Medium energy ion scattering (MEIS) study from the five-fold surface of icosahedral Ag-In-Yb quasicrystal

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Abstract. Medium energy ion scattering (MEIS) is employed to characterize the composition and structure of the five-fold surface of the icosahedral $Ag_{42}In_{42}Yb_{16}$ quasicrystal. The composition of the surface after sputtering is dominated by Ag and In, and when the surface is annealed at temperatures approaching 430°C, Yb is restored at the surface. The composition is that expected from the bulk structure if the surface is formed at bulk planes involving the centre of rhombic triacontahedral clusters, the building blocks of the system. Structural analysis of MEIS results are also consistent with a surface after annealing that is in close agreement with bulk truncation intersecting the cluster centre.

1. Introduction

The discovery of the binary icosahedral (*i*-)Cd-Yb quasicrystal[1] has led to the development of a series of isostructural ternary quasicrystalline and approximant systems that are suitable for surface studies under ultra-high vacuum (UHV). These systems include *i*-Ag-In-Yb and Ag-In-RE 1/1 approximants (RE: rare earth element Yb, Gd, Yb). The surface structure of these materials has been investigated by scanning tunneling microscopy (STM)[2-7]. The STM images were found to be either dependent on bias voltage[2] or atomic resolution was not obtained[5,6], making it difficult to analyse the images in terms of a bulk structure model. In this work, we employed medium energy ion scattering (MEIS) to characterise the structure and chemical composition of the five-fold surface of *i*-Ag-In-Yb.
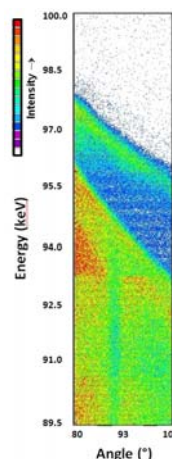
The main building blocks of the *i*-CdYb system are rhombic triacontahedral (RTH) clusters which consist of five successive atomic shells (an outer-most RTH shell composed of 92 Cd atoms, a 30-atom Cd icosidodecahedron, a smaller 12-atom Yb icosahedron, a smaller 20- atom Cd dodecahedron, and an inner 4-atom Cd tetrahedron)[8]. The cluster atoms comprise 93.8% of the total atoms in the crystal with the remaining 'glue' atoms filling the space between the RTH clusters. Cd is replaced by an equal amount of Ag and In in *i*-Ag-In-Yb. However, the exact distribution of Ag and In in the RTH cluster is still unknown. STM studies show that all the three high symmetry surfaces (five-fold, two-

fold and three-fold) of i-Ag-In-Yb truncate at the bulk planes intersecting the centre of the RTH cluster. However, the surface termination of the approximants is still under debate. The MEIS results for the icosahedral material are consistent with surface termination at cluster centres.

2. Experimental Details

The single grain sample of i-Ag-In-Yb (i-Ag$_{42}$In$_{42}$Yb$_{16}$) was grown using the Bridgman method[7]. The sample was cut perpendicular to the three-fold axis and then mechanically polished with successively finer grades of diamond suspension down to 0.25 µm. Subsequently, the surfaces were cleaned in an ultra-high vacuum (UHV) chamber with a base pressure of 2×10^{-10} mbar using repeated cycles of Ar$^+$ sputtering at 3 KeV for 30 mins and annealing at different temperatures up to 430°C for 2 hours each. MEIS data were taken after each annealing.

Figure 1. Two-dimensional MEIS spectra obtained from the clean five-fold i-Ag-In-Yb surface.

The MEIS experiments were carried out at Daresbury Laboratory[10] with a 100 keV He$^+$ ion beam incident on the surface. The angle and energy of the scattered ions were determined using a toroidal electrostatic energy analyser with position-sensitive detector and a data acquisition system which produced 2D spectra such as that shown in Fig. 1. The variation in scattered ion intensity with both scattered energy and angle is represented by a false colour map. By gating specific areas of the two-dimensional spectra and projecting onto either the energy or angle axis, one-dimensional spectra can be produced. Energy spectra typically provide information on the depth dependent composition, while angular spectra provide crystallographic information.[11]

3. Results and Discussion

Figure 1 shows a typical 2D MEIS spectrum from the five-fold surface of i-Ag-In-Yb after annealing. 1D energy and angle cuts from these 2D spectra are shown in Figures 2 and 3 and have been analysed to determine the composition and structure of the top-most layers and sub-surface region just below.

