12668 J. Am. Chem. Soc. **1998,** *120,* 12668−12669

Surface Reactivity of a Sputter-Annealed Al−Pd−Mn Quasicrystal

Cynthia J. Jenks,[†] Thomas A. Lograsso,[‡] and
Patricia A. Thiel*,[†]

Department of Chemistry, Ames Laboratory
and Department of Materials Science
Iowa State University, Ames, Iowa 50011

Received June 2, 1998
Revised Manuscript Received October 1, 1998

Quasicrystals are materials with unusual atomic structure, coupled with unusual physical properties.[1] Surface properties are particularly important, because most proposed applications quasicrystals involve low-dimensional solids—coatings, thin films, precipitates, or composites—where the ratio of surface area to volume is high.[2] Perhaps the most fundamental surface property is chemical reactivity. Studies under various environmental conditions suggest that quasicrystals are relatively unreactive and/or corrosion-resistant.[3,4]

It has been proposed that the surface chemistry of quasicrystals should be dominated by the suppression of the density of states at the Fermi level[5]—the "pseudogap"—which is characteristic of bulk quasicrystals. This hypothesis is supported by surface energy measurements conducted under atmospheric conditions, which show that the passivated surface of a quasicrystal behaves more like a covalently bonded material (e.g., Teflon) than like a metal; the polar component of the surface energy is anomalously low.[6] A low polar component suggests low surface polarizability, i.e., low free-electron density.

The present study addresses the reactivity of one particular Al-based quasicrystal, icosahedral (i-) Al−Pd−Mn, toward a series of simple molecules: H_2, CO, CH_3OH, and two iodoalkanes. Note that these molecules, and their adsorption products, form bonds to metal surfaces that are primarily covalent in nature. Hence, one might expect these adsorbates would be less sensitive to the pseudogap than to rehybridization of valence orbitals within the intermetallic. Our approach is to compare the chemistry of a clean quasicrystalline surface with the known chemistry of the clean, pure metals that comprise the intermetallic, to determine whether the quasicrystal is unusual.

The i-Al−Pd−Mn sample used in these experiments was grown at the Ames Laboratory.[7] A single grain was harvested from a boule and oriented to a 5-fold axis within 0.25° with use of Laue X-ray diffraction. Inductively coupled plasma-atomic emission spectroscopy of an adjacent sample showed a composition of $Al_{72.8}Pd_{18.6}Mn_{8.6}$. Prior to experiments, scanning Auger and electron microscopy showed the sample to be single phase.

The experiments were performed in a well-equipped ultrahigh vacuum (UHV) chamber, with a base pressure below 1×10^{-10} Torr. There, the sample was cleaned with cycles of Ar ion bombardment and annealing, to a maximum of 800 K.[8] Our method reproducibly yields low-energy electron diffraction patterns which are 5-fold symmetric after annealing at 800 K.[8] Note that our results are specific to a surface prepared in the fashion described here. There is speculation that surfaces prepared in different ways, e.g. via fracture, may exhibit different reactivities.[9]

When this surface is exposed to H_2 in UHV at 120 K, temperature-programmed reaction spectroscopy shows that no H_2 evolves. The same is true for Al(100), Al(111), Al(110), and Mn.[10,11] (All literature on surface chemistry of pure Mn describes Mn overlayers on metal substrates.) In contrast, Pd is known to dissociate H_2 readily, followed by recombination and desorption at 300−360 K.[12] Hence, the surface interaction of H_2 with i-Al−Pd−Mn is the same as with Al and Mn, but distinctly different from that with Pd.

Exposure of i-Al−Pd−Mn to CO results in a CO (*m*/*e* 28) peak at 150 K with a shoulder at about 180 K. This is qualitatively similar to Al(100), where CO desorbs at 125 K following adsorption at 70 K.[13] (Because the desorption temperature from i-Al−Pd−Mn is relatively close to the adsorption temperature (125 K), a more quantitative comparison with the literature value is not possible.) On i-Al−Pd−Mn, we find no gas-phase products other than CO; furthermore, neither carbon nor oxygen is found by Auger electron spectroscopy (AES) after repeated CO exposures and heating to 800 K. There is also no dissociation on Al(100) and Al(111).[13−15] Mn is known to partially dissociate CO.[11,16] On Pd, CO does not dissociate but desorbs at 515 K.[17] Hence, the surface chemistry of CO on i-Al−Pd−Mn resembles the chemistry on Al but not on Pd or Mn.

