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Weak bonding of Zn in an Al-based approximant based on surface measurements

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Abstract
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Keywords
quasicrystals; surface physics

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Weak bonding of Zn in an Al-based approximant based on surface measurements

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We have studied two surfaces of a new Al–Pd–Zn approximant using mass spectrometry, X-ray photoemission spectroscopy (XPS) and scanning tunneling microscopy (STM). Zn is bonded weakly in this approximant, perhaps as weakly as in elemental Zn. This is based upon three observations: (1) the low vapor pressure of Zn above the approximant (detectable in the gas phase at 600 K), (2) preferential sputtering of Zn (contrary to the usual preferential sputtering of Al in Al-rich quasicrystals), and (3) preferential surface segregation of Zn. We further show that preferential segregation – and perhaps incipient evaporation – causes the surface to roughen, preventing it from forming a terrace-step morphology. Finally, our data show that at low O₂ pressures, Al oxidizes. In air, Zn oxidizes as well. All results and conclusions are similar for the two-fold and pseudo-10-fold surfaces.

Keywords: quasicrystals; surface physics

1. Introduction

One of the interesting observations to emerge regarding the surfaces of quasicrystals and related periodic phases is that the surfaces are usually bulk-terminated, except for relaxations (changes in interplanar spacing perpendicular to the surface) [1–4]. However, it must be said that there is little understanding of why the surfaces of these complex alloys are stable against the perturbations that are common in alloy surfaces, namely, reconstruction (usually defined as major lateral deviations from bulk lattice positions) and segregation (deviation from the stoichiometric composition at the surface). An exception to the generality of bulk-termination may be decagonal Al–Ni–Co. There, preferential segregation of Al has been reported by one group [5], but other reports in the literature seem contradictory [6–9]. In the present work, we study a newly discovered Al₅₇Pd₃₀Zn₁₃ approximant to a decagonal phase [10]. We find that Zn segregates to the surface. This, together with

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evaporation of Zn at low temperature (T) and preferential sputtering, lead to the conclusion that Zn is weakly bound in this alloy, perhaps as weakly bound as in metallic Zn.

Our initial goal was to prepare a terrace-step morphology using a sputter-annealing regimen in ultrahigh vacuum (UHV). Such a surface could then be used to determine the atomic structure with STM and other tools of surface science. However, elemental Zn has a high vapor pressure. For instance, at 400 K, its vapor pressure is $2 \times 10^{-8}$ Torr [11]. This normally precludes Zn and its alloys from being used or studied in UHV, because Zn can evaporate and contaminate the chamber, leading to spurious detection of Zn in subsequent samples. Our hope, a priori, was that the chemical potential of Zn in the Al–Pd–Zn approximant would be significantly lower than in elemental Zn. As precedent, the surface of quasicrystalline Ag–In–Yb has been annealed and characterized successfully in UHV, despite the rather high vapor pressure of elemental Yb [12,13].

The Al–Pd–Zn phase is an orthorhombic $5/3$ approximant, with bulk lattice constants of $a = 2.36$ nm, $b = 3.24$ nm and $c = 1.67$ nm. Its bulk composition is 57 at% Al, 30 at% Pd and 13 at% Zn. It is structurally similar to a known Al–Os–Ir phase[14]. It melts congruently at 1045 K. The synthesis and analysis of this material will be reported elsewhere [10].

2. Experimental details

The main UHV chamber, used for STM and XPS, has been described elsewhere [15]. A second, smaller vacuum chamber was used to measure the effective pressure of Zn as a function of sample temperature. This chamber was equipped with a UTI 100C quadrupole mass spectrometer and the sample was heated within a Knudsen-type cell at a rate of 0.5 degrees per minute. The pressure recorded at the mass spectrometer was not an equilibrium pressure, since the system was dynamically pumped. In the test chamber, the Knudsen cell was a cylindrical Ta crucible with a thermocouple spot-welded on the bottom plate and a 1-mm orifice in the top cap. The Ta crucible was held within a boron nitride cylinder. A tungsten filament was wrapped around the boron nitride cylinder and heated resistively.

