Adsorption of cobalt on the ten-fold surface of d-Al₇₂Ni₁₁Co₁₇ and on the five-fold surface of i-Al₇₀Pd₂₁Mn₉

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**Adsorption of cobalt on the ten-fold surface of $d\text{-Al}_{72}\text{Ni}_{11}\text{Co}_{17}$
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Adsorption of cobalt on the ten-fold surface of $d\text{-Al}_{72}\text{Ni}_{11}\text{Co}_{17}$ and on the five-fold surface of $i\text{-Al}_{70}\text{Pd}_{21}\text{Mn}_9$

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The adsorption behaviour of Co on the ten-fold surface of $d\text{-Al}_{72}\text{Ni}_{11}\text{Co}_{17}$ and on the five-fold surface of $i\text{-Al}_{70}\text{Pd}_{21}\text{Mn}_9$ has been studied using scanning tunneling microscopy (STM), Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED). The analysis of a distinctive quasiperiodic LEED pattern for coverages from 3 - 30 ML of Co on $d\text{-Al}_{72}\text{Ni}_{11}\text{Co}_{17}$ suggests that the Co forms in a pseudomorphic row structure composed of domains of Fibonacci spaced rows having a periodic lattice parameter along the rows of 2.5 ± 0.1 Å. The same structure, though less well-ordered and with a larger lattice parameter, is formed on the five-fold surface of $i\text{-Al}_{70}\text{Pd}_{21}\text{Mn}_9$.

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I. INTRODUCTION

Quasicrystals are complex alloys, usually consisting of three or more elements arranged in a highly ordered but aperiodic fashion[1]. The effect of aperiodic ordering on the physical properties of these exotic materials is inextricably linked to those properties that arise from the comparatively large number of species present. There is therefore much interest in single-element aperiodic structures, the formation of which may be facilitated by using the aperiodic surfaces of quasicrystals as nanotemplates for the adsorption of single-element films[2-7].

In this paper we report the formation of a pseudomorphic Co layer on the ten-fold surface of $d\text{-Al}_{72}\text{Ni}_{11}\text{Co}_{17}$ at 300 K; the formation of a less well-ordered Co thin film on the five-fold surface of $i\text{-Al}_{70}\text{Pd}_{21}\text{Mn}_9$ is also reported. The quasiperiodic structure of the films is evidenced in low-energy electron diffraction (LEED) patterns, and in part from scanning tunneling microscopy (STM) measurements taken from the films.

II. EXPERIMENTAL DETAILS

The $d\text{-Al}_{72}\text{Ni}_{11}\text{Co}_{17}$ sample was produced in the Ames laboratory using the melt decantation method, and the $i\text{-Al}_{70}\text{Pd}_{21}\text{Mn}_9$ sample by the same group using the Bridgman method. The *ex-situ* and subsequent *in-situ* preparation procedures are described elsewhere[8].

Using an Omicron EFM-3 e-beam evaporator, Co was deposited onto the ten-fold $d\text{-Al}_{72}\text{Ni}_{11}\text{Co}_{17}$ surface at a rate of 6×10^{-3} ML sec^{-1} and onto the five-fold surface of $i\text{-Al}_{70}\text{Pd}_{21}\text{Mn}_9$ at the same rate (as determined by STM coverage measurements and by a comparison of the ion flux as measured by the evaporator). All deposition was carried out

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FIG. 1: (a-g); Comparison of the ten-fold $d\text{-Al}_{72}\text{Ni}_{11}\text{Co}_{17}$ surface as studied with increasing Co coverage. The coverage is respectively 0.4 ML, 1.9 ML, 3.7 ML, 5.6 ML and 7.5 ML (for (e-g)). (f) is a detail of (e), with the row structure showing more clearly. Indications of orientational order are superimposed on (e-g). A graph showing the trend of Auger peak area ratios vs coverage is also shown.

with the substrates at a temperature of 300 K. Scanning tunneling microscopy, LEED and AES measurements were taken from the resulting films. The error on the coverages quoted for $\text{Co}/d\text{-Al}_{72}\text{Ni}_{11}\text{Co}_{17}$ is estimated at 5% and for $\text{Co}/i\text{-Al}_{70}\text{Pd}_{21}\text{Mn}_9$ it is estimated at 20%.

III. RESULTS

A. Scanning tunneling microscopy and Auger electron spectroscopy

Figure 1 shows images taken from the $\text{Co}/d\text{-Al}_{72}\text{Ni}_{11}\text{Co}_{17}$ film at room temperature with an Omicron variable-temperature STM. No order is discernible at 0.4 ML coverage (determined by STM and checked with AES).

