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Iron deposition on the tenfold surface of the $Al_{72}Ni_{11}Co_{17}$ decagonal quasicrystal

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Abstract
The adsorption behaviour of Fe on the tenfold surface of the decagonal quasicrystal $Al_{72.6}Ni_{10.5}Co_{16.9}$ has been studied using scanning tunnelling microscopy, low energy electron diffraction (LEED), Auger electron spectroscopy (AES) and x-ray magnetic circular dichroism (XMCD). The results show the growth of a disordered film up to a coverage of 9 MLE (monolayer equivalent) after which polycrystalline island growth is observed. These islands are interconnected, and the LEED pattern indicates that they preferentially align along five directions. The AES results indicate that the film is composed of Fe intermixed with the substrate elements. The XMCD results point to an induced magnetic moment for Co and Ni in the intermixed layer/interface region.

1. Introduction

One of the simplest yet most profound connections in condensed matter physics is the relationship between order and physical properties. Crystalline and amorphous forms of the same element can exhibit vastly different behaviour. Quasicrystals are aperiodic structures constituting a form of solid matter distinct from periodic and amorphous materials. They are metallic alloys which have a quasiperiodic arrangement of atoms, incorporating long range order without translational symmetry [1]. Hence the investigation of physical properties of quasicrystals as archetypal aperiodic solids has been a topic of great interest since their discovery [2].

Magnetism is one of the most important of physical properties. Several calculations of quasiperiodic magnetic systems have shown that unusual magnetic structures are expected [3, 4]. However although magnetism in bulk quasicrystals has been studied extensively, strong magnetic effects are not observed. In icosahedral quasicrystals such as i-$Al_{70}Pd_{21}Mn_9$, or decagonal quasicrystals such as d-$Al_{72.6}Ni_{10.5}Co_{16.9}$ [5], magnetic elements are dispersed in a nonmagnetic framework with a multiplicity of distances between the magnetic species which leads to very effective screening.

A possible route to the formation of quasiperiodic magnetic structures is to utilize the surfaces of quasicrystals as templates to grow single element epitaxial single layers of films. This approach has been successful in elucidating the effect of induced quasiperiodic order on the electronic structure of adsorbed species: the electronic structure of a quasiperiodic Pb monolayer adsorbed on i-Al–Pd–Mn was found to display a pseudogap at the Fermi level in the electronic structure induced by aperiodic ordering [6]. Growth of magnetic films on quasicrystal surfaces offers the possibility of forming similar magnetic systems, provided that the magnetic elements order quasiperiodically on the surface.

However in all studies reported to date, such ordered growth has not been observed. Cobalt was observed to adopt a pseudomorphic one-dimensional quasiperiodic structure on both i-Al–Pd–Mn and d-Al–Ni–Co. The Co atoms order

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into crystalline rows which are spaced according to a one-dimensional Fibonacci sequence [7–9]. The adsorption of Fe on i-Al–Pd–Mn has also been studied [10]. Wearing *et al* reported that Fe produced a disordered film up to 3 MLE, and then formed nanosized islands with a 'wedding cake' structure elongated along the five-fold axes of the substrate. Weisskopf and co-workers found similar structural results for Fe, although they reported Al interdiffusion with the Fe between 4 and 8 MLE [11]. Therefore, while the results obtained to date are of interest with regards to epitaxy, they do not allow the testing of the theoretical predictions [3, 4] of magnetism in quasicrystals, which were arrived at by calculation of perfect quasiperiodic magnetic systems.

The results for Fe adsorption discussed above were obtained on the five-fold surface of the icosahedral quasicrystal i-Al–Pd–Mn. Decagonal quasicrystals such as d-$Al_{72}Ni_{11}Co_{17}$ have a very different structure: they are periodic in the direction parallel to the ten-fold symmetry axis, and quasicrystalline in planes perpendicular to this direction. They offer an alternative quasicrystalline substrate for comparison of adsorption as has been demonstrated recently for the case of Si [12, 13]. In this work we investigate the adsorption of Fe on the ten-fold surface of the d-$Al_{72}Ni_{11}Co_{17}$ quasicrystal. We have applied the techniques of scanning tunnelling microscopy (STM), low energy electron diffraction (LEED), Auger electron spectroscopy (AES) and x-ray magnetic circular dichroism (XMCD), to the study of this system. The results are presented below.

