

Surface Preparation and Characterization of the Icosahedral Al-Pd-Mn-Ga Quasicrystal

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Abstract. Auger electron spectroscopy and low-energy electron diffraction (LEED) provide basic information about the structure and composition of the fivefold surface of the quaternary quasicrystal, icosahedral $\text{Al}_{67}\text{Pd}_4\text{Mn}_{21}\text{Ga}_8$. Surface preparation techniques established previously for the icosahedral alloys Al-Pd-Mn and Al-Cu-Fe appear to be similarly effective for Al-Pd-Mn-Ga. After annealing in the range 600-950 K, the surface concentration of Ga is constant and low. After annealing in the range 900-950 K, a good LEED pattern is obtained. LEED indicates that Ga changes the surface structure significantly.

Introduction. Quasicrystals are intermetallics with long-range order but without periodicity.¹ Discovered by Shechtman in 1982 in the Al₆Mn alloy,² they are now recognized as a general phenomenon in metallic alloys, due to the fact that hundreds of different combinations of elements have been found to support quasicrystalline phases.^{3,4} Most of the known systems contain over 50 atomic % Al.^{3,4} The quest for more elemental combinations continues, and recent findings suggest that a rich field awaits in non-Al-based systems.⁵

The search for new quasicrystals is driven in part by a desire to develop and test predictors of quasicrystalline stability. (The average maximum oxidation state, or e/a ratio, is one such predictor.³) It is also driven by a desire to tailor the physical properties of quasicrystals, which are unusual. These properties—such as brittleness, hardness, low thermal and electrical conductivity, low adhesion—are clearly coupled to the unusual atomic structure. It is hoped that changing composition might provide a route to optimizing properties. However, within any given set of elements, quasicrystalline phases typically exist over a very narrow compositional range. Hence, changing composition is virtually impossible within a single system; it can be done best by spanning different systems.

In this paper, we present the basic surface preparation and characterization of a relatively new quaternary quasicrystal, icosahedral (i-) Al-Pd-Mn-Ga. This was discovered as an offshoot of the ternary, i-Al-Pd-Mn, during optimization of the growth of that material.⁶ Gallium is commonly used as flux in growth of Al-based alloys; in the case of i-Al-Pd-Mn, however, it was found that the Ga flux incorporated partially into the quasicrystal structure. The Ga replaced 4 % of the Al atoms to yield a final bulk

composition of $\text{Al}_{67}\text{Ga}_4\text{Pd}_{21}\text{Mn}_8$, and a high degree of structural perfection.⁶ (In this paper, we refer to i-Al-Pd-Mn-Ga as a quaternary, although Fisher et al. preferred the term ‘pseudoquaternary’ to acknowledge that it was unclear whether Ga occupies specific sites, or substitutes randomly for the Al.)

Surfaces of quasicrystals are interesting because some of their unusual physical properties are surface properties. However, detailed surface investigations have been carried out on only two icosahedral quasicrystals thus far: i-Al-Pd-Mn and i-Al-Cu-Fe, and these have established both similarities and differences.

The similarities between the two provide a benchmark for the present work. It is generally agreed that a clean, fivefold surface can be prepared in a classic terrace-step morphology, in which the terraces are laterally bulk-terminated.⁷⁻¹⁷ The terraces are Al-rich relative to the average bulk composition, not because of surface segregation, but because dense, Al-rich layers that exist in the bulk are preferentially exposed.^{11-13, 17, 18} The technique used to obtain such a surface is most commonly ion-sputtering, followed by annealing. Ion sputtering preferentially removes Al.¹⁹ Furthermore, the sputtered surface is very rough. Therefore, annealing is necessary to remove both chemical and physical damage.

Icosahedral Al-Pd-Mn-Ga provides a new opportunity to test the generality of observations for surfaces of Al-rich icosahedral quasicrystals. The present study lays the groundwork for, and establishes the feasibility of, future surface studies of this icosahedral quaternary.