At higher coverages (5.6 ML and above) evidence for a row structure of the film is observed. It can be seen from the emergence of straight line domain boundaries in the STM images shown in figure 1 that certain orientations are preferred for the formation of islands of Co. At higher coverages, some one-dimensional row structuring within these islands becomes apparent. Due to limitations in resolution, it cannot be shown conclusively from STM that the inter-row spacings are arranged in a Fibonacci sequence, as we have previously observed for Cu adsorption on the five-fold $i\text{-Al}_{70}\text{Pd}_{21}\text{Mn}_9$ surface. The step height of the film as determined from STM is $2.0 \pm 0.1 \text{ \AA}$, which is consistent with the interlayer separation of hcp Co(0001) previously observed with STM to be $1.95 \pm 0.10 \text{ \AA}$ [9]. The fact that the Al/Co Auger peak ratio drops to zero with increasing coverage implies that there is no alloying within the film.

Scanning tunneling microscopy images taken from the $\text{Co}/i\text{-Al}_{70}\text{Pd}_{21}\text{Mn}_9$ film revealed no definite order, at any coverage (determined by STM and checked with AES), though at higher coverages there is a suggestion of linear structures within the incomplete layers formed. Auger electron spectroscopy again implies that there is no alloying within the film. Figure 2 (a,b) indicate that the dark five-fold hollows are not a preferred nucleation site for this adsorbate (as they have been found to be in previous studies [10]) as they may still be clearly observed when there is a coverage of 0.4 ML Co on the surface, with a density of approximately half that found on the clean surface. The size of the five-fold hollows (around $8 \text{ \AA}$) indicates that they belong to the substrate.

FIG. 2: (a-d); Comparison of the five-fold surface of $i\text{-Al}_{70}\text{Pd}_{21}\text{Mn}_9$ as studied with increasing Co coverage. Coverage is (a) 0.4 ML; (b) as (a) with five-fold depressions highlighted; (c) 2.5 ML coverage, and (d) 13 ML coverage.

FIG. 3: Low-energy electron diffraction patterns from 3 systems at 2 beam energies for each system. From left to right, the coverages are: 20 ± 4 ML Co, 7.5 ± 0.4 ML Co, 4 ± 0.2 ML Cu.

B. Low-energy electron diffraction

The LEED patterns obtained from the multilayer films show more evidence for ordering. Figure 3 shows the patterns obtained at 2 different electron energies from the $\text{Co}/i\text{-Al}_{70}\text{Pd}_{21}\text{Mn}_9$ film, the $\text{Co}/d\text{-Al}_{72}\text{Ni}_{11}\text{Co}_{17}$ film (both at room temperature) and previously obtained patterns from the pseudomorphic $\text{Cu}/i\text{-Al}_{70}\text{Pd}_{21}\text{Mn}_9$ film[7] (at 85 K). The patterns on the right have been corrected for the different acceptance angle and size of the optics so they may be compared with the others. Each coverage quoted provided the optimum LEED pattern in terms of lowest background and clearest diffraction peaks. It can be observed, despite the lower quality of the patterns, that the $\text{Co}/i\text{-Al}_{70}\text{Pd}_{21}\text{Mn}_9$ diffraction is qualitatively similar to that for $\text{Cu}/i\text{-Al}_{70}\text{Pd}_{21}\text{Mn}_9$, and the $\text{Co}/d\text{-Al}_{72}\text{Ni}_{11}\text{Co}_{17}$ patterns, apart from having a different set of momentum transfers, show the same broad characteristics as both.

In diffraction obtained from the $\text{Cu}/i\text{-Al}_{70}\text{Pd}_{21}\text{Mn}_9$ film, the periodic arrangement of the streaks was attributed to

FIG. 4: (a); LEED pattern obtained from the clean surface at 120 eV. (b); LEED pattern from a 7.5 ML Co overlayer at 120 eV. Lines are superimposed to aid identification of the periodic separation of the streaks.

	Lattice parameter (Å)	NN distance (Å)	Interlayer spacing (Å) (STM)	Lattice parameter on <i>i</i> -AlPdMn (Å)	Lattice parameter on <i>d</i> -AlNiCo (Å)
hcp Co	—	2.51	1.95	2.5(3)	2.4(6)
fcc Co	3.56	2.52	1.78 (001)	—	—
bcc Co	2.82	2.44	1.41 (110)	—	—
fcc Cu	3.62	2.56	1.81 (001)	2.5(3)	—

FIG. 5: Table showing certain structural properties of copper and cobalt [13, 14]

a periodic ordering along the Fibonacci rows, and a 2D LEED analysis was carried out to determine this periodicity. Although we cannot directly observe Fibonacci ordering from STM of the Co/*d*-Al₇₂Ni₁₁Co₁₇ film, the similarity of the diffraction patterns leads us to conduct a similar investigation into this system.

Using the PhD thesis of Sharma[11], a diffraction peak of known momentum transfer ($k = 2.67 \text{ \AA}^{-1}$) indexed as $(\bar{1}2\bar{2}1)$, was identified in the *d*-Al₇₂Ni₁₁Co₁₇ diffraction pattern shown in figure 4 (a). The momentum transfer k' of the streaks in the Co/*d*-Al₇₂Ni₁₁Co₁₇ film was hence calculated from the ratio of the line length y/x using $k' = k.y/x$ and was found to be $2.56 \text{ \AA}^{-1}$. Hence the periodic spacing along the rows is found to be $2\pi/k' = 2.5 \pm 0.1 \text{ \AA}$, a figure which corresponds well to the nearest neighbour distance in the stable hcp phase of cobalt of $2.51 \text{ \AA}$.

