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Evidence for surface compaction in Al-incorporated Al-Pd-Mn quasicrystals

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The quasicrystalline order at the pentagonal surface of the icosahedral Al-Pd-Mn is monitored by low-energy electron diffraction during the vacuum deposition of aluminum. We find that thick Al layers can readily be diffused into the bulk if the substrate is kept at 770 K, with no measurable changes in the surface quasicrystalline order. In the process, the surface Debye temperature (298 K) increases by more than 100 K suggesting the filling of the vacancy-rich, open-structured pentagonal surface of the Al-Pd-Mn quasicrystal with Al.

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At finite temperatures, each atom fluctuates about its equilibrium position and, since the vibrational amplitude of surface atoms is commonly larger compared to the bulk value, surfaces show a distinctly different behavior than the bulk. Surface melting is certainly a prominent example of this class of processes.

The mean-square displacement of atoms, expressed as $\langle u^2 \rangle$, can be determined experimentally by measuring the intensity of particles, e.g., electrons, reflected from the surface as a function of temperature, because the intensity decreases exponentially with increasing temperature. This is expressed as the Debye-Waller factor e^{-2M}, where, in the high-temperature limit,[1,2]

$$2M = \frac{16\pi^2 \langle u^2 \rangle \cos^2\phi}{\lambda^2} \quad \text{and} \quad \langle u^2 \rangle = \frac{3\hbar^2 T}{m k_B \theta_D^2}. \tag{1}$$

Here, in an electron-scattering experiment, ϕ is the angle of incidence relative to the surface normal and λ is the wavelength inside the material, θ_D represents the Debye temperature, k_B is the Boltzmann constant, and m is the atomic mass of the sample. Thus, the attenuation of the reflected intensity is described by the Debye-Waller factor, which can be used to determine θ_D. In low-energy electron-diffraction (LEED) the electron energy is kept in the range of 30–250 eV, and the experiments are extremely surface sensitive owing to the short mean free path.[3] Thus, θ_D becomes characteristic of the surface.

Temperature-dependent LEED experiments contain a wealth of information on structural properties of surfaces. Viljoen and co-workers[4] have determined θ_D for the three low-index surfaces of Al and derived thermal-expansion coefficients of crystallographic planes near the surface.

In contrast to crystals, quasicrystals (QC's) are characterized by rotational symmetries, such as fivefold, which are incompatible with the translational symmetry of ordinary crystals.[5] Nevertheless, they exhibit high-energy electron-diffraction and x-ray-diffraction patterns characteristic of a well-ordered atomic structure of the bulk material. In an x-ray-diffraction experiment, Colella *et al.*[6] have determined θ_D to be 312 K of the bulk icosahedral (i-) Al-Pd-Mn along the twofold-symmetry axis. Distinct LEED patterns are routinely obtained from properly prepared pentagonal surfaces of Al-Pd-Mn (Ref. 7). Lüscher *et al.*[8] have found a θ_D of 298 ± 7 K for the pentagonal surface which is very close to the bulk value. Here, we have introduced additional Al by vacuum deposition onto this surface, kept at 770 K. The high substrate temperature provides rapid diffusion of Al into the volume. We have determined θ_D at the surface as a function of the amount of deposited Al.

The i-QC with a bulk composition of $Al_{70}Pd_{20}Mn_{10}$ has been grown using the Bridgman technique.[9] After orienting it by means of the x-ray Laue method along one of the pentagonal directions, it has been cut by spark erosion. The sample with dimensions of $\approx 4 \times 3 \times 1$ mm^3 is subsequently mounted on a goniometer, allowing for polar and azimuthal rotations, and inserted into an ultrahigh vacuum (5×10^{-9} Pa) chamber where it is cleaned using cycles of Ar$^+$ ion sputtering at 1.5 keV and heat treatment at 850 K. The sample is heated from the backside, and the temperature is measured with an accuracy of ± 2 K using a chromel-alumel (K-type) thermocouple, pressed onto the front surface. In order to minimize systematic errors, the temperature is simultaneously measured with a second thermocouple of the same kind in contact with another position on the sample. Al is vapor deposited using an electron-beam heated source. In an independent experiment, the evaporation rate of Al was determined as 1.30 ± 0.05 Å/min by recording the exponential reduction of the Cu signal at 920 eV in Auger electron spectroscopy (AES) during growth of Al on Cu. In this procedure we used 12 Å for the mean free path of 920-eV Cu Auger electrons in Al.[3] The calibration of the flux from the atom source has been done by comparing the changes in the AES signals with the changes in the mass of a quartz microbalance for a given condition of operation of the source.[10] This calibration is periodically confirmed and is consistent with the mean free path used here. Any deviation in the calibration will adversely influence the accuracy of the evaporation rate, but not the main conclusions drawn here. In the present work, Al is evaporated onto the QC surface at elevated substrate temperatures at which Al readily diffuses into the bulk. For practical and conventional reasons, we still refer to the Al amount in units of thickness.

