Published in Surface Science 433-435, 302-306, 1999
which should be used for any reference to this work

Temperature-induced phase transition observed at a fivefold icosahedral quasicrystalline AlPdMn surface

D. Naumović [a,*], P. Aebi [a], C. Beeli [b], L. Schlapbach [a]

[a] *Institut de Physique, Université de Fribourg, Pérolles, CH-1700 Fribourg, Switzerland,*
[b] *Laboratorium für Festkörperphysik, ETHZ, CH-8093 Zürich, Switzerland.*

Abstract

A switch in symmetry from fivefold to tenfold has been observed at the surface of a monograin icosahedral AlPdMn quasicrystal cut perpendicularly to a fivefold axis as a function of annealing temperature and/or annealing time at a constant temperature. A continuous change in stoichiometry was simultaneously monitored by X-ray photoelectron spectroscopy. The surface structure study was performed using full-hemispherical X-ray photoelectron diffraction and low-energy electron diffraction.

Keywords: Alloy; AlPdMn; Low-energy electron diffraction; Quasicrystal; Surface phase transition; X-ray photoelectron diffraction

From their discovery quasicrystals continue to rouse the interest of scientists. They exhibit not only extraordinary crystallographic structures (especially including forbidden symmetry axes as 5-, 8-, 10- or 12-fold), but also most remarkable electronic and mechanical properties. (For a review see, for example Refs [1–4].) Among them, unusually low friction, wetting and oxidation characteristics of quasicrystalline surfaces are particularly attractive for industrial applications. As yet, quasicrystals can only be used as coatings due to their brittleness. Crucial questions concerning the stability of the quasicrystalline surfaces under different treatment as annealing or oxidation are specifically addressed to (or can be solved by) surface scientists. Recently, for instance, different studies have reported on crystalline reconstructions occurring after ion sputtering and, eventually, annealing the sample at temperatures between 200 and 400°C, what is below the temperature necessary to recover a bulk-terminated surface after sputtering [5–10].

In the present study we intend to describe one of the possible surface reconstructions which occurs after annealing a quasicrystalline icosahedral AlPdMn (*i*-AlPdMn) surface. Icosahedral quasicrystals exhibit two-, three- and fivefold axes as it is the case for an icosahedron. The annealing temperatures are chosen in a range between 500 and 750°C. 500°C is just high enough to recover a bulk-terminated surface after sputtering and 750°C is close to the melting point.

Surface techniques probing the very surface geometrical structure, as scanning tunneling microscopy (STM) [11], secondary-electron imaging (SEI) [12] and low-energy electron diffraction (LEED) [13,14], have only been applied recently. STM and SEI are both sensitive to local order, whereas LEED, is a diffraction technique operating

---

* Corresponding author. Fax: +41-26-300-97-47.
E-mail address: dusanka.naumovic@unifr.ch (D. Naumović)

in reciprocal space. None of them, however, is chemically selective. In this paper, besides LEED, we used X-ray photoelectron spectroscopy (XPS) to study the chemical composition at the surface and, in particular, an XPS derived method, full-hemispherical X-ray photoelectron diffraction (XPD). Some XPD results on the *i*-AlPdMn quasicrystal surface cut perpendicularly to a two- or fivefold symmetry axis have already been presented elsewhere [10,15]. XPD is chemically selective and sensitive, providing at the same time local and site-specific, real-space information of the near-surface region. The photon energy used in the present study (Mg Kα at 1253.6 eV) is such that the kinetic energies of photoelectrons from the examined core levels are >500 eV, namely Al 2s at 1136 eV, Pd $3d_{5/2}$ at 917 eV and Mn $2p_{3/2}$ at 615 eV. Only diffractograms of the Pd $3d_{5/2}$ signal will be shown. Owing to a strong focusing of photoemitted electrons along dense atomic rows or planes in this kinetic energy regime (for a review see, for example, Refs [16–19]), the mapping of the core-level electron intensity over the hemisphere above the sample surface results in a projection of the atom–atom directions, along which the photoelectrons are focused, starting from the core level of the emitting chemical species [20,21]. By choosing a particular emission line or emitting atom (Pd, Al or Mn) this specific real-space environment is probed. So, the diffractogram obtained from a particular emitter gives a very specific and unique view of its local real-space environment. Therefore, XPD is particularly suitable to probe surface reconstructions and phase transitions occurring at surfaces of monocrystals or monograin quasicrystals.

