Photoelectron spectra of an Al$_{70}$Pd$_{21}$Mn$_9$ quasicrystal and the cubic alloy Al$_{60}$Pd$_{25}$Mn$_{15}$


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Photoelectron spectra of a fivefold quasicrystalline alloy Al$_{70}$Pd$_{21}$Mn$_9$ and a related cubic alloy Al$_{60}$Pd$_{25}$Mn$_{15}$ reveal two noteworthy features. The first is that the Pd 3$d$ lines fall at binding energies which are 2.2 eV higher than in pure Pd. A similar shift is observed for Pd in other alloys. The second noteworthy feature is that the Mn 2$p_{3/2}$ line is very sharp in the quasicrystal. Fitting the experimental peaks with a Doniach-Sunjic line shape suggests that the position and density of Mn states near $E_F$ is very sensitive to the structural and/or chemical environment of Mn in the alloys, and that this accounts for the shape of the 2$p_{3/2}$ Mn line. The sharpness of the Mn line may be a fingerprint of the quasicrystalline phase within the AlPdMn family. [S0163-1829(96)06232-7]

I. INTRODUCTION

Quasicrystalline films$^{1-7}$ can have properties which render them useful. These properties include attractive tribological characteristics, and apparent oxidation resistance.$^{8-14}$ The fact that such properties are controlled mainly by surface and interface phenomena provides an impetus to examine these phenomena on an atomic scale.

A primary, common method of surface analysis is x-ray photoelectron spectroscopy (XPS). The main purpose of this paper is to analyze the peak positions and shapes of the spectra obtained with XPS, for a clean, fivefold surface of AlPdMn. Such an analysis can shed light upon the electronic properties of the material, particularly when compared with the spectra of related crystalline materials. The material which is the primary focus of our study is a ternary quasicrystal alloy, Al$_{70}$Pd$_{21}$Mn$_9$. The materials we choose for comparison are a cubic AlPdMn alloy with a composition similar to the quasicrystal, and samples of the pure metal constituents Al, Pd, and Mn.

A few basic facts regarding the electronic structure of the quasicrystalline (icosahedral) alloy are known already. The quasicrystal is metallic, but the density of states is low at the Fermi energy $E_F$.$^{15,16}$ A "pseudogap" at the Fermi edge is mentioned frequently.$^{17-22}$ Consequently, the alloy exhibits high electrical resistivity.$^{16,23,24}$ The crystalline, cubic alloy Al$_{60}$Pd$_{25}$Mn$_{15}$, is also a poor conductor.$^{25}$ This stands in contrast to the constituent metals. Aluminum is a nearly free-electron metal with a moderate density of states at the Fermi level, while Pd and Mn are transition metals with larger densities of states at the Fermi level.

Further detail on the electronic structure of the AlPdMn quasicrystal is available from various photoelectron and x-ray-absorption techniques which probe the valence bands,$^{21,22,26}$ and from electronic structure calculations.$^{27}$ These show that the Mn 3$d$ states are located near, and on both sides of, $E_F$, hybridized with Al valence states. The Pd 4$d$ states lie several eV below $E_F$. A corresponding level of information is unavailable for the cubic alloy.

II. EXPERIMENTAL DETAILS

The quasicrystal sample used in our studies is a single grain in the shape of a flat wafer, approximately $3\times6\times1$ mm$^3$ in size, cut with a fivefold axis normal to the surface. It is mechanically polished to a mirror finish with 1 µ diamond paste. The response of the fivefold Al$_{70}$Pd$_{21}$Mn$_9$ surface to treatment in vacuum, and to oxidizing environments, is known.$^{28,29}$ The sample is cleaned by cycles of ion bombardment and vacuum anneals at temperatures of 870 K. This treatment yields a high-quality fivefold pattern in low-energy electron diffraction, and a surface composition close to that of the bulk.$^{30}$ A Pd-rich secondary phase is present at a level of 0.7% by volume, based upon examination with scanning electron and scanning Auger microscopies.$^{29}$

The sample of the cubic alloy has nominal bulk composition Al$_{60}$Pd$_{25}$Mn$_{15}$, and has a surface composition—measured with XPS after ion bombarding, annealing to 870 K and recooling to room temperature—of Al$_{56.2}$Pd$_{36.2}$Mn$_{7.6}$.$^{30}$ The sample is a single crystal, with a structure of the B2 space group (CsCl structure), determined experimentally by x-ray diffraction, and with a lattice constant 3.02 Å. The sample is roughly $15\times6\times1$ mm$^3$ in size. Its surface happens to be oriented 9.5° from the (111), 29° from the (110), and 48° from the (100). Its Van der Pauw resistivity at room temperature is 0.132±0.001 mΩ cm.$^{25}$ It is ferromagnetic with a Curie temperature of −150°C.$^{31}$ Well below the temperature at which our measurements are made. Both the quasicrystal and the cubic alloy are grown at the Materials Preparation Center of the Ames Laboratory, by Dr. T. Lograsso and D. Delaney. No secondary phases can be detected with scanning electron and scanning Auger microscopies.$^{29}$

