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Cleaved surfaces of d-AlNiCo and ξ′-AlPdMn

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Abstract

Decagonal Al–Ni–Co quasicrystals were cleaved in ultrahigh-vacuum and the resulting surfaces were investigated by dynamic scanning force microscopy. The samples were cleaved perpendicular to the tenfold axis and perpendicular to one of the twofold axes. Both surfaces show a rough structure with lateral features on the nanometer scale and height differences of angstroms to nanometers. While the corrugation of the tenfold surface does not show any correlation to the quasiperiodic bulk structure, the twofold surface exhibits row-like corrugations, which indicate the existence of columnar structure motifs along the direction of the tenfold axis as expected from structure models. Images from surface regions tilted with respect to the twofold plane strongly indicate the existence of inclined netplanes. In addition, we studied surfaces of an ξ′-(Al–Pd–Mn) quasicrystal approximant, which was cleaved perpendicular to the pseudo-tenfold b-axis. These surfaces show a corrugated structure as well, similar to the results obtained from the decagonal Al–Ni–Co surfaces. There is no indication of a correlation to the periodicity or other structural features of this orthorhombic, crystalline material.
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1. Introduction

Quasicrystalline structures can be described by cluster models, in which the structure is considered to be built up from clusters as structural units [1]. These are arranged quasiperiodically, according to underlying tilings. In the case of decagonal quasicrystals these are columnar clusters of about 2 nm in diameter, which are arranged quasiperiodically and can also overlap in the structure, depending on the model [2–4]. In the case of icosahedral quasicrystals the structure contains quasi-periodically arranged Pseudo-Mackay Icosahedra or Bergman Clusters of about 1.2 nm in diameter [5]. There are contrary opinions concerning the meaning of these clusters in the real structure, mainly regarding their stability. On the one hand, the electronic stabilization of quasicrystals by the cluster structure has been intensely

discussed and can be considered as confirmed [6–8]. On the other hand, it is not clear if the clusters are indeed building units exhibiting extraordinary mechanical or structural stability or if they are just useful theoretical elements for the description of quasicrystalline structures [2,6,9]. The investigation of cleaved surfaces should provide information which might enlighten this question. In the case of an exceptional mechanical stability the clusters should be preserved during the cleavage process and it might be possible to image them as quasiperiodically arranged corrugations at the cleavage plane. Scanning tunneling microscopy (STM) investigations of cleaved icosahedral Al–Pd–Mn quasicrystals have been published by Kluge et al. [10]. They report a cluster-subcluster structure and relate the smallest clusters to a fundamental structural entity of the quasicrystal [11]. However, no quasiperiodic arrangement of these structures has been reported, which would be an essential condition for relating the features in the images to clusters.

In this paper we present results obtained by dynamic scanning force microscopy (SFM) [12] investigations

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of cleaved surfaces of decagonal Al–Ni–Co quasicrystals (d-AlNiCo) and an ξ'-(Al–Pd–Mn) approximant (ξ'-AlPdMn) [13]. Dynamic SFM is a surface characterization technique that is unrivalled for imaging insulators with a resolution capability down to the atomic scale [14]. In the context of investigating surfaces of quasicrystals, this method is interesting as tip–surface interactions leading to an image contrast are fundamentally different compared to those involved in tunneling microscopy. While the information obtained in tunneling microscopy is mainly related to the local variation of the electronic density of states, short-range interactions important for contrast formation in dynamic SFM are of chemical nature. Atomic resolution SFM imaging requires the reversible forming and breaking of bonds between tip and surface that results in atomic contrast. However, on surfaces that are not atomically flat, this contrast is superimposed by other strong components due to long-range interactions (e.g. van der Waals interaction). As the investigated cleavage surfaces do not exhibit large atomically flat terraces, atomic resolution in force imaging can not be expected. It can be anticipated that the apparent surface topography obtained in force microscopy is influenced by the surface electronic structure in a different way than that obtained in STM measurements. Thus, dynamic SFM yields information that is complementary to conventional scanning probe microscopies like STM and contact-mode SFM.

2. Experimental

Samples of about $4 \times 4 \times 10$ mm^3 were cut from a large d-AlNiCo quasicrystal grown by the Czochralski method [15] and from a Bridgman-grown ξ'-AlPdMn approximant [16] with the axis of interest oriented along the long axis of the prisms. In the case of d-AlNiCo these have been the tenfold [00001] axis (according to the indexing system by Steurer et al. [17]) and the twofold axis oriented perpendicular to the naturally growing twofold {10000} surface plane, while the ξ'-AlPdMn approximant sample was oriented along the pseudo-tenfold [010] axis. The nominal compositions of the investigated samples were $Al_{72.8}Ni_{15.2}Co_{12.0}$ and $Al_{74}Pd_{22}Mn_{4}$. The samples were cleaved in ultrahigh-vacuum (UHV) (base pressure 2.5×10^{-8} Pa) using a sharp blade mounted on a wobble stick. The cleavage surfaces were investigated with a commercial UHV-scanning force microscope (Omicron) operated in the dynamic mode [12]: the cantilever was excited at its resonance frequency (cantilever spring constant 6 Nm^{-1}, resonance frequency 80 kHz) and the detuning induced by the tip–surface interaction was used as a control parameter [18,19].