2. Experimental details

The sample was produced at Ames laboratory, using the melt decantation method. The sample was cut (spark etched) perpendicular to the ten-fold axis. It was then mechanically hand polished using 6, 1 and 1/4 μm diamond paste. An atomically flat surface with large flat terraces was obtained through cycles of 3 keV Ar^+ sputtering for 45 min at room temperature followed by annealing for four hours at a temperature of 1070 K, at a base pressure of 1.5×10^{-10} mbar. The annealing was performed by electron bombardment of the sample. The temperature was monitored through an infra red pyrometer.

Scanning tunnelling microscopy (STM) was performed in ultra high vacuum (UHV) at a base pressure of 3×10^{-11} mbar using an Omicron variable temperature STM. Iron was deposited using an Omicron EFM-3 electron beam evaporator. The sample was at room temperature during deposition and measurement. The deposition rate was calibrated by applying a density slice to STM data taken at submonolayer coverages. As the coverage was determined from observation the deposition and hence coverage are quoted in terms of monolayer equivalent (MLE). One MLE corresponds to the completion of a layer as monitored using STM. The deposition rate during STM experiments was found to be 0.038 ± 0.005 MLE s^{-1}, and the error on the coverage is estimated to be 13%. The surface order was monitored using LEED, and AES was used to determine sample cleanliness using the LEED apparatus as an analyser in retarding field mode.

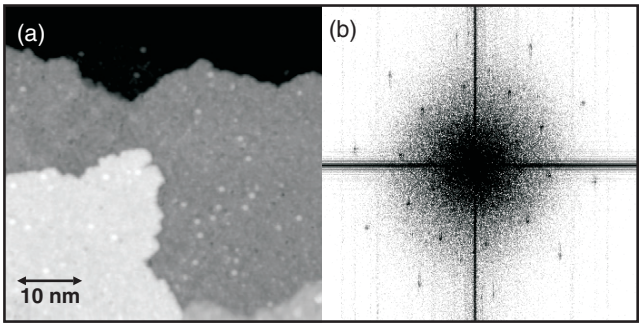

Figure 1. Left: 50 nm × 50 nm STM image of the clean surface of d-Al–Ni–Co. A quadratic compensation was applied to the image and the contrast was enhanced resulting in the apparent exclusion of the terrace at the top. Right: a FFT of the main image.

Auger measurements were performed in a separate system under a base pressure of 1.5×10^{-10} mbar using the same evaporation source. A Perkin Elmer double pass cylindrical mirror analyser operated at a beam energy of 2 keV was used to provide high quality Auger spectra to obtain information about the growth mode. The deposition rate was calculated to be 0.029 ± 0.005 MLE s^{-1} using the calibration obtained from the STM measurements and adjusted for the different sample/source distance in both systems.

X-ray magnetic circular dichroism (XMCD) measurements were undertaken on beamline ID08 of the European Synchrotron Radiation Facility. The photon energy is tunable in the range of 0.4–1.6 keV, with an energy resolution close to $\mathrm{d}E/E = 5 \times 10^{-4}$ at 850 eV. XMCD spectra were obtained at the Fe and Co $L_{2,3}$ edges in total electron yield mode using circularly polarized (**P**) light with 99% polarization in magnetic fields up to ±7 T with the sample at $T = 5$ K. XMCD was recorded by switching both the polarization vector of the circularly polarized light **P** and the sample magnetization **M**. In these experiments Fe was deposited at room temperature from a rod source using an Omicron EFM-3 electron beam evaporator, with coverage calibrated using a quartz crystal microbalance.

3. Results

Bulk Al–Ni–Co has a structure consisting of ABAB periodic stacking of aperiodic planes along a ten-fold symmetry axis [14]. The ten-fold surface of d-Al–Ni–Co therefore consists of two near identical surface terminations each related to its neighbour plane by a $\pi/5$ rotation [15–18]. Each of the terminations has five-fold symmetry, and are related by inversion symmetry to produce a ten-fold diffraction pattern. The structure is periodic in the direction orthogonal to the ten-fold surface. The surface of d-Al–Ni–Co has been characterized using dynamic LEED [18]. A bulk terminated structure was found, with a degree of relaxation of the outermost layer of approximately 10%.