3.1. Surface composition

Figure 2(a) show 1D MEIS energy spectra taking from the five-fold i-Ag-In-Yb surface after sputtering and annealing at different temperatures. The characteristic features observed in the spectra are result of ions scattered from Ag, In and Yb. The peak at lower energy represents both Ag and In due to their similar mass. Only the small step at approximately 90.5 keV provides information on the relative contributions of In and Ag and then only for the top-most layers. As such, whilst the proportion of Yb can be determined with confidence, In and Ag have much larger relative uncertainty.

Figure 2(b) shows the normalised intensities of these elements with respect to their cross-sections (effectively the square of their atomic number) for the top-most layers (within around 4 Å of the surface). Figure 2(c) shows similar data for the sub-surface region (for these measurements, typically 10 to 15 Å below the top-most layers). The concentration of Yb after sputtering is about 15% in the sub-surface region and about 10% in the top-most layers, which is less than bulk composition, suggesting that Yb is selectively removed. The preferential sputtering of Yb and In was also observed

by XPS from the same surface[12]. Both of these elements are heavier than Ag, however, their surface free energy is less. Therefore, the selective sputtering may be related to surface energy of the constituent elements rather than their mass. Elements with low surface free energy are likely to segregate to the surface and can then be sputtered by the incoming ions. The i-Al-Pd-Mn[13] and decagonal Al-Cu-Fe[14] quasicrystals show a depletion of Al upon sputtering. Al is the lightest element but also has the lowest surface free energy among the constituents in both systems. Another factor that may cause the selective sputtering is surface binding energy of the elements[14].
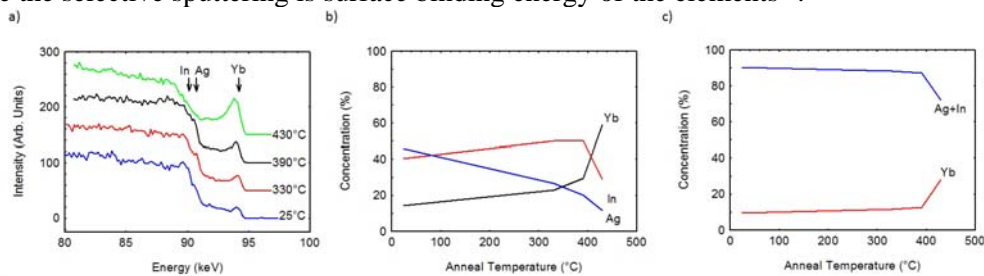

Figure 2. (a) 1D energy spectra from the five-fold i-Ag-In-Yb surface after sputtering and annealing at different temperatures. Peaks relating to Yb, Ag and In are highlighted. (b) Concentrations of Yb, Ag and In in the top-most layers versus annealing temperature extracted from (a) by fitting with the SIMNRA simulation program. (c) Concentrations of Yb and Ag + In combined for the sub-surface region

As the annealing temperature increases, the concentration of Yb increases and Ag/In decreases. At 430°C, the concentration of Yb is roughly 30% in the sub-surface region and about 60% in the top-most layers. These values are higher than the bulk concentration, i.e., also higher than the concentration determined by XPS[12]. For the top-most layers, MEIS is more surface sensitive than XPS, which averages over a slightly larger depth range. The composition of the top-most layers determined from the model structure is $Ag_{11.5\pm2.1}In_{45.7\pm8.7}Yb_{42.8\pm10.8}$. The model surface was selected at bulk planes which intersect the cluster centre and the concentration was determined considering atoms in a slab of 0.5 Å thickness are in a single plane. This thickness was chosen because the maximum projected atomic density in this region is comparable to that of the closed-packed Yb surface. The concentration of Yb would go down if a thicker slab is considered. The measured concentration of Yb in the top-most layers is above this, but the sub-surface region is slightly less than the value expected from the model. This might imply that the sample was annealed to a slightly higher temperature than desirable to obtain the ideal surface compositional profile. As previously stated, the close masses of Ag and In make them difficult to resolve in the MEIS spectra, precluding a similar analysis.

3.2. Structural Analysis

Angular spectra from the quasicrystalline sample after annealing are shown in Figure 3. The spectra exhibit significant noise as a result of the low flux of ions incident on the surface during the experiment. However, for the sub-surface data the three major blocking dips are still observed at 69°, 90° and 110.5°. An angular spectrum has been simulated using the VEGAS analysis code[13] and is included as Figure 3(c) for comparison. For the simulation, we used the atomic positions from the ideal model of the i-Cd-Yb quasicrystal[8] with the model containing an 8 Å slab. Due to the complexity of the model, the theoretical spectrum was limited to an angular resolution of 0.5°. The major blocking dips observed by experiments are reproduced in the calculation both in terms of position and amplitude, evidencing a close similarity between the theoretical and actual atomic positions.