IV. DISCUSSION

On the five-fold surface of *i*-Al₇₀Pd₂₁Mn₉, there is no suggestion of order in the STM images until a relatively high coverage of Co is reached and even then it is not well resolved. This order is also not apparent in diffraction patterns taken from the film until similar high coverages are reached. The growth as determined by STM is most closely approximated by the layer-by-layer model, though the layers are rough, and the island size small (tens of angstroms).

The Co/*i*-Al₇₀Pd₂₁Mn₉ film produces a diffraction pattern that, within the error introduced by the correction for optics, and indeed the quality of the patterns themselves, is extremely similar to that from the Cu/*i*-Al₇₀Pd₂₁Mn₉ film. Assuming the streaks observed in the pattern from the Co film indicate periodicity, as they do for the Cu film, then we may conclude that they correspond to the same periodicity, as far as is permitted within the accuracy of such an analysis. The NN distance in bulk fcc Cu is $2.56 \text{ \AA}$. Our LEED analyses of the Cu film and of the Co films yield a periodicity along the rows of $2.5 \pm 0.1 \text{ \AA}$. We have used this analysis to assist our assertion elsewhere[12] that the structure of the Cu phase present on *i*-Al₇₀Pd₂₁Mn₉ consists of five orientational domains composed of rows of atoms arranged according to a one-dimensional Fibonacci sequence.

On the ten-fold surface of *d*-Al₇₂Ni₁₁Co₁₇, deposited Co appears to form an initial complete layer upon which smaller domains of row-structured material take shape. With each subsequent layer, the lateral island size decreases. The growth is therefore neither strictly layer-by-layer nor 3D, though layer-by-layer growth is the closest approximation. At the highest coverages studied (15ML), the size of the Co islands was on the order of hundreds of angstroms.

The streaks present in the diffraction pattern from the Co/*d*-Al₇₂Ni₁₁Co₁₇ film can immediately be seen to correspond to a smaller period (due to the significantly larger separation of the streaks on the pattern). The NN distance in bulk hcp Co is 2.51 Å. Our LEED analysis of the Co/*d*-Al₇₂Ni₁₁Co₁₇ film yields a periodicity along the rows of 2.5 ± 0.1 Å. The momentum transfer extracted for the separation of the streaks on the Cu/*i*-Al₇₀Pd₂₁Mn₉ was 2.48 Å^{-1} [12]. To the extent that the values of the momentum transfers derived from the bulk structures are correct for these surfaces, we can see that the difference in the momentum transfers for the two films is $(2.56/2.48 = 1.03)$ and this translates to a difference in lattice parameter of 3%. We can thus determine that the periodicity for Co on *i*-Al₇₀Pd₂₁Mn₉ is 3% larger, in one dimension, than that on *d*-Al₇₂Ni₁₁Co₁₇. Bulk fcc Cu has a NN distance 2% larger than that of bulk hcp Co. The table in figure 5 lists these properties.

V. CONCLUSIONS

We find that, when deposited onto the ten-fold surface of *d*-Al₇₂Ni₁₁Co₁₇, Co grows in a predominantly layer-by-layer fashion, forming a film with a number of orientational domains. These domains have a row structure visible in STM images, and are shown by a LEED analysis to be consistent with a one-dimensional Fibonacci arrangement of rows, with a periodic arrangement of atoms perpendicular to the Fibonacci direction. The NN distance along these rows has been determined to be 2.5 ± 0.1 Å, and has also been shown to be smaller than the periodicity of the Cu/*i*-Al₇₀Pd₂₁Mn₉ structure by around 3%. This is consistent with the NN distance in bulk hcp and fcc Co; however, due to the interlayer spacing observed by STM, it is suggested that the structure adopted by the Co on this surface is composed of rows of hcp structured material with the (1000) hcp orientation along the rows. It has also been observed that a film of Co deposited on *i*-Al₇₀Pd₂₁Mn₉ appears to have the same broad structure and periodicity as a film of Cu deposited onto the same surface. However, the Co film is far less ordered than the Cu film on this surface, and also less ordered than the Co film deposited on *d*-Al₇₂Ni₁₁Co₁₇.

In the regime of pseudomorphic growth, there have been to date three multilayer films formed on quasicrystal substrates: the copper film on *i*-Al₇₀Pd₂₁Mn₉ [7] and the studies under discussion. Although the structural properties of the two substrates are very different (*i*-Al₇₀Pd₂₁Mn₉ is an icosahedral quasicrystal with three-dimensional aperiodicity, whereas *d*-Al₇₂Ni₁₁Co₁₇ is periodic along one direction and decagonal and aperiodically ordered perpendicular to that direction), common features emerge in the films deposited: the atoms order themselves in row structures according to orientations present within the substrate, and these row structures are themselves ordered according to a one-dimensional Fibonacci sequence.

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