3.1. Scanning tunnelling microscopy and low energy electron diffraction

The starting surface in this experiment displayed large flat terraces, shown in figure 1. The inset shows a fast Fourier

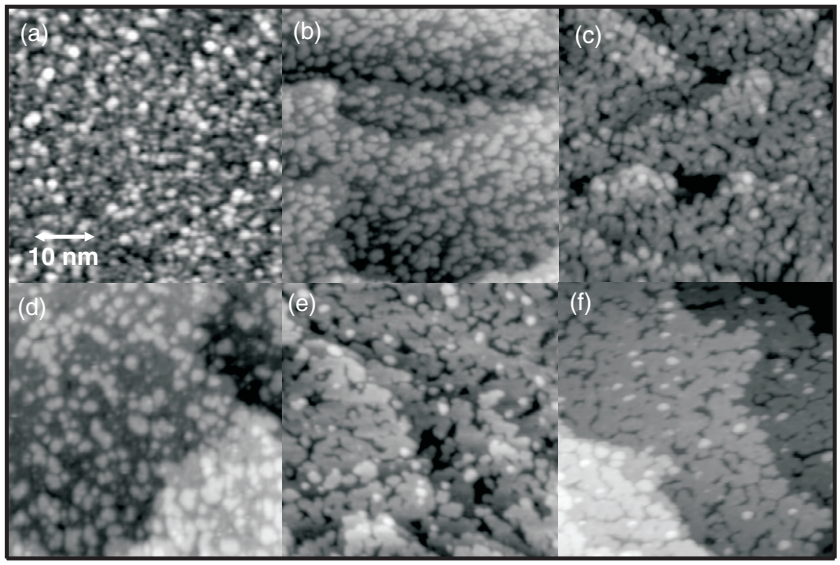

Figure 2. 50 nm × 50 nm STM images of the d-Al–Ni–Co surface after the deposition of (a) 0.13 MLE, (b) 0.4 MLE, (c) 0.8 MLE, (d) 1.2 MLE, (e) 2.3 MLE and (f) 6 MLE of Fe.

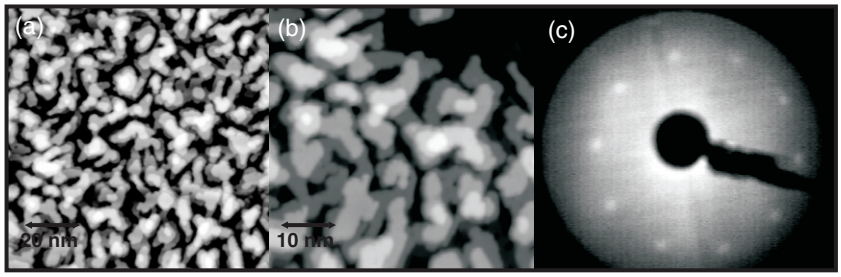

Figure 3. (a) 100 nm × 100 nm and (b) 50 nm × 50 nm STM images of the surface after the adsorption of 9 MLE of Fe on d-Al–Ni–Co; (c) LEED pattern taken with a beam energy of 120 eV.

transform (FFT) taken from this image. The sharpness of the spots indicates a well-ordered substrate.

Figures 2(a)–(c) show the growth process at submonolayer coverages of Fe. At the lowest coverage observed, Fe adsorbs onto the substrate in clusters of average apparent diameter 1.4 ± 0.5 nm. Further deposition increases the density of these clusters, until they join and form an interconnecting array at a coverage of 0.8 MLE. Figures 2(d)–(f) show the continuation of the growth process up to a coverage of 6 MLE. At 1.2 MLE the first layer is fully complete. A faint LEED pattern identical to that of the clean surface is visible at a beam energy of 76 eV. The growth mode during this phase is predominantly layer by layer, with the formation of the second layer occurring as clusters merge together. At 2.3 MLE (figure 2(e)) a nearly complete second layer is formed as the third layer begins to develop. This pattern of growth continues up to a coverage of 6 MLE (figure 2(f)), where no LEED pattern is observed.