Experimental Description.

The Al-Pd-Mn-Ga sample was grown as described previously. After growth, standard preparation and characterization were carried out.²⁰ After introduction to ultrahigh vacuum, the sample was cleaned by repeated Ar⁺ bombardment and sequential annealing.^{20, 21} Annealing times were 30 to 60 minutes in the temperature range 400 to 850 K. The most tenacious contaminant was oxygen. For all data reported herein, the surface oxygen concentration was 2% or less. Oxygen concentration fell during the course of the experiments and was eventually undetectable. Oxygen concentrations higher than about 5% interfered significantly with the detection of Ga by Auger electron spectroscopy (AES). The data reported herein were all obtained on a single sample of i-Al-Pd-Mn-Ga.

During heating, mass spectrometry did not show the presence of Ga vapor (or other metals from the alloy).

Experimental Results and Interpretation.

First, we investigate the evolution of surface composition with temperature using AES. Figure 1 shows the variation in surface compositions, measured by AES, for the i-Al-Ga-Pd-Mn quasicrystal. Qualitatively, the trends are very similar to those observed for i-Al-Pd-Mn. Recalling that the bulk composition is $\text{Al}_{67}\text{Ga}_4\text{Pd}_{21}\text{Mn}_8$, ion bombardment at 300 K produces a surface that is depleted in Al and enriched in Pd—in fact, the concentrations of the two are essentially equal at about 48 atomic %. Both the Mn and Ga concentrations are very low. In fact, it is often impossible to detect Ga on the surface immediately after sputtering, and the Mn concentration is about 2%. With increasing temperature, the compositions change and generally approach the bulk values. The concentrations of Al, Mn, and Ga all increase, while Pd falls. An annealing temperature

of about 550 K is necessary to detect Ga reproducibly. After annealing at temperatures of 900 to 950 K for 1 to 5 hours, the average surface composition is $\text{Al}_{63.7 \pm 1.6}\text{Ga}_{10.4 \pm 0.8}\text{Pd}_{20.9 \pm 1.5}\text{Mn}_{4.7 \pm 0.8}$, where the averages and standard deviations are derived from 8 AES measurements.

The surface compositions do not exactly match the bulk compositions (except for Pd). Specifically, the measured surface Al concentration is low, and the Ga and Mn concentrations are high. This could have one of three sources. First, the surface concentrations are calculated from AES data using sensitivity factors calibrated for individual elements, which could easily introduce absolute errors of several percent.²² Second, there could be some real surface segregation of e.g. Ga. Third, the surface may have the bulk composition, but terminations could be favored that are enriched e.g. in Ga and depleted in Al. These terminations would contribute heavily to the measured surface concentrations, due to the exponential attenuation of electrons in the bulk.

After annealing at 900-950 K, an excellent pattern develops in low-energy electron diffraction (LEED), as illustrated in Fig. 2. The different parts of the figure show patterns at different electron beam energies, all at normal incidence. At some energies, such as 130 eV, the pattern appears tenfold, while at other energies, especially 91 eV, the pattern is fivefold. This indicates that the surface is fivefold symmetric. These diffraction patterns are very similar, qualitatively, to those observed for the fivefold surface of the ternary quasicrystal, i-Al-Pd-Mn,^{8, 9, 11, 12, 14, 15, 20, 21, 23} except for the electron energies at which they occur.