In addition to the AlPdMn samples, three pure samples of metallic Al, Pd, and Mn are used. Their preparations are described in another paper.$^{29}$ For each of these three metals, we compare photoelectron spectra of the metals present in the alloy quasicrystal, with the spectra they exhibit as pure (elemental) samples. By making these measurements in house, we avoid problems which could arise by citing data for the pure metals available in the literature, since literature...
values would be generated in a variety of laboratories using a variety of instrumentation and cleaning procedures. The photoelectron data are acquired using a Perkin-Elmer Multitechnique Chamber, Model 5500, and with PHI-ACCESS software. The base pressure of the chamber is $3 \times 10^{-10}$ Torr or better. The x-ray source provides monochromatized Al $K\alpha$ radiation at a power of 250 W. The takeoff angle used in these experiments is 45°. Binding energies are calibrated against two different samples, Au using the 4$f_{7/2}$ photoelectrons at 84.0 eV and Cu using the 2$p_{3/2}$ photoelectrons at 932.7 eV. The measured resolution is 0.65 eV, for a 29.5-eV pass energy, and for the 3$d_{5/2}$ electrons of Ag. All photoemission spectra are recorded at room temperature.

### III. PHOTOELECTRON SPECTRA AND DISCUSSION

The photoelectron spectra are compiled in Fig. 1, while the widths and positions of the core-level peaks are specified in Table I. The core-level spectra of the two alloys depend upon the conditions of their preparation. This is shown for the quasicrystal by comparison of the top two rows of Fig. 1. The top row [panels (a)–(c)] shows spectra obtained after ion bombarding the quasicrystal at room temperature, and the second row [panels (d)–(f)] shows spectra after treatment (vacuum annealing, or ion bombardment) at 870 K. Figure 1 and Table I show that the Al and Pd peaks are nearly identical in shape and location after these two treatments, but that the Mn peaks are much sharper after high-temperature treatment. This may be related to the fact that ion bombardment at room temperature perturbs the surface composition, presumably via preferential sputtering, leaving the surface highly enriched in Pd.28,30 Such a surface is also structurally perturbed, since it does not yield a fivefold pattern in low-energy electron diffraction (LEED).28 (Structural perturbation by ion bombardment, leading to damping or extinction of the characteristic LEED pattern, is well known for single crystals.) Either of these perturbations—chemical or structural—could be responsible for the difference in line shapes between Figs. 1(c) and 1(f). However, it is interesting to note that our data show that line shapes and linewidths in pure Mn do not depend at all upon whether the sample is sputtered at room temperature or annealed. The spectrum shown in Fig. 1(l) is of pure, clean, annealed Mn; the spectrum of the sputtered, unannealed surface is not shown, but it exhibits precisely the same shape and width. This may suggest that chemical effects are more important than structural ones in causing variations in the Mn peak shape. The cubic alloy behaves in a fashion which is qualitatively similar to the quasicrystal, undergoing strong Pd enrichment during ion bombardment at room temperature, and exhibiting a much

![XPS spectra for Al, Pd, and Mn core levels.](image)

**Figure 1.** XPS spectra for Al, Pd, and Mn core levels. The top row of panels shows results from the quasicrystal surface after ion bombardment at room temperature, without annealing. The second panel shows results after ion bombardment, or after annealing in vacuum, at 870 K. The third panel shows data for the cubic alloy, annealed at 870 K. The bottom row shows results for the pure metals, annealed at 810–870 K. The vertical lines mark the peak positions of the pure metals, to facilitate comparisons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al 2$p$</th>
<th>Pd 3$d$</th>
<th>Mn 2$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_0$</td>
<td>FWHM</td>
<td>$E_0$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quasicrystal sputtered at 300 K [Figs. 1(a)–1(c)]</td>
<td>73.1</td>
<td>1.05</td>
<td>342.2</td>
</tr>
<tr>
<td>Quasicrystal sputtered at 870 K [Figs. 1(d)–1(f)]</td>
<td>73.0</td>
<td>1.04</td>
<td>342.6</td>
</tr>
<tr>
<td>Cubic alloy annealed at 870 K [Figs. 1(g)–1(i)]</td>
<td>73.1</td>
<td>1.07</td>
<td>342.4</td>
</tr>
<tr>
<td>Pure metal annealed $T&gt;800$ K [Figs. 1(j)–1(l)]</td>
<td>72.9</td>
<td>0.96</td>
<td>340.4</td>
</tr>
</tbody>
</table>

**Table I.** Positions (binding energies, $E_0$) and full widths at half maximum (FWHM) of the XPS peaks. Both quantities are in units of eV. Values are extracted from data such as those shown in Fig. 1.
broader Mn peak after preparation in this manner than that obtained after annealing.

