of a rough structure quite similar to that observed in our experiments.

The cluster elements and their particular arrangements are considered an inherent feature of the AlPdMn icosahedral quasicrystal. An elevated degree of disorder or, even more so, the destruction of the clusters induces a phase transition. This means that, as long as surface phase transformations are excluded, the quasicrystal surface should always be rough with respect to the arrangement of the fundamental clusters. This may have a bearing on a low coefficient of friction of quasicrystals. As shown in a recent study of surface oxidation of AlPdMn quasicrystals by x-ray photoelectron spectroscopy the surface forms an overlayer which is essentially aluminum oxide [22]. Nevertheless, the coefficient of friction [23] is up to an order of magnitude lower than that of oxidized aluminum [24]. We suggest that this is due to a different structure of the oxide layer if it grows on the rough quasicrystal surface.

In conclusion, the investigation of surfaces produced by cleaving AlPdMn single quasicrystals has demonstrated that the quasicrystal structure is dominated by aggregates of an elementary cluster. As a consequence the surfaces are rough on a scale of a few nanometers. In brittle fracture the rigid clusters and their aggregates are avoided by the advancing crack. This results in intercluster cleavage.

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