3. Results

3.1. d-AlNiCo quasicrystals

3.1.1. Tenfold axis

The surface produced by cleavage perpendicular to the tenfold [00001] axis (i.e. parallel to the quasiperiodic plane) of d-AlNiCo shows a cloudy structure with the smallest lateral features of 2–3 nm in diameter and several angstroms up to a few nanometers in height (Fig. 1(a)). In order to conclude that this structure is correlated to the underlying quasicrystalline structure of the material, the protrusions visible in Fig. 1(a) would have to be arranged quasiperiodically. However, this is not the case for any of the images that we obtained from this cleavage surface. They do not show features suggesting a correlation to the tenfold surface, and autocorrelation function calculations do not either. The latter would have to show five- or tenfold symmetry in the case of an existing correlation. Therefore, we cannot demonstrate any correlation between the protrusions in the images and the structure of the tenfold surface, and hence cannot give any evidence for the existence of clusters as stable units at the cleavage surface.
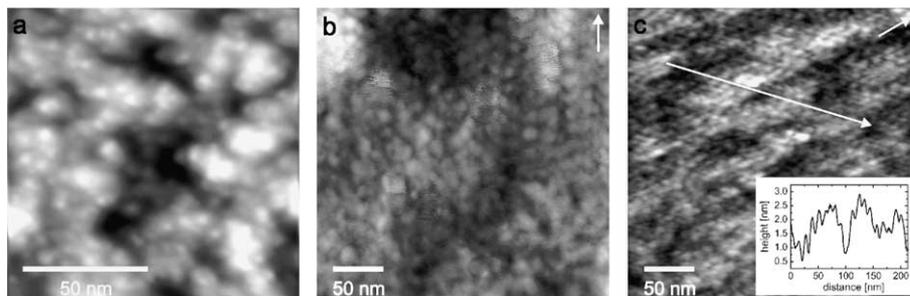

Fig. 1. Dynamic SFM images (mean detuning $\Delta f \sim 10$ Hz) of the tenfold surface (a) and the twofold surface (b) of d-AlNiCo; (c) shows a surface plane tilted and rotated with respect to the tenfold axis matching the orientation of an inclined netplane. The inset shows the cross-section along the large arrow.
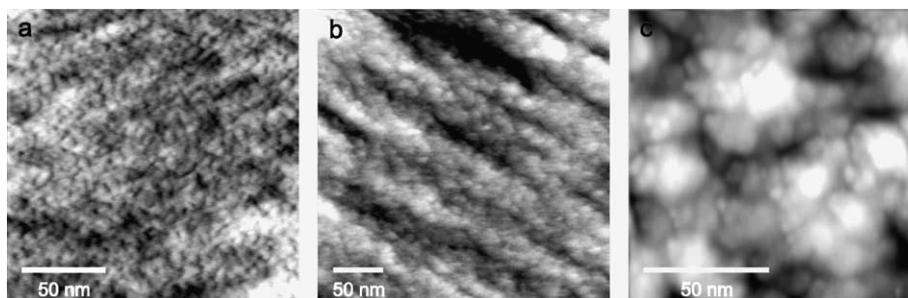
Fig. 2. Dynamic SFM images (mean detuning $\Delta f \sim 15$ Hz) of the surface obtained by cleavage perpendicular to the pseudo-tenfold axis of ξ'-AlPdMn: (a) shows the pseudo-tenfold surface plane, (b) and (c) originate from planes tilted with respect to the pseudo-tenfold surface.

3.1.2. Twofold axis

Fig. 1(b) shows an image obtained from the twofold (1 0 0 0 0) plane of d-AlNiCo. This surface is rough as well; the features are 7–10 nm in diameter, height differences range between several angstroms and a few nanometers. The direction of the tenfold axis is clearly visible (indicated by the white arrow in Fig. 1(b)) and the structures along this direction seem to be regular. In this case we observe an obvious correlation of the features visible in the image to the structure of the twofold plane in decagonal AlNiCo quasicrystals. It remains unclear, however, why the features are on the nanometer scale and why regularity is visible on this scale.