In this work we show the following. After sputtering and prolonged annealing the fivefold surface of *i*-AlPdMn at temperatures >650°C (i.e. above the temperature usually applied to obtain a quasicrystalline surface [5–11,15,22]), XPD and LEED displays the appearance of a new surface phase characterized by tenfold symmetry. Simultaneously changes in stoichiometry of the surface are evident from XPS. The temperature-induced phase created at the surface is irreversible. An ordered, cubic surface alloy forms with its (110) direction aligned parallel to the surface normal of the quasicrystal. Nevertheless the quasicrystalline surface can be easily recovered by sputtering and annealing under adequate conditions.

A monograin *i*-AlPdMn quasicrystal has been grown using the Czochralsky method (CECM-CNRS, Vitry-sur-Seine, France). The bulk stoichiometry was determined to be $Al_{70.3}Pd_{21.4}Mn_{8.3}$. The sample was cut perpendicularly to a fivefold axis within 3° and polished with diamond paste. From the 2 mm thick half disk we selected a default-free circular area with a diameter of 8 mm. Surface preparation and photoemission experiments were performed in a VG ESCALAB Mark II ultra-high vacuum spectrometer with a base pressure in the 10^{-11} mbar range and equipped with a LEED apparatus. Clean *i*-AlPdMn surfaces were prepared by repeated cycles of Ar^+ (1 keV) sputtering (30–60 min) and short annealing up to ca 700°C (“standard preparation”). After this treatment LEED indicates a well-ordered surface showing well-defined and sharp spots for energies between 12 up to 120 eV (Fig. 1a). Temperature was measured with a pyrometer, which was calibrated previously by comparing with the values given by a chromel–alumel thermocouple in direct contact with the sample. Surface contaminations and concentrations were checked with XPS. For the evaluation of the concentrations we compared the intensities of Al 2s or 2p, Pd 3d and Mn 2p photoemission lines weighted with the corresponding cross sections (I_0/σ). Thus the average XPS concentration found at the surface was “$Al_{71.3}Pd_{24.3}Mn_{4.4}$” after the standard preparation. This XPS concentration compared to the bulk concentration might appear as out of the range of the quasicrystalline phase. However, it cannot be directly compared with the value obtained from the phase diagram without calibrating XPS more precisely and accounting for the structure describing the chemical composition as a function of depth. Nevertheless, XPD and LEED patterns for this XPS concentration are characteristic for an icosahedral bulk-terminated surface (see below). Furthermore the changes of the XPS concentrations (described below) are real and significant for changes in the surface region.

Typical data acquisition times for the full-hemispherical intensity maps were several hours. The