Exposure of i-Al−Pd−Mn to CH_3OH results in desorption of molecular CH_3OH at 155 K. Several decomposition products are also observed. H_2 desorbs with CH_3OH at 155 K.[18] Between 400 and 650 K, CH_4 evolves in two additional peaks, based on the ratio of *m*/*e* 16 to 15. There is no evidence of CO desorption. AES shows that oxygen remains on the surface after methanol desorption. Residual carbon is not obvious after a single adsorption−desorption cycle, presumably due to overlap between the C and Pd AES peaks. However, carbon is clearly present after repeated cycles. These data are comparable to those reported for Al(111)[19] and polycrystalline Al,[20] where a methoxy species forms at low temperature and decomposes around 500 K to form methane. For Al(111), methoxy formation is associated with concurrent H_2 and methanol desorption at 145 K; methane evolution is observed at about 445 K. Our data are different than

---

[†] Department of Chemistry and the Ames Laboratory.

[‡] Department of Materials Science and the Ames Laboratory.

(1) Janot, C. *Quasicrystals: A Primer*, 2nd ed.; Clarendon Press: Oxford, 1994.

(2) Dubois, J. M. In *New Horizons in Quasicrystals: Research and Applications*; Goldman, A. I., Sordelet, D. J., Thiel, P. A., Dubois, J. M., Eds.; World Scientific: Singapore, 1997; pp 208−215.

(3) Massiani, Y.; Yaazza, S. A.; Crousier, J. P.; Dubois, J. M. *J. Non-Cryst. Solids* **1993**, *159*, 92−100.

(4) Massiani, Y.; Ait Yaazza, S.; Dubois, J.-M. In *Proceedings of the 5th International Conference on Quasicrystals*; Janot, C., Mosseri, R., Eds.; World Scientific: Singapore, 1995; pp 790−793.

(5) Rivier, N. *J. Non-Cryst. Solids* **1993**, *153/154*, 458−462.

(6) Dubois, J. M.; Plaindoux, P.; Belin-Ferre, E.; Tamura, N.; Sordelet, D. J. In *Proceedings of the 6th International Conference on Quasicrystals*; Takeuchi, S., Fujiwara, T., Eds.; World Scientific: Singapore, 1998; pp 733−740.

(7) Delaney, D. W.; Bloomer, T. E.; Lograsso, T. A. In *New Horizons in Quasicrystals: Research and Applications*; Goldman, A. I., Sordelet, D. J., Thiel, P. A., Dubois, J. M., Eds.; World Scientific: Singapore, 1997; pp 45−52.

(8) Jenks, C. J.; Pinhero, P. J.; Shen, Z.; Lograsso, T. A.; Delaney, D. W.; Bloomer, T. E.; Chang, S.-L.; Zhang, C.-M.; Anderegg, J. W.; Islam, A. H. M. Z.; Goldman, A. I.; Thiel, P. A. In *Proceedings of the 6th International Conference on Quasicrystals*; Takeuchi, S., Fujiwara, T., Eds.; World Scientific: Singapore, 1998; pp 741−748.

(9) Ebert, P.; Feuerbacher, M.; Tamura, N.; Wollgarten, M.; Urban, K. *Phys. Rev. Lett.* **1996**, *77*, 3827−3830.

(10) Winkler, A.; Pozgainer, G.; Rendulic, K. D. *Surf. Sci.* **1991**, *251/252*, 886−890.

(11) Sieben, B.; Bonzel, H. P. *Surf. Sci.* **1993**, *282*, 246−254.

(12) Behm, R. J.; Christmann, K.; Ertl, G. *Surf. Sci.* **1980**, *99*, 320−340.

(13) Paul, J.; Hoffmann, F. M. *Chem. Phys. Lett.* **1986**, *130*, 160−163.

(14) Jacobi, K.; Astaldi, C.; Geng, P.; Bertolo, M. *Surf. Sci.* **1989**, *223*, 569−577.