LEED experiments are performed using a three-grid back-view display system operating with a beam current in the low μA range.[11] Diffraction intensities are collected on the fluorescent screen, recorded with a 16-bit charge-coupled device camera,[12] and are analyzed by integration after removal of an inelastic background, which is determined independently as a function of temperature. The pattern presented for the purpose of visual inspection is generated by flat fielding,[12] i.e., after normalization of spot intensities by the overall response function of the LEED optics. The latter is obtained by scattering at the polycrystalline sample holder, which yields a homogeneous intensity distribution. There is a reduction of diffraction intensity caused by surface contamination during the experiment. Compared to the rapid determination of θ_D this effect can be taken as linear in time. We have independently evaluated this function under the same conditions and eliminated it from the intensity data.

As temperature rises, the distance between atomic planes grows and Bragg peaks shift to lower energies.[13] In order to maintain the conditions of constructive interference, the incident electron energy is reduced by 0.1 eV/27 K between 350 and 594 K. This shift allows us to determine the thermal-expansion coefficient of atomic layers to be $(24.5\pm 2.0)\times 10^{-6}$ 1/K at the pentagonal surface of Al-Pd-Mn assuming that the quasicrystalline structure consists of planes such as ordinary crystals do.[8] This value is almost by a factor of 2 larger than corresponding bulk values obtained from isotropic x-ray scattering experiments[14] and is consistent with observations made on ordinary crystals.[15]

Owing to the absence of nonoverlapping low-energy Auger transitions for all three constituents of the alloy, no reliable stoichiometry for the surface can be extracted from AES data. This information is therefore taken from the structural determination of the similarly prepared QC by Gierer and co-workers.[7] In an information depth of 5 Å typical for our present experiment, which corresponds to nine surface layers of the QC, an average stoichiometry of $Al_{72}Pd_{21}Mn_7$ and finally an atomic mass of 7.575×10^{-26} kg is obtained, which is used in Eq. (1).

We observe two distinctly different phenomena during evaporation of Al onto the pentagonal surface of Al-Pd-Mn. At temperatures below 320 K, diffusion of Al into the substrate is negligibly small and Al nanocrystals grow in cubic facets of five different sets of domains with preferred orientational alignment.[16] At higher substrate temperatures, diffusion of Al into the bulk increases, and deposition of Al above ≈ 550 K prevents the growth of an Al layer for experimental conditions similar to those used here. We have evaporated between 5 and 195 Å of Al onto the pentagonal surface of the Al-Pd-Mn, kept at a temperature of 770 K, providing efficient diffusion of Al into the bulk. Interestingly, we have observed that the quasicrystalline order is not affected by the deposition and diffusion processes. On the contrary, the structural order is well preserved within the range of the evaporated quantity of Al. Furthermore, no distinctly measurable changes in surface-sensitive, low-energy Auger transition intensities of Al (68 eV) and Pd (330 eV) have been detected during and after evaporation.[17]

Figure 1 displays a LEED pattern recorded at 68 eV for near-normal electron incidence obtained after vacuum deposition of 65 Å of Al at 770 K and subsequent cooling of the sample to room temperature. The pattern indicates the good quality of the structural order, which is maintained after Al deposition. For recording the intensity of the specular reflection the sample is tilted by 7° from this position, and the energy is lowered to 43 eV. This scattering condition renders relatively high specular intensity that provides confident data collection. In order to calculate the energy of electrons inside the QC and thus determine true ϕ and true λ, an inner potential of 12 eV is chosen. This value is reasonable assuming 4.5 eV for the work function and taking 7.5 eV for the width of the valence band of the alloy from photoemission experiments.[18] Hence, true ϕ and true λ are calculated to be 6.2° and 1.66 Å, respectively.

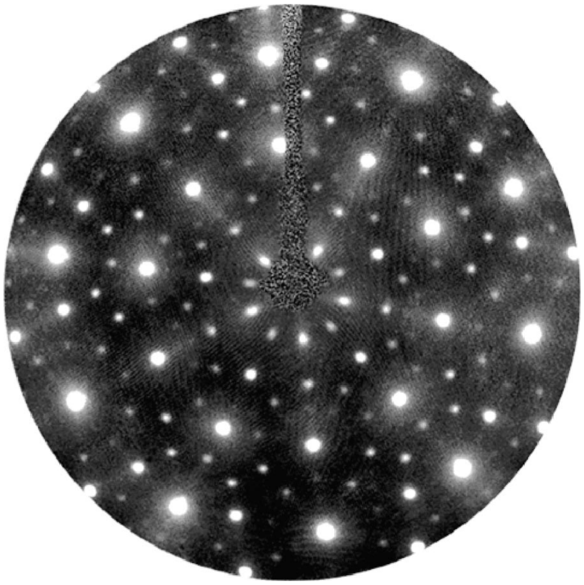

FIG. 1. LEED pattern recorded at 68 eV electron energy and near-normal incidence after vacuum deposition of 65 Å Al onto the pentagonal surface.