The quantitative variations of diffraction spot intensity with electron energy (intensity-voltage, or I-V, curves) are shown in Fig. 3. The solid curves represent experimental data for i-Al-Pd-Mn-Ga, whereas the gray curves compare experimental data for i-Al-Pd-Mn. Some difference is expected due simply to the different scattering properties of Ga vs. Al; however, the differences should be small, since the surface concentration of Ga is rather small. In Fig. 3, the main effect of Ga is to move the peaks to higher energies. Normally, such a shift means a reduction in interlayer spacings. A reduction would be consistent with the fact that Ga is smaller than Al (metallic radius of 1.35 Å for Ga vs. 1.43 Å for Al, with Pd 1.38 Å and Mn 1.35 Å), so that simple substitution would indeed tend to shrink interlayer spacings. A reduction is inconsistent with bulk data reported previously, which showed, in a comparison of two specific samples, that the bulk quasilattice constant of the Ga-containing alloy is larger (by 1.5%), not smaller, than that of the Ga-free alloy.⁶ However, the values for the two alloys fell within the range of quasilattice constants measured and reported in the literature for a variety of samples of the pure ternary, suggesting that the difference of 1.5% may not have been significant.²⁴ Of course, more complex explanations may also contribute to the differences induced by Ga in Fig. 3.

4. Discussion.

The AES data are best used as indications of trends in surface composition with temperature, rather than measures of absolute concentration. The data in Fig. 1 illustrate that the surface of i-Al-Pd-Mn-Ga is depleted in Al and Ga after ion bombardment at room temperature, but reaches an ‘equilibrium’ composition between about 600 and 950 K. In this temperature range, it appears that the surface can equilibrate with the bulk via long-range diffusion, as is true also for the ternary.²¹

Between 600 and 950K, the concentration of Ga is constant and low, irrespective of temperature or annealing time in this range. This suggests that the Ga remains part of the solid, rather than segregating into the elemental liquid, moving out and spreading over the surface.

There is no evidence of Ga evaporation from this surface. The vapor pressure of Ga is of the same order of magnitude as that of Al (Fig. 4). In the ternary quasicrystal, Mn evaporates first,²⁵ consistent with its relatively high vapor pressure as shown in Fig. 4, and we expect this phenomenon to occur for the quaternary as well. However, evaporation of Mn is detectable from the ternary at $T > 950$ K in ultrahigh vacuum, above the temperature range investigated here. Hence, it is reasonable that Ga evaporation is negligible under our conditions.

The main conclusion from the above paragraphs is that i-Al-Pd-Mn-Ga is tractable and amenable to surface preparation and analysis in ultrahigh vacuum. The surface preparation techniques established previously for i-Al-Pd-Mn and i-Al-Cu-Fe appear to be similarly effective for i-Al-Pd-Mn-Ga.

Finally, the LEED I-V data in Fig. 3 indicate that {Michel: The following sentences are obviously inconsistent with what was written previously. I need your input on how to interpret the LEED data before I try to make things consistent, thanks.} Ga changes the surface structure significantly. Figure 4 shows the surface energies²⁶ of the 4 elements that comprise the quaternary, as a function of their vapor pressures at fixed temperature. Ga has the lowest surface energy, as much as a factor of two below that of Al. It is therefore likely that Ga can change the relative surface energies of different types of terminations, possibly leading to preferential exposure of different types of planes. Another possibility is surface segregation of Ga. Either could account, qualitatively, for the changes in the LEED I-V data illustrated in Fig. 3. The former possibility—preferential exposure of different types of planes—is intriguing and worthy of further investigation.

Conclusions.

Acknowledgments.