Other structures could be observed at other positions of this fracture surface. Fig. 1(c) shows a plane that is tilted about 30° from the (1 0 0 0 0) plane towards the tenfold [0 0 0 0 1] axis. In addition, this plane is rotated 30–40° around the tenfold [0 0 0 0 1] axis. One should keep in mind that at 36° of rotation a symmetrically equivalent twofold axis is located, since the symmetry group is invariant with respect to rotations of 36° around the [0 0 0 0 1] axis. The roughness in this image is about the same as in Fig. 1(b), but the features are 3.5–5 nm in diameter, which are about half the size of the structures visible at the twofold plane. The direction of the projection of the tenfold axis is clearly visible (indicated by the small white arrow in Fig. 1(c)) and the structures along this direction seem to be regular again. However, this image does not only show the direction of the projection of the tenfold axis, but other preferential directions are clearly visible as well. This result strongly indicates the existence of inclined netplanes [20]. The orientation with respect to the tenfold axis suggests that this plane is an inclined netplane itself (namely the $(0\,\bar{1}\,\bar{1}\,0\,1)$ after [20]); the other preferential directions visible may indicate further sets of inclined netplanes. The inset in Fig. 1(c) shows the line profile along the large white arrow in the image, which is lying along such a direction inclined about 45° with respect to the projected tenfold direction. The average distance of the structures in this direction is about 10 nm and rather regular.

3.2. ξ'-AlPdMn approximant

3.2.1. Pseudo-tenfold axis

The ξ'-phase of Al–Pd–Mn is an orthorhombic approximant phase with a unit cell containing 320 atoms, arranged in partial Mackay icosahedra [13]. The samples were cleaved perpendicular to the pseudo-tenfold axis (unit cell parameters in this plane: $a = 23.541$ Å, $c = 12.339$ Å). Fig. 2(a) shows an image obtained from the pseudo-tenfold surface plane. The features are 4–8 nm in size and show height differences between several angstroms and a few nanometers. No clear preferential direction and no periodicity are visible in this image; therefore no correlation to the underlying structure can be evidenced.

The surfaces produced by fracture were rough on a macroscopic scale. Different regions on this fracture surface exhibit quite different surface structures (Fig. 2(b) and (c)). This is due to the fact that these images originate from different planes that are tilted with respect to the pseudo-tenfold plane.

4. Discussion

The cleavage technique applied resulted in macroscopically rough surfaces, so that planes with orientations different from the intentional cleavage planes could be additionally investigated. On a smaller scale the fracture surfaces exhibit a root mean square roughness of about one nanometer in all cases. The data obtained from the dynamic SFM images do not give any evidence of the existence of mechanically stable clusters, neither for d-AlNiCo nor for ξ'-AlPdMn. In the case of the d-AlNiCo tenfold plane and the ξ'-AlPdMn pseudo-tenfold plane no correlation to the underlying structure could be identified, while the images of the d-AlNiCo twofold surface clearly show the direction of the tenfold axis. Furthermore, this cleavage surface exhibits regions that strongly indicate the existence of inclined netplanes.

Some of our images show a striking similarity to the images of icosahedral Al–Pd–Mn published by Ebert

et al. [11], although the scale and the structural nature of the material under investigation are completely different. This is a quite unexpected result, which is difficult to explain. One may contemplate whether the observed structures may be incidental roughness, rather than strongly influenced by the materials structure. This notion is corroborated by the fact that no correlation to the underlying structure could be found except in the case of the d-AlNiCo twofold axis (Fig. 1(b) and (c)). The size of the smallest structures found at the tenfold surface of the d-AlNiCo sample (Fig. 1(a)), on the other hand, agrees with what is expected for a single structural cluster column imaged with dynamic SFM (taking a tip–surface structure convolution into account). It is therefore tempting to interpret these structures as clusters. Ebert et al. indeed relate their smallest features to a fundamental structural entity of the quasicrystal [11]. However, since no quasiperiodic arrangement of the structures is observed, we are cautious in associating the word *cluster*.

Theoretical investigations of crack propagation in quasicrystals suggest that clusters act as structure-intrinsic obstacles, which lead to a rough fracture surface exhibiting parts of clusters and material in between [9]. This result questions the possibility to image and identify single preserved clusters at fracture surfaces even if they exist as stable units. Former and recent investigations of sputter-annealed surfaces provided impressive STM images [21], however without evidence for the existence of mechanically stable clusters. Surfaces annealed at lower and medium temperatures showed cluster-like corrugations, but no five- or tenfold symmetric Fourier transform or autocorrelation function images were reported, which could evidence the quasiperiodic arrangement of the structures. Annealing at high temperatures resulted in atomically flat, terraced surfaces, which show structural features at the atomic scale. In this case tenfold autocorrelation and Fourier transform images clearly evidence the quasiperiodic ordering of these surfaces. Apparently the formation of atomically flat surfaces is energetically favored compared to the reconstruction of clusters at sputter-annealed surfaces.

5. Conclusions

The results we obtained from cleaved surfaces did not allow for any conclusion concerning the existence of mechanically stable clusters in the quasicrystalline and approximant structures under investigation. Ongoing experiments will hopefully enlighten the question whether this fracture behavior is intrinsic to quasicrystalline structures containing clusters or whether it is typical for structurally complex alloy phases (SCAPs), alloys in general or even metals. Overall we conclude that the evaluation of data obtained from cleaved surfaces should be done elaborate with respect to the real orientation of the investigated regions.

Acknowledgements

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