The second and third rows of Fig. 1 and Table I show the data for the clean, annealed quasicrystal surface and for the clean, annealed crystalline surface. It can be seen that the Al and Pd features are virtually identical in shape and position, whereas the Mn peak, especially the 3/2 component at 638.4–638.8 eV, is significantly broader in the crystalline phase.

Turning now to a comparison between the two alloys and their pure metal constituents, the fourth row of Fig. 1 shows XPS spectra for the pure elemental components after annealing. Comparing the second and third rows (the annealed alloys) with the fourth row (the annealed, pure metals) shows that the Al peaks are almost unchanged in both shape and position, upon going from the alloys to the pure metal. The other two metals, Pd and Mn, show significant differences, however, when analogous comparisons are made. Most striking are the difference in peak position for Pd, and the difference in peak shapes and widths—especially in the 3/2 peak—for Mn. We will discuss the peak position for Pd first.

For pure Pd, our measured values of the peak position, or binding energy $E_0$, are 340.4 and 335.1 eV, for the 3/2 and 5/2 components, respectively. The latter number agrees closely with literature values, which are 335.2 eV for the bulk component measured on a 110 face of Pd (Ref. 32) and 335 eV for the bulk component measured on a 100 face. 43 The shifts for the Pd core levels in the alloys, relative to the pure metals—2.2 eV higher in the quasicrystal and 2.0 eV higher in the cubic alloy—are large, but Pd core-level shifts tend to be large upon alloying. 34,35 The observed shifts are very close to the 2.15 eV found for Pd in dilute solution in Al which might be expected to resemble these alloys.

It is known that $E_0$ can differ between a metal in its pure form, and a metal contained in an alloy or compound, due to differences in local charge environment or oxidation state (initial-state effect),36,37 or photohole screening (final-state effect),38 or both.39 The shift in the dilute alloy Pd-Al has been explained38 with a commonly used model in which the core-level peaks in all metallic samples arise from a final state that is fully screened, which allows the final-state core-hole lifetime to be replaced by that of the ground state of the next element in the periodic chart—the ionized charge distribution to be replaced by that of the state that is fully screened, which allows the final-state core-level peaks in all metallic samples arise from a final state that is fully screened. The approximations which we report here should be regarded as parameters which we report here should be regarded as phenomenological values which probably reflect, primarily, bulk properties.

The best fits for the annealed quasicrystal are shown in the top two panels of Fig. 2, for the cubic alloy in the middle two panels, and for the elemental metals in the bottom two panels. In each panel, the quality of the fit can be judged by the residual, which is the top curve in the panel. Focussing first on the Pd peaks, shown in the left-hand column, it can be seen that the Doniach-Sunjic fit is rather poor in all cases, with a clear structure in the residual. For the pure metal, the poor fit has been reported previously,33 and attributed to the need for a more complex density of states near the Fermi level.34,45 A similar concern may apply to the alloys as well, especially given the pseudogap in the quasicrystal, where the density of states goes through a minimum at $E_F$ (a more complicated shape than anything considered previously).

Better fits are obtained for the Mn 2p photoelectron lines, as shown in the right-hand column of Fig. 2. Interestingly, we can find no corresponding analysis of Mn core-level photo-
A similar reason may account for the low value of $\alpha$ in the cubic alloy (0.09). Although photoelectron data which could reveal the DOS at $E_F$ is not available for the cubic alloy, a low DOS at $E_F$ would be consistent with its high resistivity. Note that the value of $\alpha$ for the Pd peaks of the alloys is quite robust. Table II shows that it does not vary significantly in the alloy samples, regardless of temperature of preparation, and regardless of whether the alloy is cubic or icosahedral.

The trend in the value of $\alpha$ for the Mn peaks is quite different, with the annealed quasicrystal exhibiting a value which is clearly lower than that of any of the other three samples. This accounts for the reduction in intensity of the high-energy tail noted previously, and thus accounts, at least in part, for the distinctive peak shape. However, if this were the only important factor, one would expect the $2p_{1/2}$ and $2p_{3/2}$ peaks to show comparable relative reductions in width, since the value of $\alpha$ is set equal for both in any given sample. This expectation is not borne out by the full width at half maximum (FWHM) values in Table I, suggesting that an additional factor is at play in determining the peak shape.