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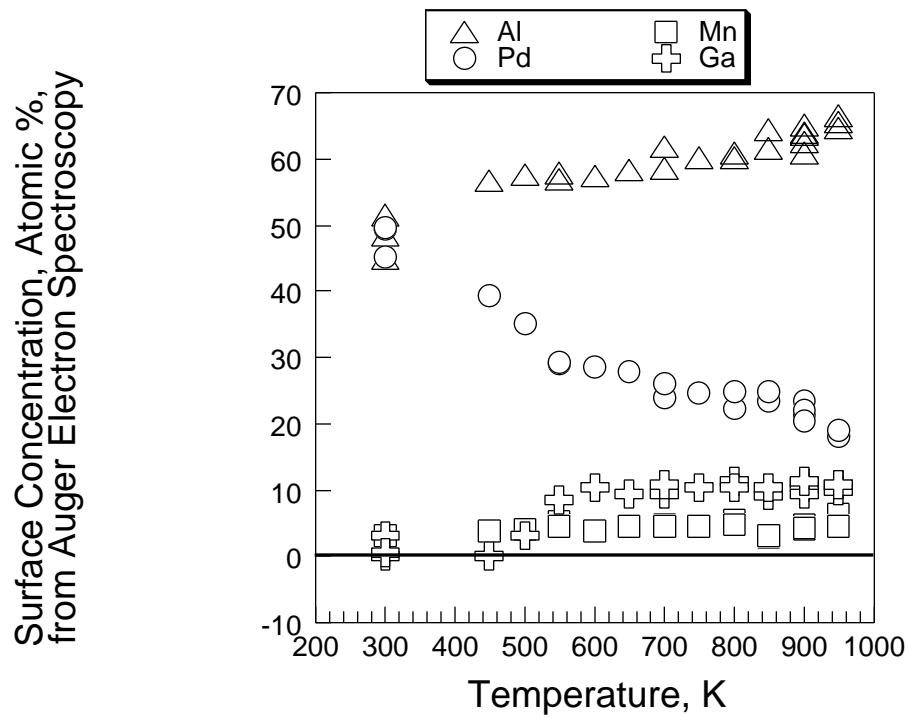


Figure 1: Variation in surface composition as a function of annealing temperature for the quaternary quasicrystal. Between 400 and 850 K, the annealing times were 0.5 to 1 hour. Between 900 and 950 K, annealing times were 1 to 5 hours.

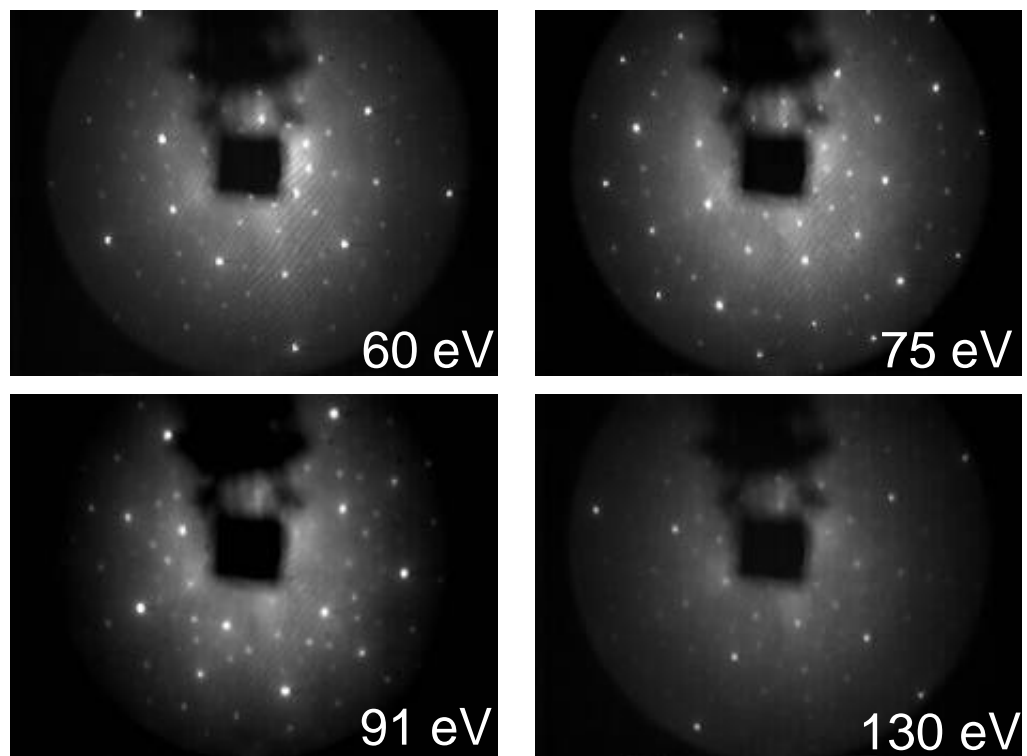


Figure 2: LEED patterns of the fivefold surface of i-Al-Pd-Mn-Ga, following treatment at 900-950 K. The sample is cooled to liquid nitrogen before the data are acquired.

