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Surface study of the (100) and (010) faces of the quasicrystal approximant $\text{Al}_4(\text{Cr,Fe})$

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Abstract. Low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM) results are used to study the pseudo-6-fold nature of the (100) surface of the orthorhombic quasicrystal approximant $\text{Al}_4(\text{Cr, Fe})$. LEED patterns are also presented from the pseudo-10-fold (010) surface of this material. In each case the results are compared with the known bulk structure of this complex metallic alloy.

1. Introduction

Complex metallic alloys (CMAs) are characterised as having large unit cells (or, in the case of quasicrystals, infinite unit cells), the presence of well-defined atomic clusters and some inherent disorder in their ideal structure [1]. It is of fundamental interest to understand why combinations of relatively simple elements should lead to such structural complexity. It is also thought that the existence of the cluster sub-structure may give rise to interesting physical properties resulting from the competition between the different length-scales of the clusters and the unit cell [1].

Such materials are generally ternary alloys. Because of their structural complexity, there have been a limited but growing number of studies of the bulk structure of such materials. However, the majority of this work has focussed on quasicrystal surfaces [2] and there have hardly been any surface structural studies on periodic CMA surfaces. Indeed surface studies on alloys have generally focussed on simple binary metallic alloys [3, 4]. The best-studied periodic CMA surface is the ξ' -Al–Pd–Mn (010) face [5–6, 7]. Here the interest is the comparison with the five-fold surface of the icosahedral Al–Pd–Mn quasicrystal.

In this work we discuss the surface structure of a decagonal quasicrystal approximant. The phase diagram of Al–Cr–Fe is particularly rich. Metastable icosahedral quasicrystals have been found in the Al-rich corner of the diagram [8, 9], and stable approximants of a decagonal phase

were found in the Al-poor part [10–13]. A structural model for orthorhombic $\text{Al}_4(\text{Cr,Fe})$ was proposed [14, 10] by comparing high-resolution electron microscopy images with the well-known structure of $\mu\text{-Al}_4\text{Mn}$ [15]. It has since been the subject of an X-ray diffraction study [16]. Its physical properties are also of interest [17, 18]. The structure of the unit cell showing the (100), (001) and (010) facets is shown in Fig. 1. The unit cell dimensions are $a = 12.5006$ nm, $b = 12.6172$ nm and $c = 30.6518$ nm. In this paper we attempt to link the surface structure of the (100) and (010) faces of this intermetallic compound to the previously-determined X-ray structural model.

2. Experimental methods

The $\text{Al}_4(\text{Cr, Fe})$ single crystals were grown by the Czochralski technique from Al-rich off-stoichiometric melts ($\text{Al}_{87}\text{Cr}_7\text{Fe}_6$ to $\text{Al}_{88}\text{Cr}_7\text{Fe}_5$) at about 1050 °C which is well below that of the peritectic transformation. To minimize melt surface oxidation the growth chamber was fully metal-sealed and filled with Ar at ambient pressure. Use was made of native seeds prepared from previous Czochralski experiments. Due to the incongru-

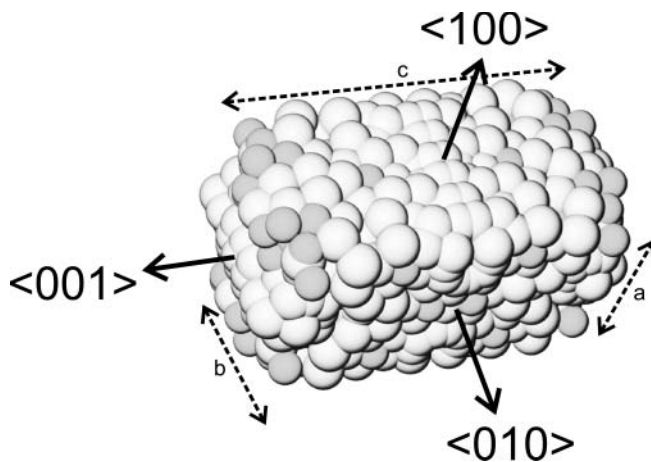


Fig. 1. Representation of the unit cell of the X-ray determined structure of $\text{Al}_4(\text{Cr,Fe})$ [16]. Al atoms are shown in white and transition metal atoms in light grey. Unit cell vectors a , b , and c are indicated.