Taken together, the trends in $\alpha$ for the Pd and Mn peaks suggest that the density of states near $E_F$ varies less for Pd than for Mn, within the range of alloy samples and preparation routes studied here. In other words, the density of Mn states near $E_F$ (the 3d states) appears more sensitive to the structural and/or chemical environment than does the density of Pd states. This is consistent with the fact that Mn 3d states form 3d bands around $E_F$ in metallic Mn, and remain near $E_F$ (although hybridized with Al states) in the quasicrystal.\(^{21,22,26,27}\) On the other hand, the Pd states lie several eV below $E_F$ in the quasicrystal; as noted above, the invariance of $\alpha$ in going from the quasicrystalline to the crystalline alloy suggests that the Pd states lie well below $E_F$ in the crystalline alloy as well.

The other major fitting parameter is $\gamma$, which, to zero order, determines the peak half-width. A smaller value of $\gamma$ corresponds to a narrower peak and a longer lifetime of the photohole, indicating that the photohole is less effectively quenched. For this parameter, the most interesting trend revealed by Table II is the distinctively small value of $\gamma$, 0.07, for the $2p_{3/2}$ Mn peak in the annealed quasicrystal. This reveals that the second factor responsible for the sharpness of the $2p_{3/2}$ peak is a long photohole lifetime. The value of $\gamma$ in

**TABLE II.** Fitting parameters for the Pd and Mn peaks, corresponding to the data of Fig. 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pd 3d $3/2$</th>
<th>Pd 3d $5/2$</th>
<th>Mn 2p $1/2$</th>
<th>Mn 2p $3/2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$</td>
<td>$E_0$</td>
<td>$2\gamma$</td>
<td>$E_0$</td>
</tr>
<tr>
<td>Quasicrystal sputtered at 300 K</td>
<td>0.09</td>
<td>342.3</td>
<td>0.16</td>
<td>336.9</td>
</tr>
<tr>
<td>Quasicrystal sputtered at 870 K</td>
<td>0.07</td>
<td>342.6</td>
<td>0.34</td>
<td>337.3</td>
</tr>
<tr>
<td>Cubic alloy annealed at 870 K</td>
<td>0.09</td>
<td>342.4</td>
<td>0.02</td>
<td>337.1</td>
</tr>
<tr>
<td>Pure metal annealed $T&gt;800$ K</td>
<td>0.25</td>
<td>340.3</td>
<td>0.60</td>
<td>335.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table II for elemental Mn (fourth row) agrees well with that predicted for atomic Mn. 48 It is somewhat surprising, therefore, that the line in the quasicrystal is even sharper than that (expected) for the free atom.

This may be rationalized as follows. The lifetime of a photohole is dominated by Auger processes. According to McGuire’s calculations, 49 roughly half of the total transition probability for filling the 2p 3/2 hole in Mn involves 3d electrons, i.e., L 2,3 , C, M 4,5 , and L 2,3 , M 4,5 , M 4,5 , M 4,5 processes. This can be seen in the relative strength of Auger lines in the spectrum reported by Väyrynen. 50 Lying in the valence band, Mn can be seen in the relative strength of Auger lines in the probability for filling the 2p 3/2 hole. The 3d population must be lower, and/or the residual distribution at these states must be larger, in the annealed quasicrystal than in the free atom or in solid elemental Mn, in order for the photohole lifetime to be longer.

In short, for the Mn 2p 3/2 line, both of the fitting parameters α and γ appear to reflect characteristics of the Mn 3d states in the annealed quasicrystal. The low value of α is associated with the change in peak shape (specifically, the reduction in relative intensity of the high-energy tail), and the low value of γ reflects a reduction in the intrinsic linewidth. It is their combined influence which makes the experimental 2p 3/2 line distinctively sharp in the quasicrystal, relative to the other samples studied here.

IV. CONCLUSIONS

Photoelectron spectra of a fivefold quasicrystalline alloy, Al 70 Pd 21 Mn 9 , reveal two noteworthy features. The first is that the Pd 3d lines fall at binding energies which are 2.2 eV higher than in pure Pd. A similar effect is known to occur for Pd in other alloys, where it is attributed to a combination of initial- and final-state effects. 54 The second noteworthy feature is that the Mn 2p 3/2 line is very sharp in the quasicrystal. Fitting the experimental photoelectron peaks with a Doniach-Sunjic line shape suggests that both the position and population/residual distribution of the Mn states near E_F (the 3d states) is very sensitive to the structural and/or chemical environment of Mn in the alloys. However, the results of the fitting should be regarded with some caution, due to the lack of experimental resolution between bulk and surface states, and to the simplistic form assumed for the density of states near E_F. The latter concern is particularly relevant to the Pd fits.

In a very practical sense, the interesting result is that the sharpness of the Mn 2p 3/2 line may be a useful fingerprint of the quasicrystalline phase within the AlPdMn system. This appears to be true within the range of samples and preparation methods studied here; further comparisons are necessary, however, to see how far this conclusion may be extended.

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