Two Al–Pd–Zn samples were used. The first was flux-grown and cut parallel to a two-fold growth facet. The second was Bridgeman-grown and cut to expose a pseudo-10-fold surface. The results were very similar, so sometimes we will show data for only one of the samples.

In the XPS experiments, the X-ray source was Mg K$\alpha$. The XPS source was perpendicular to the sample surface and the take-off angle (defined as the angle between the entrance axis of the analyzer and the sample surface) was 45°.

The STM data were often used to derive the surface root-mean-square (rms) roughness. In several cases, we checked whether the roughness depended upon tunneling parameters by varying the bias voltage between ±1 V, in 0.5 V increments. The rms roughness did not depend on tunneling conditions in this range.
3. Experimental results and interpretation

Figure 1 gives the effective pressure of Zn over an Al–Pd–Zn sample as a function of sample temperature. The gas-phase Zn level first rose above its baseline reading of \(5 \times 10^{-10}\) Torr at 600 K, thereby setting an upper limit on the temperature to be used in subsequent UHV work. Given the configuration of the test chamber, we can estimate that a measured Zn pressure of \(2 \times 10^{-10}\) Torr above baseline (the detection limit) corresponds to a pressure at the Knudsen cell of about \(10^{-4\pm1}\) Torr, which is close to the equilibrium vapor pressure of elemental Zn (\(10^{-3}\) Torr) at 600 K. Thus, the vapor pressure of Zn above the approximant is the same as for the elemental metal, within about one order of magnitude.

Figure 2 shows how the composition of an air-exposed surface evolves during sputtering with Ar\(^+\) in UHV. Bulk compositions are shown for reference by the horizontal dashed lines. Initially, there are high concentrations of carbon and oxygen, typical contaminants from air. With time, these peaks disappear, and the Al and Pd peaks intensify. The Zn concentration remains constant at about 3 at%, which is quite small relative to its bulk value of 13 at%.

After extensive sputtering, the surface compositions of the two samples approach asymptotic limits in the range of Al\(_{62-67}\)Pd\(_{29-32}\)Zn\(_{3-6}\). Thus, they are Al-rich by 5–10 at% and Zn-poor by 7–10 at%, relative to the bulk composition of Al\(_{57}\)Pd\(_{30}\)Zn\(_{13}\). This reveals preferential sputtering of Zn, contrary to the preferential sputtering of Al that is usually seen in Al-rich quasicrystals and which is attributed to optimal energy transfer between the sputtering gas and an Al atom, compared with other kinds of metal atoms in the alloys [16]. However, it is known that weak bonding also favors preferential sputtering [17]. Since Zn is a poorer mass-match than Al, its preferential sputtering most likely reflects weaker bonding in the solid.

Sputtered surfaces were annealed to determine whether a bulk-like, or at least stable, composition could be regained. This was done both after air exposure and after treatment in UHV. Figure 3 shows surface compositions after heating to various temperatures. Each data point in Figure 3 represents a surface that had been sputtered at 300 K, annealed at the given temperature for 2 h (except the highest-temperature point, where the surface was annealed for only 10 min),
cooled, and subjected to XPS. Higher temperatures were not used, to avoid Zn evaporation. These data show that Zn concentration begins to increase rather abruptly above 400 K, accompanied by decreasing Al and Pd concentrations. The fact that the Zn concentration eventually exceeds its bulk concentration by a significant amount – more than a factor of two – means that Zn segregates to the surface, replacing or covering both Al and Pd, at least in part.

Figure 2. XPS depth profile of O, C, Al, Pd and Zn after the pseudo-10-fold sample was introduced from air to UHV. The photoelectrons are emitted from Zn2p3/2, Pd3d, Al2p, C1s, and O1s core levels.