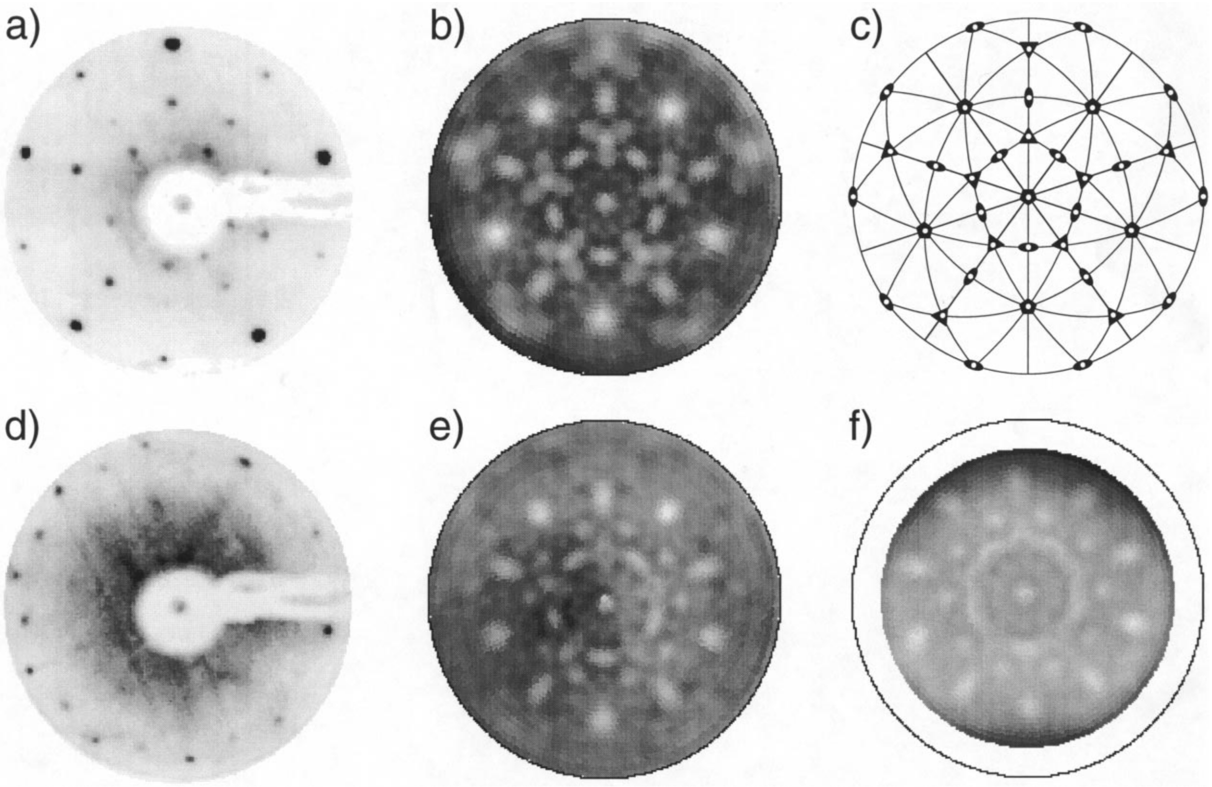

Fig. 1. The bulk-terminated surface of *i*-AlPdMn cut perpendicularly to a fivefold symmetry axis obtained after standard preparation (sputtering and flash annealing at 650°C): (a) LEED pattern (negative) taken at 23.5 eV; (b) experimental XPD pattern of the Pd $3d_{5/2}$ ($E_{\mathrm{kin}}=917$ eV); (c) stereographic projection of the icosahedral symmetry elements, that is, axes of two- (ellipses), three- (triangles) and fivefold (pentagons) symmetry. A tenfold-symmetric reconstruction of the surface appears after annealing the sample at 750°C: (d) LEED pattern (negative) taken at 23.5 eV; (e) experimental XPD pattern of the Pd $3d_{5/2}$ ($E_{\mathrm{kin}}=917$ eV) taken after 30 min of annealing at 750°C; (f) as (e) but after 70 min of annealing. Note that the outer ring of the XPD patterns represents the grazing-angle emission; normal emission is located at the centre. The pattern (f) was measured up to 78° off normal.

different emission lines were measured by integrating the intensity on the maximum of the line and subtracting the background intensity measured in front of the peak. Typically, intensity was accumulated for several seconds on each emission line before moving to the next angular setting. The complete map counts >4000 angular settings. Data are displayed with no symmetry averaging as grey-scaled intensity maps (white, maximum; and black, minimum of intensity) stereographically projected.

In Fig. 1 we present the LEED pictures and the experimental full-hemispherical photoelectron intensity maps of the Pd $3d_{5/2}$ signal ($E_{\mathrm{kin}}=$ 917 eV) measured over the fivefold symmetric surface of *i*-AlPdMn. By simple inspection of Fig. 1a and b, we immediately see that, after standard preparation, the surface of *i*-AlPdMn is fivefold symmetric. In Fig. 1b clear and well-defined forward-focusing maxima are observed as well as a considerable amount of fine structure which is due to interference. Comparing the pattern with the stereographic projection of the icosahedral symmetry elements (Fig. 1c) we can clearly identify axes of five-, three- and twofold symmetry. Furthermore one can observe (Fig. 1b) that the fivefold axes have the shape of a fivefold star, the threefold axes look like trefoils and the twofold axes are elongated maxima. From now on, the surface of *i*-AlPdMn will be considered as *bulk-terminated* if the following three criteria are fulfilled:

1. fivefold-symmetric LEED pattern (Fig. 1a);
2. fivefold-symmetric icosahedral XPD diffractogram (Fig. 1b); and
3. an average surface composition (XPS) of $Al_{71.3}Pd_{24.3}Mn_{4.4}$.