Figure 2 contains the logarithmic plot of the diffraction intensity of the (00) beam at a given temperature normalized to the intensity at 350 K as a function of sample temperature after evaporation of 65 Å. We note that the logarithm of the relative intensity is proportional to the temperature up to

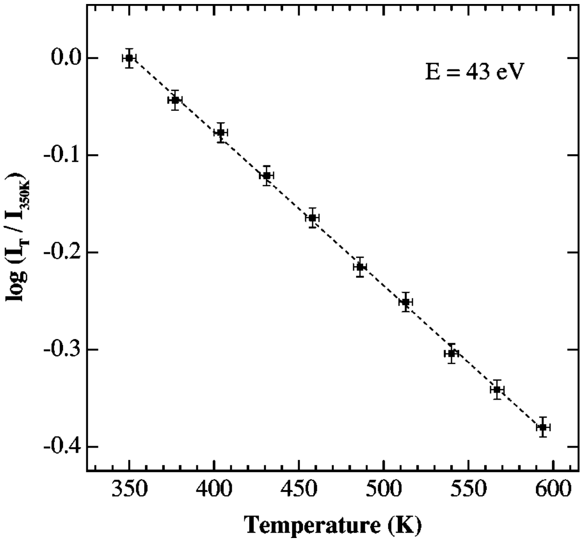

FIG. 2. Plot of the logarithm of the relative intensity of the specular beam at 43 eV energy and 7° angle of incidence as a function of temperature, obtained after 65 Å Al evaporation.

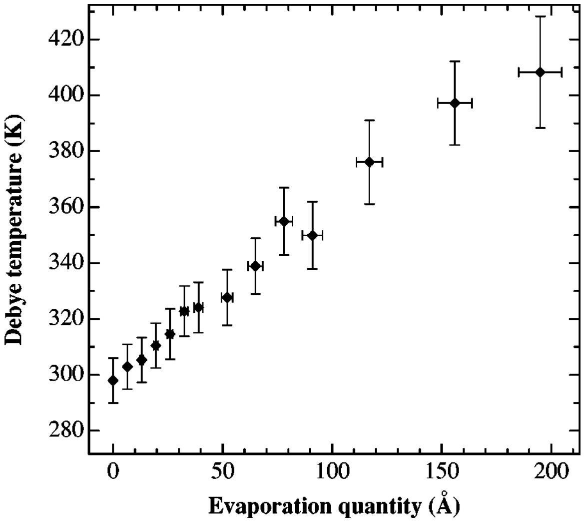

FIG. 3. The surface Debye temperature θ_D vs the evaporated amount of Al.

600 K. At higher temperatures, inelastic scattering increases significantly and the data become uncertain. The slope of the linear plot is found as $-0.001\,581$ 1/K, which is proportional to the square of the inverse of θ_D. Using Eq. (1), 339 ± 8 K is found for θ_D. This procedure is repeated successively after vacuum deposition of increasing amounts of Al. Figure 3 shows the resulting values of surface Debye temperatures. We note that θ_D increases almost linearly at a rate of 0.64 ± 0.05 K/Å. As the Al quantity is increased above ≈ 100 Å, the evaporation times become so long, e.g., it takes about 2 h for 150 Å, that the contamination level introduces significant uncertainties in the extraction of θ_D. We were, therefore, unable to observe a clear saturation. Some contamination on the surface does not adversely affect either the quality of LEED patterns or the linear trend of θ_D values in agreement with Chang and co-workers[19] who have reported that some oxygen on the surface would affect the diffraction intensities, but not the overall quality of the LEED pattern.

QC's are stable only in a limited region of their phase diagram,[20] and even a small change in the chemical composition can induce a structural phase transformation. Since the evaporation process does not affect the quasicrystalline order and no measurable changes in the Al concentration have been found at the surface after evaporation at 770 K, either diffusion or desorption of Al must be present which makes Al disappear from the surface. Schmithüsen *et al.*[21] have found that Al does not evaporate below 1000 K. Therefore, it must be diffusion into the bulk that makes Al disappear from the surface to within a few percent and preserves the structural order at the surface as seen in Fig. 1.