(15) Ryberg, R. *Phys. Rev. B* **1988**, *37*, 2488−2490.

(16) Hrbek, J. *J. Phys. Chem.* **1990**, *94*, 1564−1570.

(17) Stuve, E. M.; Madix, R. J.; Brundle, C. R. *Surf. Sci.* **1984**, *146*, 155−178.

(18) Jenks, C. J.; Thiel, P. A. *J. Mol. Catal. A* **1998**, *131*, 301−306.

(19) Chen, J. G.; Basu, P.; Ng, L.; Yates, J. T., Jr. *Surf. Sci.* **1988**, *194*, 397−418.

(20) Rogers, J. W., Jr.; Hance, R. L.; White, J. M. *Surf. Sci.* **1980**, *100*, 388−406.

10.1021/ja981916x CCC: $15.00

Table 1. Comparison of the Reactivity of i-Al−Pd−Mn to Its Pure Constituents[a]

molecule	pure Mn refs 11, 16	pure Pd refs 12, 17, 21−23, 26	pure Al refs 10, 13−15, 19, 20, 25, 27	i-Al−Pd−Mn ref 18
H_2	does not dissociate	evolves at 300−360 K	does not dissociate	does not dissociate
CO	partially dissociates, evolves at 900 K	evolves at 515 K	desorbs <150 K	desorbs <150 K
methanol	n/a	dissociates, H_2 evolution at 350 K, CO evolution at 450 K	dissociates, H_2 evolution at 145 K with CH_3OH, CH_4 at 445 K	dissociates, H_2 evolution at 155 K with CH_3OH, CH_4 at 435 and 600 K
iodoethane	n/a	ethylene evolves at 270−325 K	ethylene evolves at 480−580 K	ethylene evolves at 600 K
1-iodopropane	n/a	n/a	propylene and H_2 evolve at 520−535 K	propylene and H_2 evolve at 585 K

[a] Temperatures are not corrected for different heating rates.

those reported for Pd(111) and Pd(110), where adsorption of CH_3OH yields H_2 at 300−350 K, and CO at about 475 K.[21−23] We were unable to find literature studies of CH_3OH on Mn. In short, the surface chemistry of methanol on i-Al−Pd−Mn resembles that on Al, but not on Pd; comparison to Mn is not possible.

Two linear iodoalkanes were also studied: iodoethane and 1-iodopropane. Because of the weak C−I bond strength, these molecules typically dissociate at low temperatures on transition metals, and on Al, to yield adsorbed iodine and the corresponding alkyl species. A variety of reaction pathways are then available to the alkyl species including β-H elimination, reductive coupling, and carbon−carbon bond cleavage.[24] Thus, the formation of various gas-phase products at higher temperatures may be useful as a signature of bonding.

On the quasicrystal, molecular iodoethane desorbs at 275 K while 1-iodopropane desorbs at 290 K. On both Al and Pd, iodoalkanes desorb molecularly below 200 K.[25,26] On the quasicrystal, there is abundant evidence that the C−I bond can cleave for both iodoalkanes, as expected. Carbon and iodine remain on the surface after heating to 800 K. The presence of carbon at such high temperature indicates that there has been some C−C bond breaking in the alkyl fragment. Furthermore, the alkyl fragment can undergo β-H elimination, based upon observation of the corresponding alkenes at 585−600 K. H_2 was not detected concurrent with ethylene desorption, but was detected with propylene desorption.

β-H elimination is also a major mechanistic pathway for pure Al and pure Pd.[25−27] However, there are also differences between the surface chemistry of the quasicrystal and the pure metals. Perhaps the most significant is that C−C bond breaking is not reported for either Al or Pd. This may be related to the peak desorption temperatures of the major products, the alkenes, which reflect the temperatures at which the adsorbed alkyl fragments react. For Al(100), ethylene desorbs from iodoethane at 480 K at saturation, and propylene desorbs from 1-iodopropane at 520 K.[25] On Al films, propylene evolves from 1-iodopropane at 535 K.[27] These temperatures are all at least 100 K lower than observed for i-Al−Pd−Mn, when a correction for the heating rate is applied (our heating rates being lower by a factor of 7). On Pd, the difference is even larger. There only iodoethane has been studied, and ethylene evolves at 270−325 K.[26] Literature on Mn is unavailable. In short, the peak temperatures of alkene desorption from the quasicrystal are higher than from Al, and higher still than from Pd, indicating that the alkyl fragment is more stable than on either pure metal. Its enhanced stability may allow C−C cleavage to compete effectively with β-H elimination, assuming that the activation barrier to the former is the highest.