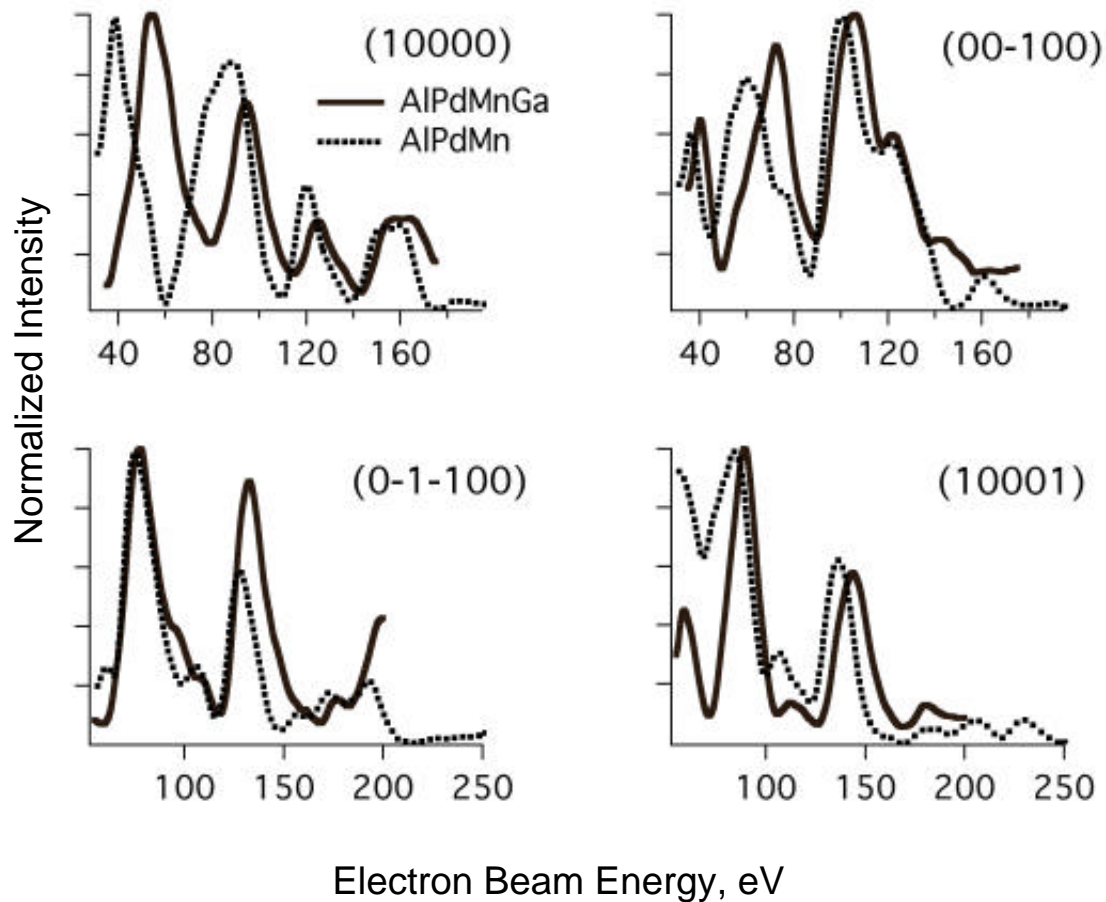


Figure 3: I-V curves of LEED spots in the patterns of Fig. 2, taken at normal incidence. The sample is cooled to liquid nitrogen before the data are acquired. Each curve is a smoothed average over all accessible symmetry-equivalent spots. Intensity values for each curve are normalized. Al-Pd-Mn fivefold sample treatment: Ar+ sputtered, then annealed at 800 K for 1.5 hours. Al-Pd-Mn-Ga fivefold sample treatment: Ar+ sputtered, then annealed at 950 K for 2.5 hours