Figure 3. Compositional evolution during heating, from XPS. The photoelectrons are emitted from Zn2p3/2, Pd3d, and Al2p core levels. The surfaces are (a) pseudo-10-fold and (b) two-fold. At each temperature, the samples are heated for 2 h, except for the final temperature of the pseudo-10-fold surface, which was maintained only for 10 min. The error bars at 300 K represent the full range of surface concentrations after five similar sputtering preparations.
Note that XPS provides a depth-weighted average composition over the top few nm of material, i.e. over several tens of atomic layers. It is, therefore, possible that Zn covers the entire surface above 400 K, and that Al and Pd XPS signals mainly originate below the Zn layer.

The data show that Zn segregates to the surface. In general, three factors promote surface segregation of one metal over other constituents in an alloy: large atomic radius, low surface energy and low bond energy in the alloy. Zn is actually the smallest of the atoms in Al–Pd–Zn, so size is not responsible. Elemental Zn has the lowest surface energy, but it is only slightly lower than Al (0.99 J/m² for the close-packed surface of Zn versus 1.2 J/m² for Al and 1.9 J/m² for Pd) [18]. It is reasonable that weak bonding for Zn within Al–Pd–Zn also promotes the segregation of Zn in this system.

In both samples, the surface composition reached that of the bulk at about 460–470 K. This observation prompted a set of experiments, in which the samples were held at 460–470 K for extended periods of time in the hope that the bulk phase could stabilize at the surface. However, in these experiments, the Zn concentration continued to increase above its bulk value, while the Al and Pd concentrations fell below their bulk values, with time. This shows that the crossing point in Figure 3 is not stable.

Representative STM images are shown in Figure 4. The surface is very rough, with no evidence of a terrace-step type structure even after heating to the highest $T$, 545 K. Quantitative evaluation of the roughness is illuminating. Before presenting the roughness as a function of annealing temperature, it should be noted that roughness always depends upon image size [19]. Figure 5 shows the rms roughness, $w$, as a function of image area for individual experiments. As expected, $w$ always increases toward an asymptotic value at large image size [19]. Subsequent analysis will be based on images with sizes on the asymptote.

Normally, one expects $w(T)$ to be a decreasing function for a surface that is initially prepared by sputtering. In other words, one expects annealing to heal the damage induced by sputtering and smoothen the surface. Figure 6 shows that this expectation is met for three other metallic samples that have been studied in our laboratory: (1) the (110) surface of a crystalline binary alloy, NiAl [15],

![STM Images](image_url)
(2) a Zr–Ni–Cu–Al metallic glass [20], and (3) the two-fold surface of a quasicrystal, decagonal Al–Cu–Co [21]. However, the roughness of the two Al–Pd–Zn surfaces behave differently. For them, $w(T)$ starts high and increases strongly. Their limiting values of $w$ in Figure 6, 2–4 nm, are very large relative to the roughness of the other surfaces. The main difference is that, in the other samples, there is no evidence for surface segregation. This suggests that, in the Zn-containing samples, segregation of Zn (possibly coupled with incipient sublimation) substantially enhances surface roughness. In other words, when surface segregation of Zn increases in the Al–Pd–Zn samples, surface roughness also increases.

Figure 5. Root-mean-square roughness, $w$, as a function of image size, for the Al–Pd–Zn samples under different conditions.

Figure 6. Root-mean-square roughness, $w$, as a function of annealing temperature, for the Al–Pd–Zn samples and also for three other metallic samples. At each temperature, the two-fold surface was held for 2 h and the pseudo-10-fold surface was held for 15 min.
We have also studied surface oxidation of Al–Pd–Zn, where oxidation occurred both via air exposure, and via oxygen exposure within the UHV chamber. In the latter case, oxygen pressures of $10^{-8}$–$10^{-7}$ Torr were used.

Following a well-established approach [22], we use XPS peak intensities to determine qualitative changes in surface metal concentration, and peak positions to determine which element is engaged in chemical bonding. Peak positions are illustrated by the XPS data in Figure 7. We also determined qualitative changes in surface oxygen concentration, but here it should be noted that the O1s peak at 532 eV overlaps the Pd3p3/2 at 531 eV binding energy. To disentangle the oxygen signal intensity, we use the ratio of the (O1s plus Pd3p3/2) to the Pd3d peak intensities, and subtract the ratio for the clean surface from the ratio measured after oxygen exposure.