In Fig. 1d–f, the transformation of the surface is characterized with LEED and XPD during the phase transition induced by annealing the sample at high temperatures. After annealing the sample at 750°C for 30 min, a new LEED pattern (Fig. 1d) arises in some regions of the surface, besides the fivefold LEED pattern (Fig. 1a) still present at some other parts of the surface. The new LEED picture is tenfold symmetric (Fig. 1d). At this stage the symmetry of the XPD pattern (Fig. 1e) remains fivefold but changes appear in the shape of the trefoil along the threefold symmetric axes. The central triangular maximum of the trefoil is replaced by a minimum. The three leaves are not equivalent anymore. Two detached maxima replace the external leaves. A minimum appears in the centre of the innermost petal. We also note that the anisotropy close to the outer border of the pattern disappeared nearly completely (e.g. the external threefold symmetry axes). From LEED and XPD, we guess the appearance of a new phase at the surface, but this latter is not yet uniformly developed over the surface. With XPS, we observed also a clear change in the stoichiometry of the surface. The composition is given by $Al_{65.8}Pd_{32.4}Mn_{1.8}$. The diffractogram presented in Fig. 1f, has been taken after repreparing the *i*-AlPdMn surface and annealing it at the same temperature (750°C) but over 70 min (the external black areas are due to a different mounting of the sample). In this state, the symmetry of the pattern is nearly perfectly tenfold (the fivefold symmetry of the bulk is still remanent in the centre of the pattern since normal emission is more sensitive to the bulk). The nearly-equivalent ten outermost intensity maxima are visible instead of the alternation of two- and fivefold axes observable in Fig. 1b and e. Ten other maxima closer to the centre and a bright ring replaced the succession of two- and threefold axes (trefoils). Here the LEED pattern is purely tenfold (Fig. 1d). From LEED and XPD, we established that the temperature-induced phase is extended uniformly over the surface. With XPS, we observe a surface composition of $Al_{67.7}Pd_{31.8}Mn_{0.9}$. Note that the decrease of the Mn signal is confirmed while the ratio between Al and Pd remains almost constant. As a consequence the absolute surface composition is not anymore within the range of the quasicrystalline phase. The temperature-induced tenfold phase is most probably formed by five equivalently distributed domains of a cubic (110), Cs–Cl-type Al–Pd surface alloy rotated by 72° with respect to each other. Calculations simulating the scattering process during emission of the photoelectron fit the experiment quite well [10].

Fig. 2 gives more indications concerning the change of the stoichiometry at the surface due to segregation and/or partial evaporation during the annealing process. The concentrations of Al, Pd and Mn are plotted after annealing the previously sputtered sample at constant temperatures for

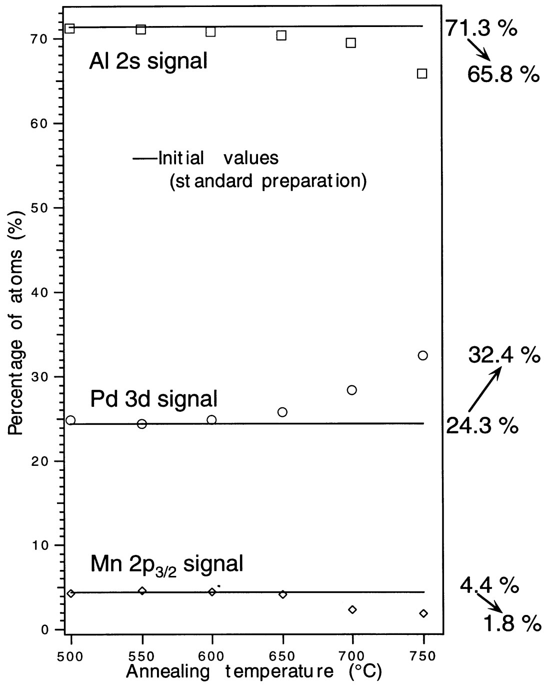

Fig. 2. The Al, Pd and Mn concentrations of *i*-AlPdMn are plotted after annealing the sample for 30 min at the given temperatures. The percentages have been extracted from XPS measurements performed at room temperature. The intensities of the photoemission lines mentioned in the figure have been weighted with the corresponding cross sections.

30 min. The experiment was repeated for six different temperatures between 500 and 750°C. After each annealing step, XPS spectra have been taken and XPD and LEED patterns (not shown) have been measured. We observe that the surface composition starts do deviate from $Al_{71.3}Pd_{24.3}Mn_{4.4}$, the standard composition value obtained after flash annealing at 650°C, after annealing the sample at the same temperature but for 30 min. Such a prolonged annealing at 750°C leads to a surface stoichiometry of $Al_{65.8}Pd_{32.4}Mn_{1.8}$. Note that XPD and LEED patterns taken after annealing at temperatures between 500 and 700°C showed a fivefold-symmetric pattern similar to Fig. 1a and b. A switch to the tenfold symmetric pattern arose only after annealing the sample at 750°C (see above Fig. 1d and f).

To summarize, a switch in symmetry from fivefold to tenfold is observed at the fivefold symmetric surface of *i*-AlPdMn after annealing the sample at 750°C for 30 min or more. With XPS we evidenced a change in surface stoichiometry after annealing the sample at 650°C already. Very probably annealing the surface at temperatures <750°C for >30 min would also lead to a surface reconstruction. We interpret the changes by the formation of five domains of a cubic Al–Pd(110) alloy.