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ent melt, the liquidus temperature changes with proceeding growth which has to be compensated by a progressively decreasing temperature program as to maintain near-equilibrium growth conditions. The pulling rates were as low as 0.05 to 0.25 mm/h for kinetic and mass transport reasons.

Precisely oriented slices were cut from the grown single crystals using a wire saw. The (100) and (010) surfaces were polished with 7 μm , 1 μm and 0.25 μm diamond paste to obtain a mirror-like surface before cleaning in an ultra-sonic bath and eventual insertion to UHV.

The experiments were carried out in ultra high vacuum chambers where the base pressure of the system was 1×10^{-10} mbar. The local atomic arrangement was probed by using an Omicron STM, calibrated in a standard procedure using a Si(111)-(7 \times 7) sample. The alloy surfaces were prepared by *in-situ* sputtering and annealing processes. Details of the optimum preparation procedures for each face are given in following Section.

3. Results and discussion

In this section we present results of the optimization of the in-vacuum preparation procedures and the LEED and STM data acquired.

3.1 $\text{Al}_4(\text{Cr,Fe})(100)$

This surface underwent cycles of 45 minutes Ar ion sputtering at 500 eV followed by 5 hours annealing to 650 $^{\circ}\text{C}$ up to a total of 40 hours annealing. At this point it was introduced to an Omicron RT-STM 1. As shown in Fig. 2(a) the surface was of high quality, exhibiting step/terrace morphology over a wide length scale. Fig. 2(b) shows a LEED pattern obtained from the surface, showing clearly the pseudo-six-fold structure along with the larger scale two-fold underlying substructure.

High quality STM data were acquired from this surface. These data are shown in Fig. 2(a). Although atomic resolution is not obtained, the cluster-based structure and orientation of the surface are clearly visible, and the aspect ratio of features again corresponds to that expected from the model. The model is based on a sequence of

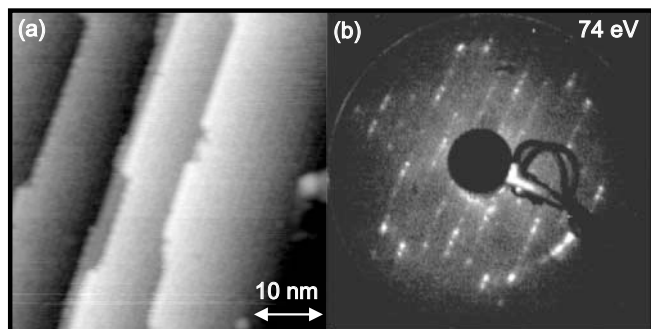


Fig. 2. (a) 750 \times 750 \AA STM image of the (100) face of $\text{Al}_4(\text{Cr,Fe})$, indicating the large terraces formed following the optimised preparation procedure. (b) LEED pattern taken at 74 eV incident beam energy showing both the local six-fold symmetry and the underlying larger-scale two-fold symmetry of the surface.

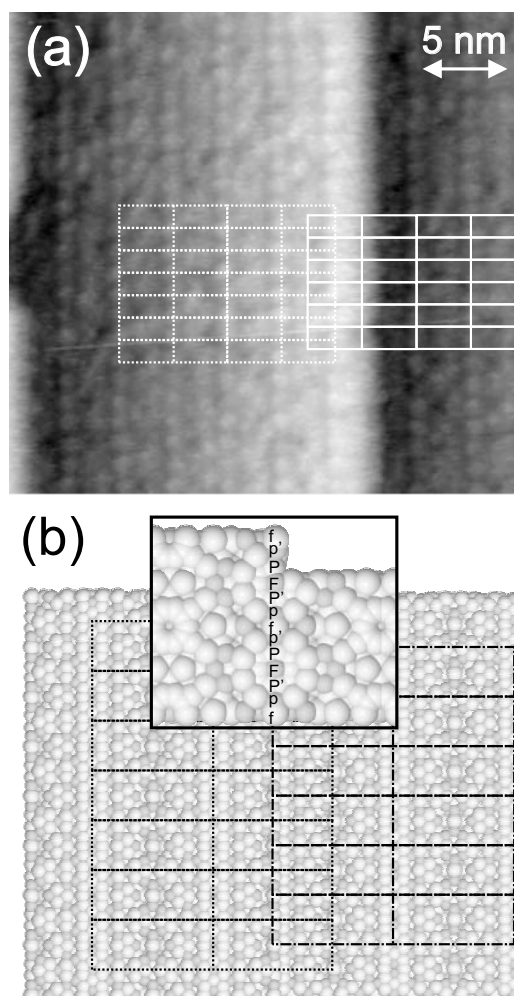


Fig. 3. (a) 300 \times 300 \AA STM image of the (100) face of $\text{Al}_4(\text{Cr,Fe})$, showing a structural terrace. The step-height as measured by STM is 5.8 ± 0.2 \AA . (b) An extended part of the model showing a half-unit-cell step height (6.25 \AA). The inversion symmetry of adjacent terraces is thus demonstrated.