As film growth continues up to 9.2 MLE, there is a transition from layer-by-layer growth to multilayer island growth. These islands have a more angular appearance (figures 3(a) and (b)), with large flat bases approximately 8 nm in lateral extent. These form the foundation of subsequent increasingly smaller layers to produce an interconnected terraced structure, consisting of up to four tiers. A monatomic step height of 0.20 ± 0.01 nm was measured using a line profile analysis. The islands align along five-fold directions as shown by LEED (figure 3 (c)); the LEED pattern can be interpreted as resulting from five cubic domains rotated by 72°. Atomic resolution of these islands was not achieved using STM.

3.2. Auger electron spectroscopy

The growth process was also characterized using AES in a separate experiment. Figure 4 shows the magnitude of the peak to peak Auger signal for the Al LMM (68 eV), Co LMM (775 eV) and Fe LMM (651 eV) transitions as a function of Fe coverage. The Ni LMM (716 eV) peak is included in the figure for completeness. Trend lines are added as a visual aid as discussed below.

There is a large surface science literature on the interpretation of the growth mode from AES curves. In the most favourable cases the growth curves can be fitted to extract definitive information on the growth mode [19]. The AES trends can also be qualitatively compared with the expected shapes for various growth modes. Figure 4 shows that after an initial decrease, the Al and Co Auger intensities do not decay

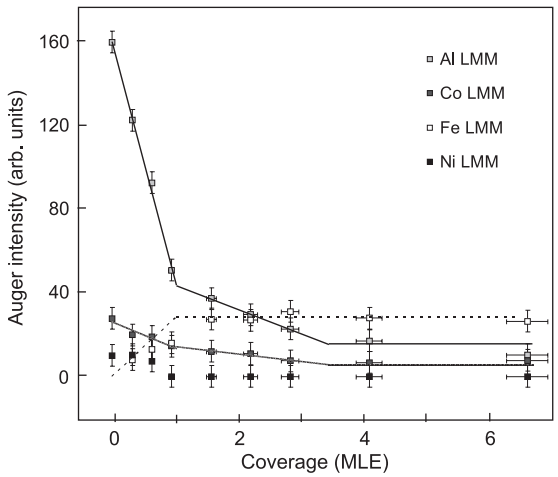

Figure 4. A plot of the Al LMM (68 eV) Fe LMM (651 eV), Ni LMM (705 eV) and Co LMM (775 eV) Auger peak intensity as a function of increasing coverage in MLE as defined in the text. Trend lines are added as a visual aid.

further but remain at a constant value, and the Fe signal initially increases sharply but then also plateaus. This behaviour is indicative of intermixing leading to the formation of a surface alloy [19]. The results are comparable to those of previous studies when surface alloying has been inferred, e.g. for Pb deposited on Au [20].

The completion of the first monolayer is clearly observed as a break in the AES plot for all elements present. The linear rise/fall in the adsorbate/substrate signal indicates a constant sticking probability up to the development of a monolayer. During the formation of subsequent layers, adsorbed Fe intermixes with the substrate. Therefore after the monolayer break it is not possible to observe further line breaks corresponding to the completion of layers, as such breaks are a result of the bulk signal attenuating at a constant rate with each forming layer, which does not occur when intermixing is taking place. The point at which the bulk Auger signals become negligible and the concentration of substrate and adsorbate atoms appears constant, occurs at about 3 MLE. This is indicated by a change in slope in the trend lines shown, although no clear break is observed in the data. Thereafter, no change is seen up to a coverage of 11 MLE, which was the highest coverage measured in this experiment. The data are shown only up to 6 MLE in figure 4, to emphasize the changes taking place in the low coverage regime.

3.3. X-ray magnetic circular dichroism

XMCD was employed as a probe of the magnetic properties of the d-Al–Ni–Co substrate and the deposited Fe film [21]. Circularly polarized radiation can be characterized by a polarization vector (**P**) which points either parallel or antiparallel to the x-ray propagation direction. The magnitude of the XMCD response is given by the projection of **M** onto **P** so that at normal incidence ($\theta = 0°$) the x-rays probe only an out-of-plane magnetization; at $\theta = 60°$, predominantly in-plane magnetization is probed. XMCD is therefore an element specific probe of **M** and, in addition, elegant sum-rules can reveal details of the spin and orbital contributions to the magnetic moment. In this study, however, XMCD is used to extract qualitative comparisons of in-plane and out-of-plane easy axes and the presence of induced magnetic moments.