The data from the top-most layers also show the same blocking dips, but with reduced amplitude. This may in part be because of greater illumination of these layers, which is typical for all materials, but enhanced for aperiodic materials where shadowing of the underlying atoms by surface atoms is less. Another possible contribution to the reduced amplitude is the presence of some Yb atoms that are

not sitting in the predicted lattice sites, since this would be consistent with the excess Yb at the surface as evidenced by the compositional data. There is also a slight shift in the positions of the blocking dips towards lower scattering angle. This is evidence that some of the atoms in the top-most layers have relaxed inward towards the bulk. From simple geometric calculations the likely contraction can be deduced to be approximately 8% or around 0.1 Å. However, the lack of any additional features in the surface data suggests that no gross reconstruction of the surface. The MEIS data are consistent with an essentially bulk-like termination at the RTH cluster centres, but with a slight inward relaxation of the outermost atoms. This bulk-like termination is in agreement with STM observations[2].
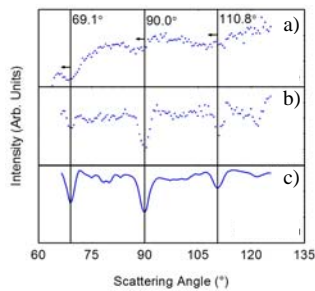

Figure 3. One-dimensional spectra taken along the angle axis, showing the intensity of scattered ions as a function of angle. (a) For the top-most layers (b) for the sub-surface region and (c) a simulated spectrum of the same material.

4. Conclusions

MEIS was used to study the atomic composition and structure of the five-fold surface of *i*-Ag-In-Yb. The surface after sputtering shows Yb depletion which is restored after annealing. This composition is expected for the surface formed at bulk planes intersecting the centre of RTH clusters, the building blocks of the system. Structural analysis is also consistent with bulk truncation at these planes, but with a slight inward relaxation of the top-most atoms.

References
[1]   A P Tsai, J Q Guo, E Abe, H Takakura, and T J Sato 2000 *Nature* **408**, 537
[2]   H R Sharma, M Shimoda, K Sagisaka, H Takakura, J A Smerdon, P J Nugent, R McGrath, D Fujita, S Ohhashi, and A P Tsai 2009 *Phys. Rev. B* **80**, 121401(R)
[3]   C Cui, P J Nugent, M Shimoda, J Ledieu, V Fournée, A P Tsai, R McGrath, and H R Sharma 2012 *J. Phys.: Condens. Matter* **24**, 445011
[4]   P J Nugent, J A Smerdon, R McGrath, M Shimoda, C Cui, A P Tsai and H R Sharma 2011 *Phil. Mag.* **91**, 2862
[5]   C Cui, P J Nugent, M Shimoda, J Ledieu, V Fournée, A P Tsai, R McGrath, and H R Sharma 2014 *J. Phys.: Condens. Matter* **26** 015001
[6]   C Cui, P J Nugent, M Shimoda, J Ledieu, V Fournée, A P Tsai, R McGrath and H R Sharma 2012 *J. Phys.: Condens. Matter* **24**, 445011
[7]   S S Hars, H R Sharma, J A Smerdon, T P Yadav, A Al-Mahboob, J Ledieu, V Fournée, R Tamura, and R McGrath 2016 *Phys. Rev. B* **93**, 205428
[8]   H Takakura, C P Gomez, A Yamamoto, M de Boissieu, and A P Tsai 2007 *Nature Materials* **6**, 58
[9]   C Cui and A P Tsai 2010 *J. Cryst. Growth* **312**, 131
[10]   P Bailey, T C Q Noakes, and D P Woodruff 1999 *Surf. Sci.* **426**, 358
[11]   J.F. van der Veen 1985 *Surf. Sci. Rep.* **5**, 199
[12]   H R Sharma, M Shimoda, S Ohhashi, and A P Tsai 2007 *Phil. Mag.* **87**, 2989
[13]   C J Jenks, J W Burnett, D W Delaney, T A Lograsso, and P A Thiel 2000 *Appl. Surf. Sci.* **157**, 23
[14]   J A Barrow, V Fournée, A R Ross, P A Thiel, M Shimoda, and A P Tsai 2003 *Surf. Sci.* **539**, 54
[15]   J F Frenken, J F van der Veen and R M Tromp 1986 *Nucl. Inst. Methods Phys. Res. B* **17**, 334