Acknowledgements

The authors wish to thank Y. Calvayrac (CECM-CNRS, Vitry-sur-Seine, France) for providing the monograin quasicrystal, all the members of the XPD group from the University of Fribourg for many stimulating discussions, and the mechanical workshop staff for their skilful technical assistance. This project has been supported by the Fonds National Suisse de la Recherche Scientifique.

References

[1] C. Janot, Quasicrystals: A Primer, 2nd ed., Oxford University Press, Cambridge, 1994.

[2] F. Hippert, D. Gratias (Eds.), Lectures on Quasicrystals, Les Editions de Physique, Les Ulis, 1994.

[3] J.M. Dubois, Phys. Scr. T49 (1993) 17.

[4] Proceedings of the 6th International Conference on Quasicrystals, ICQ-6, S. Takeuchi, T. Fujiwara (Eds.), Yamada Conference XLVII, World Scientific, Singapore, 1998.

[5] Z. Shen, C.J. Jenks, J. Anderegg, D.W. Delaney, T.A. Lograsso, P.A. Thiel, A.I. Goldman, Phys. Rev. Lett. 78 (1997) 1050.

[6] Z. Shen, P.J. Pinhero, T.A. Lograsso, D.W. Delaney, C.J. Jenks, P.A. Thiel, Surf. Sci. 385 (1997) L923.

[7] F. Shi, Z. Shen, D.W. Delaney, A.I. Goldman, C.J. Jenks, M.J. Kramer, T. Lograsso, P.A. Thiel, M.A. Van Hove, Surf. Sci. 411 (1998) 86.

[8] M. Zurkirch, M. Erbudak, A.R. Kortan, in: Proceedings of the 6th International Conference on Quasicrystals, ICQ-6, S. Takeuchi, T. Fujiwara (Eds.), Yamada Conference XLVII, World Scientific, Singapore, 1998, p. 67.

[9] F. Schmithüsen, Diplomartbeit, Rapport de stage DEA, ESRF, Grenoble, 1998.

[10] D. Naumović, P. Aebi, L. Schlapbach, C. Beeli, T.A. Lograsso, D.W. Delaney, in: Proceedings of the 6th International Conference on Quasicrystals, ICQ-6, S. Takeuchi, T. Fujiwara (Eds.), Yamada Conference XLVII, World Scientific, Singapore, 1998, p. 749.

[11] T.M. Schaub, D.E. Bürgler, H.-J. Güntherodt, J.-B. Suck, Phys. Rev. Lett. 73 (1994) 1255.

[12] M. Erbudak, H.-U. Nissen, E. Wetli, M. Hochstrasser, S. Ritsch, Phys. Rev. Lett. 72 (1994) 3037.

[13] T.M. Schaub, D.E. Bürgler, H.-J. Güntherodt, J.-B. Suck, Z. Phys. B 96 (1994) 93.

[14] S.-L. Chang, W.B. Chin, C.-M. Zhang, C.J. Jenks, P.A. Thiel, Surf. Sci. 337 (1995) 135.

[15] D. Naumovic, P. Aebi, L. Schlapbach, C. Beeli, in: A.I. Goldman, D.J. Sordelet, P.A. Thiel, J.M. Dubois (Eds.), New Horizons in Quasicrystals, Research and Applications, World Scientific, Singapore, 1997.

[16] C.S. Fadley, in: R.Z. Bachran (Ed.), Synchrotron Radiation Research: Advances in Surface Science, Plenum, New York, 1989.

[17] W.F. Egelhoff Jr, Crit. Rev. Solid State Mater. Sci. 16 (1990) 213.

[18] S.A. Chambers, Surf. Sci. Rep. 16 (1992) 261.

[19] J. Osterwalder, P. Aebi, R. Fasel, D. Naumović, P. Schwaller, T. Kreutz, L. Schlapbach, Surf. Sci. 331–333 (1995) 1002.

[20] J. Osterwalder, T. Greber, A. Stuck, L. Schlapbach, Phys. Rev. B 44 (1991) 13764.

[21] D. Naumović, A. Stuck, T. Greber, J. Osterwalder, L. Schlapbach, Phys. Rev. B 47 (1993) 7462.

[22] C.J. Jenks, D.W. Delaney, T.E. Bloomer, S.-L. Chang, T.A. Lograsso, Z. Shen, C.-M. Zhang, P.A. Thiel, Appl. Surf. Sci. 103 (1996) 485.