For a thin film, the internuclear axes are preferentially oriented along the plane of the sample surface. In the absence of a strong interface magnetocrystalline anisotropy, the magnetostatic energy is minimized when atomic magnetic moments align parallel to the internuclear axis leading to an in-plane easy-axis of magnetization. Figure 5 shows hysteresis curves taken at the Fe L_3 edge for 3 MLE of Fe deposited on d-Al–Ni–Co at 5 K clearly indicating that the easy-axis of magnetization is in-plane for the Fe thin film.

There have been several studies of the magnetism of bulk d-Al–Ni–Co performed on single grain samples. Magnetization is described by the equation

$$M = \chi_0 H + M_0. \tag{1}$$

Markert and co-workers [22] found a weak ferromagnetic component of the magnetization $M_0(H)$ and a weak susceptibility $\chi_0 = \Delta M/\Delta H$. The magnetization was found to be slightly anisotropic in-plane and out-of-plane (i.e. perpendicular and parallel to the ten-fold axis). Yamada *et al* also reported a small ferromagnetic component and a weak diamagnetic susceptibility [23]. Jeglič and Dolinšek concluded from a nuclear magnetic resonance study that Co is in a nonmagnetic state in this material [5]. Our measurements of the Co XMCD signal from the clean surface of d-Al–Ni–Co are consistent with these previous studies. The dichroic response, shown in figure 6 (top) for the in-plane geometry, is vanishingly small, but nevertheless present. A similar result was also obtained for the Ni signal (not shown). When the same measurements are performed after the deposition of 3 MLE of Fe, a large increase in the Co XMCD is found (figure 6 (bottom)). A similar increase in the XMCD was also found at the Ni $L_{2,3}$ edges.

There are two possible origins of the increased Co XMCD: (i) the in-plane Fe interface magnetization has induced a large magnetic moment on the neighbouring Co and Ni interface atoms or (ii) Co and Ni atoms which are intermixed with the Fe thin film give rise to the observed XMCD. The second explanation is certainly consistent with the Auger results described in section 3.2 above. Contributions from both of these sources cannot be ruled out in this study.

4. Discussion

The structure of the Fe film observed on the ten-fold surface may be compared to that observed on the five-fold surface of i-Al–Pd–Mn [10]. A similar growth mode was observed in each case; the formation of a disordered layer-by-layer film, followed by a transition to island growth. Nanosized 'wedding cake' like islands are observed in both cases which have roughly the same dimensions, are aligned preferentially along five directions, have a monatomic step height and produce identical LEED patterns. While the films are structurally similar, they are chemically very different. The formation of

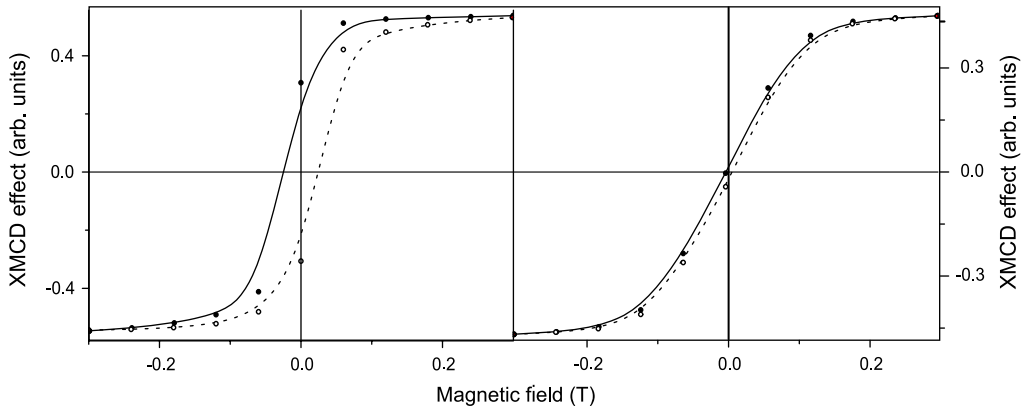

Figure 5. In-plane (left) and out-of-plane (right) hysteresis curves for 3 MLE of Fe deposited on d-Al–Ni–Co at 5 K. The points represent the peak of the Fe XMCD intensity normalized to the pre-edge intensity.