layers pfp'/PFP', where p or P indicates a puckered layer and f or F a flat layer. p' indicates an inversion of p and PFP' an inversion of pfp'. This indicates that there are two equivalent (100) surfaces within each cell unit, and therefore that two terminations ought to be visible in STM, each related to the other by inversion symmetry. This is the case, as is shown in Fig. 3(a). The step height as measured by STM of 5.8 ± 0.2 \AA is close to the value of 6.25 \AA expected from the model given the argument for two terminations presented above.

3.2 $\text{Al}_4(\text{Cr,Fe})(010)$

Several preparation procedures were attempted for this surface. It was found that annealing to a temperature above 600 $^{\circ}\text{C}$ produced a surface that gave LEED patterns with evidence of microfacetting in the movement of spots with beam energy. Lower temperatures (around 550 $^{\circ}\text{C}$) yielded a high-quality LEED pattern without microfacetting. No surface preparation procedure that was tried resulted in a step/terrace morphology suitable for study by STM.

Although the preparation of the (010) surface did not result in a surface suitable for STM, high-quality diffrac-

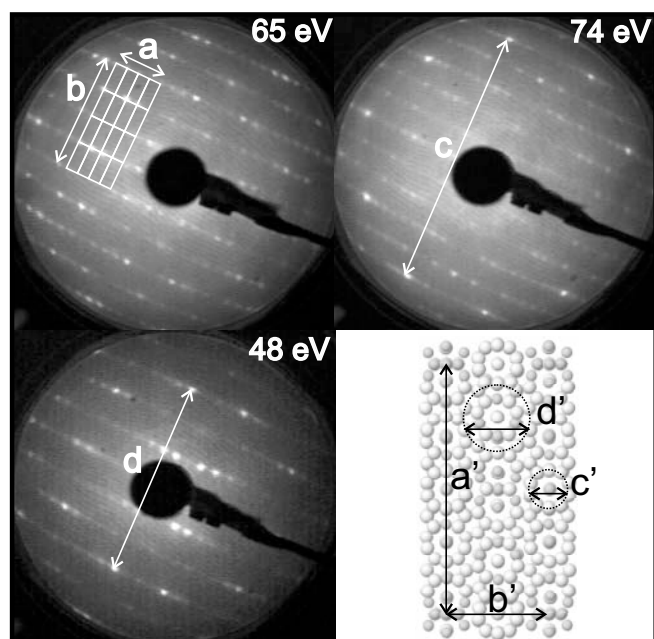


Fig. 4. LEED patterns from the clean (010) surface at various incident beam energies showing clearly the unit cell surface mesh and the pseudo-decagonal symmetry. Certain characteristic distances are highlighted in the images and in the model shown bottom right.

tion patterns were obtainable. These are shown in Fig. 4. The pseudo-decagonal symmetry is clearly manifested in the ten-fold rings observable in the figure, and the large unit cell is evidenced by the dense two-fold mesh. The aspect ratio of the smallest feature visible in the LEED patterns matches that expected from the X-ray structure solution [16].

4. Conclusions

The (100) surface of the orthorhombic phase of $\text{Al}_4(\text{Cr, Fe})$ has been studied using LEED and STM. The surface preparation in this case has proved successful for the purposes of collecting STM data. These data reveal that the unit cell has two terminations at the surface. These terminations appear to be equally favoured. LEED and STM results are consistent with the model proposed by Deng *et al.* [16].

The (010) surface of the orthorhombic phase of $\text{Al}_4(\text{Cr, Fe})$ has also been studied using LEED. A useful surface preparation procedure has been identified, though it will need some optimisation to produce a surface suitable for STM, as evidenced by the microfacetting of the surface observed in LEED patterns.

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