Oxygen exposure within the UHV chamber at 300 K produces three effects: (1) oxygen adsorbs, reaching saturation at about 10 Langmuir exposure; (2) Al oxidizes, while the other two metals do not. This is illustrated by the change in peak position for Al, but not for Zn and Pd, in comparing Figures 7b and c; (3) the oxide of aluminum covers the other two metals. This is consistent with studies of other Al-rich quasicrystals such as Al–Cr–Fe, Al–Cu–Fe, Al–Pd–Mn, and Al–Cu–Fe–Cr, which all show that Al is the only metal that oxidizes in vacuum and forms a passivating layer of pure or nearly-pure alumina on top of the other metals, accompanied by surface segregation of Al [22,23].

After oxidation in air at room temperature, there is evidence that Zn oxidizes in addition to Al. The Zn2p3/2 peak after air exposure is at 1023 eV. Sputtering causes
the peak to shift to 1021.5 eV, as shown in Figure 7. Reference values for ZnO are in the range 1021.8–1022.5 eV, and for Zn metal they are 1021.5–1021.8 eV [24]. Thus, the air-exposed surface contains ZnO, which is removed by sputtering, thereby exposing metallic Zn.

The data indicate that the susceptibility to oxidation is in the order Al > Zn > Pd. This hypothesis is consistent with the sequence of enthalpies of formation of oxides of Al, Zn and Pd. At room temperature, they are $-1632$ kJ/mol for Al$_2$O$_3$, $-348$ kJ/mol for ZnO, and $-85$ kJ/mol for PdO [25]. The trend remains unchanged if these enthalpies are normalized to the number of metal–oxygen bonds in the oxide.

4. Discussion and conclusions

The main goal of this study was to determine whether the Al–Pd–Zn approximant could be prepared in a terrace-step morphology. Our conclusion is that it cannot, for two reasons. First, Zn strongly segregates to the surface. In our experiments, the surface exceeds the bulk concentration of Zn at 400 K. Second, Zn evaporates at relatively low temperature. It is detectable in the gas phase at 600 K. Hence, it appears that Zn segregation and evaporation preempt rearrangement of the surface and near-surface region into the necessary terrace-step morphology. The effect is even worse than just preventing the surface from smoothening into a terrace-step arrangement – it appears that Zn segregation, possibly accompanied by incipient evaporation, actually exacerbates surface roughness.

However, the data allow us to reach an unexpected and possibly useful conclusion. That is, Zn is weakly bound in this material, perhaps as weakly as in elemental Zn. This conclusion is based upon preferential segregation, preferential sputtering and the low vapor pressure of Zn. This may be useful for understanding the factors that stabilize this bulk phase. It also may be useful in surface studies of other Al-rich alloys, in the following sense. If indeed preferential segregation and preferential sputtering (in this case of Zn) are linked by a common cause (weak bonding), then one should be especially watchful for one effect if the other is present. Usually, preferential sputtering is easy to determine, but preferential segregation can be more difficult, especially in multi-component systems where the bulk composition varies layer-by-layer. In Al-based alloys or intermetallics, we suggest this: if Al is not preferentially sputtered, then surface segregation of a non-Al constituent is more likely.

Finally, we find that oxidation of this alloy is similar to that of other Al-rich quasicrystals and related materials, in the sense that Al is preferentially oxidized. This might be somewhat surprising, given the premise that Zn is weakly bound. However, even if Zn is as weakly bound as in elemental Zn, thermodynamics of the constituent elements still favor oxidation of Al quite strongly.

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Note

1. In this paper, the terms “alloy” and “intermetallic” are used to denote multicomponent metallic systems. For some scientists, the two terms denote extrema in the continuum of multicomponent metals, where the chemical identity of an atom occupying any given site is either random (alloy) or fixed (intermetallic). In this sense, quasicrystals and approximants are more similar to intermetallics than to alloys.

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