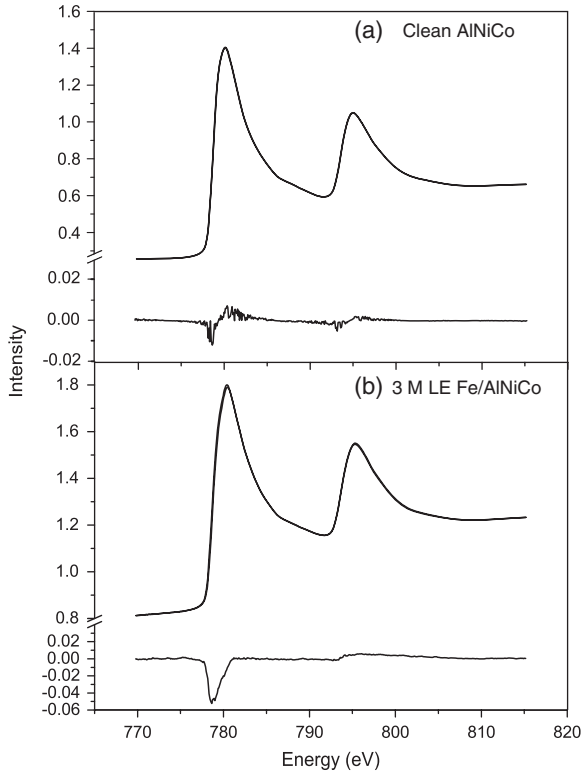

Figure 6. (a) X-ray absorption and associated XMCD spectra at the Co $L_{2,3}$ edges for the clean Al–Ni–Co surface. The geometry is in-plane ($\theta = 60°$), and the measurements were performed at an applied field of 2 T at 300 K. (b) As for (a) after deposition of 3 MLE of Fe.

a pure Fe film is observed for Fe/Al–Pd–Mn, where substrate Auger signals decay exponentially indicating the formation of Fe islands. For Fe/Al–Ni–Co the formation of a surface alloy is observed, up to the maximum coverage studied (11 MLE).

The transition from layer-by-layer growth which occurs at about 9 MLE reflects a change in energetics in the system. This happens when the energy barrier to diffusion down step edges (the Ehrlich–Schwoebel barrier [24]) exceeds the surface diffusion barrier on the flat surface. Perhaps most surprising is that the resulting islands preferentially align along five directions. While it is was not possible to correlate these directions with high symmetry directions of the substrate due to the necessity to move the sample from the STM to the LEED system, it is reasonable to assume that this preferential alignment stems from the influence of the substrate persisting up to these coverages. A study using a depth-dependent structural and compositional technique such as medium energy ion scattering [9, 25, 26] could help clarify this point and also help determine the exact composition of the intermixed film.

These observation of the growth of a multilayer intermixed film indicates that in this system a quasiperiodic single element system is not realized. Taken in conjunction with similar results for Fe on i-Al–Pd–Mn [11], Ni on i-Al–Pd–Mn [10, 27] and the observation of a quasiperiodically modulated periodic row structure for Co on i-Al–Pd–Mn and d-Al–Ni–Co [28], this is further evidence that the ferromagnetic transition elements do not produce quasiperiodic 2d or 3d overlayer systems.

5. Conclusions

STM, LEED and AES measurements of Fe deposited on d-Al–Ni–Co indicate that a disordered film forms up to a coverage of 9 MLE after which multilayered, interconnecting polycrystalline islands are observed. Intermixing of Fe with substrate elements is observed in the film, and after approximately 3 MLE, the relative concentration of elements remains constant. The XMCD results are in agreement with this picture; Fe has a predominantly in-plane magnetization, and Co and Ni both display magnetic moments consistent with their incorporation in the intermixed film, although a contribution from induced magnetism at the interface is not excluded.

Acknowledgments

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