Surface Energies of Elemental

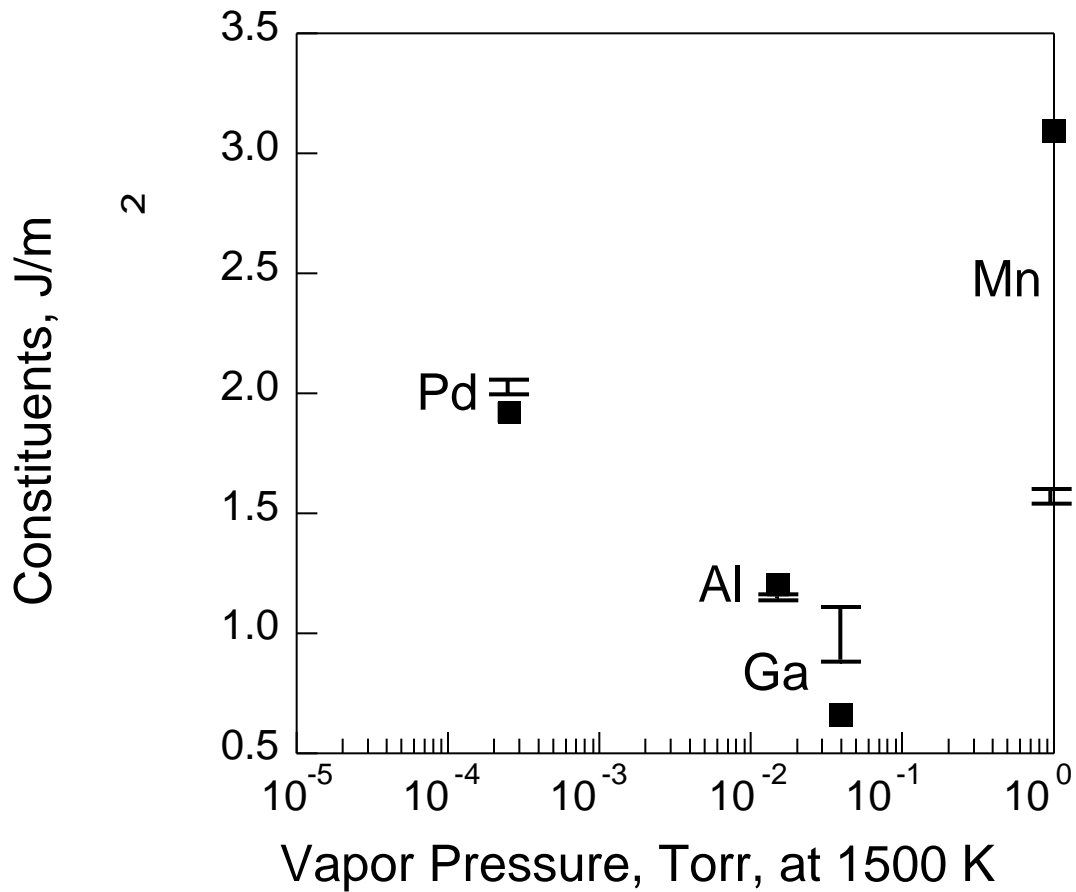


Figure 4: Surface energies of the constituent elements ²⁶ as a function of vapor pressure. Black squares are theoretical calculations for the close-packed face of the solid element. Bracketed lines show the range of experimental data cited in ²⁶.