Other differences between our data and the literature for pure Al concern the product distribution (some ethane forms from iodoethane on pure Al(100),[25] whereas no alkane forms on the quasicrystal) and the stability of residual atomic iodine (iodine remains on i-Al−Pd−Mn after heating to 800 K, whereas it disappears from pure Al upon heating to 700 K).

Our results are summarized in Table 1. For the molecules studied here, the reactivity is clearly dominated by the presence of Al as opposed to Pd which tends to be more aggressive than Al at breaking bonds. The resemblance to Al is reasonable. For a quasicrystal, many types of surface terminations, each with a different composition, are possible. The termination type favored on the sputter-annealed surfaces has 85 atomic % Al, i.e., nature selects an Al-rich termination.[28] This also means that any Pd or Mn sites exposed are probably not able to form the extended ensembles that would be necessary to exhibit chemistry resembling that of the pure metal.

The results of Table 1 are also reminiscent of our previous work with oxygen adsorption, which showed that this quasicrystal oxidizes much like Al, forming a passivating layer of pure, or nearly-pure, aluminum oxide.[29,30]

The exceptions to the analogy with Al all come from the iodoalkanes. The atomic iodine and the alkyl fragments are stable to higher temperatures than on pure Al. The latter may explain the presence of C−C bond breaking in addition to β-H elimination. In any case, this exception would indicate that surfaces of quasicrystals are *more*, not less, reactive than their pure metal constituents, in the sense that the quasicrystals tend to form *stronger* bonds to other species.

This work is a fundamental study of a model system. Our main conclusion is that an oxide-free quasicrystal surface is not unusually “inert”; its surface chemistry is very similar to that of pure Al. Of course, unique features may still be discovered when other aspects of surface chemistry are examined (e.g. kinetics or structure), when surfaces are prepared differently (e.g. via fracture), or for different quasicrystalline materials. Adsorbates which probe differently the surface density of states might provide additional insight into these materials. Finally, the surface chemistry of quasicrystals in normal environments undoubtedly will be affected by the ubiquitous surface oxide.

Acknowledgment. This work was supported by the Ames Laboratory, which is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82.

JA981916X

---

(21) Chen, J.-J.; Jiang, Z.-C.; Zhou, Y.; Chakraborty, B. R.; Winograd, N. *Surf. Sci.* **1995**, *328*, 248−262.

(22) Rebholz, M.; Kruse, N. *J. Chem. Phys.* **1991**, *95*, 7745−7759.

(23) Hartmann, N.; Esch, F.; Imbihl, R. *Surf. Sci.* **1993**, *297*, 175−185.

(24) Bent, B. E. *Chem. Rev.* **1996**, *96*, 1361−1390.

(25) Bent, B. E.; Nuzzo, R. G.; Zegarski, B. R.; Dubois, L. H. *J. Am. Chem. Soc.* **1991**, *113*, 1137−1142.

(26) Kovács, I.; Solymosi, F. *J. Phys. Chem.* **1993**, *97*, 11056−11063.

(27) Bent, B. E.; Kao, C.-T.; Zegarski, B. R.; Dubois, L. H.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 9112−9119.

(28) Gierer, M.; Van Hove, M. A.; Goldman, A. I.; Shen, Z.; Chang, S.-L.; Pinhero, P. J.; Jenks, C. J.; Anderegg, J. W.; Zhang, C.-M.; Thiel, P. A. *Phys. Rev. B* **1998**, *57*, 7628−7641.

(29) Chang, S.-L.; Anderegg, J. W.; Thiel, P. A. *J. Non-Cryst. Solids* **1996**, *195*, 95−101.

(30) Chang, S.-L.; Chin, W. B.; Zhang, C.-M.; Jenks, C. J.; Thiel, P. A. *Surf. Sci.* **1995**, *337*, 135−146.