In order to study the diffusion of Al from the surface into the bulk Al-Pd-Mn, we have grown Al layers of around 27.5-Å thickness on the quasicrystalline surface at room temperature. The Al film thickness was monitored by the Pd Auger signal at 330 eV. Subsequently, the decrease of Al at the surface was measured as a function of time for different substrate temperatures. In the range of 320–370 K, we have found that the diffusivity of Al in Al-Pd-Mn shows an Arrhenius-type behavior. We have extracted from data ≈ 1.1 eV for the activation energy of Al diffusion with a preexponential factor D_o of 3×10^{-5} m^2/s (Ref. 22). These values are characteristic for the type of the diffusion process and establish that Al diffusion is fast and proceeds via vacancies[23] as it is known for the nontransition metals Zn, Ge, and In. Kanazawa and co-workers[24] have suggested that Al diffuses following the Al subnetwork. Further, high-temperature ($T>528$ K) diffusion studies have been performed on the *i*-Al-Pd-Mn, using the radiotracer method.[25,23] It has been found that for most of the tracer elements diffusion in QC's is not significantly different from that in related crystalline systems where vacancy-mediated diffusion is generally accepted as the basic mechanism.[23]

The diffusion data allows us to estimate the mean diffusion depth given by $\sqrt{Dt}$ of Al evaporated at 770 K onto the sample. For the range of evaporation times, this quantity is found to be in the order of several tens of microns resulting in a concentration of 15–70 ppm in that region. The diffusion-derived concentration profile for excess Al in the bulk is flattened by further annealing and reaches the dimensions of the sample leading to an almost homogeneous distribution.

Each data point presented in Fig. 3 was obtained from a freshly prepared surface, which was subsequently exposed to Al. This procedure was applied in order to avoid surface contamination due to prolonged exposure times. It is remarkable that regardless of how much Al was previously deposited, the freshly prepared surfaces all had the same initial value of θ_D. The first step of the preparation procedure is sputtering, which strongly depletes Al in a near-surface region of several tens of angstroms. This region has a chemical composition of nearly $Al_{50}Pd_{50}$ and a cubic structure. Subsequent annealing at 850 K causes migration of Al from deeper layers of the bulk towards the surface which, however, changes the bulk Al concentration only in the range of some parts per million per cycle. Furthermore, this change is not appreciably different if previously Al is deposited onto the sample. We may expect that such a minute variation of the Al concentration will not have a measurable influence on θ_D at the surface. Hence, a well-defined chemical composition and a corresponding vacancy concentration at the surface is established after each sputter-anneal cycle. The evolution of the surface structure during the preparation process has been studied in several occasions[26] and interpreted in terms of diffusion of vacancies from the bulk towards the surface as well as diffusion of alloy constituents.[27] Kluge *et al.*[28] have also suggested the presence of defects and/or vacancies in the bulk.

The semiquantitative arguments given above are based on a continuum approximation with a mean averaging length of about $\sqrt{Dt}$. However, in the determination of θ_D using LEED, a thin surface layer of only a few angstroms is sampled. In this region of discrete atomic distribution, strong deviations from the bulk behavior, such as the continuous diffusion process, are expected. Consequently, the Al-treated surface must be regarded differently from the bulk. At the surface, an Al enhancement up to a few percent is not unreasonable at which the quasicrystalline order is still preserved. This situation can qualitatively account for the increase of θ_D at the surface with the addition of Al. However, its linearity still awaits for a satisfactory explanation. Surprisingly, annealing without sputtering of these surfaces does not lower θ_D, previously determined. Furthermore, repeated determinations of θ_D, which anyway involve measurements at elevated temperatures, deliver the same value. This is an additional evidence that once quasicrystalline surfaces are well-prepared (with or without additional Al), they remain structurally stable under further heat treatment. The latter only flattens the *averaged* concentration profile of Al with negligible influence on the enriched surface.

The freshly prepared specimen has a θ_D of 298 K at the pentagonal surface, which corresponds to an average vibrational amplitude of ≈ 0.10 Å. By evaporating 195-Å thick Al, the surface Debye temperature is significantly raised. The highest attained value of θ_D is ≈ 400 K at the surface of Al-treated QC which implies that the vibrational amplitude has decreased by more than 20%. Thus, the quasicrystalline surface structure has gained additional rigidity by the introduction of Al. The arguments presented above lead to the assumption that this is accomplished by quenching of vacancies in a region of a few surface layers. Considering our limit of detectability,[17] we can thus give 1–2% as an upper limit for the vacancy concentration in this region, in agreement with Sato *et al.*[29] Hence, although our Al-Pd-Mn QC has perfect long-range orientational order and is thermodynamically stable, its surface structure can still be appreciably improved by the addition of Al.

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