

Article



Rónán McGrath is Professor of Nanoscale Physics at the University of Liverpool. He is also a Principal Scientist in the University's Surface Science

Research Centre. His group has been involved in research on quasicrystal surfaces since 1997, and the current focus of their research is on the use of these surfaces as templates for the growth of novel symmetry nanostructures and thin films. He gave the Annual Materials Lecture of the Royal Microscopical Society in 2005 and this article is a resumé of that presentation.

Lydie Leung is a post-doctoral research associate in the Surface Science Research Centre. Her research interests are on the application of scanning



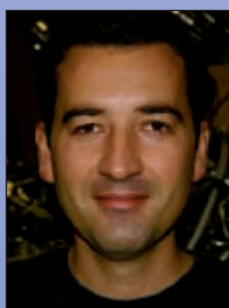
tunnelling microscopy and spectroscopy to quasicrystal surfaces.



Steve Barrett is a Senior Lecturer in the Department of Physics and a Principal Scientist in the Surface Science Research Centre at the University of Liverpool.

He is the author of the Macintosh image analysis software package "ImageSXM" which is optimised for scanning probe microscopy images.

Julian Ledieu was a PhD student and post-doctoral research assistant at Liverpool before moving to the CNRS Laboratoire de Science et Génie des



Matériaux et de Métallurgie (LSG2M) based at the École de Mines in Nancy. His research area is the complex metallic alloys, including quasicrystals and their approximant phases.

Imaging quasicrystal surfaces using scanning tunnelling microscopy

R. McGrath^{1#}, L. Leung¹, S.D. Barrett¹ and J. Ledieu²

¹Department of Physics and Surface Science Research Centre, University of Liverpool, Liverpool, L69 3BX, UK

²LSG2M, CNRS UMR 7584, Ecole des Mines, Parc de Saurupt, 54042 Nancy Cedex, France

Summary

Quasicrystals are a family of complex bi- and tri- metallic alloys having non-crystallographic symmetries and novel, physical and electronic properties. In this article we introduce these materials, describing their discovery and unusual structure. We discuss the advantages of using scanning tunnelling microscopy (STM) to study their surfaces, and we demonstrate the application of various image analysis techniques to extract quantitative information on their surface structure. Lastly we point out some current directions in research on these fascinating materials.

Introduction

The subject area entitled "Solid State Physics" or "Condensed Matter Physics" deals almost entirely with one class of solid materials, those which are crystalline. A cursory glance at any advanced undergraduate textbook will confirm this: Kittel, (Kittel, 1996) for example, devotes only a short chapter to another important class of solids, i.e. the amorphous materials. A third class of materials, the quasicrystals, merits only a passing mention. This is because the methodology of solid state physics is based almost entirely on the assumption of periodicity. In general, the properties of periodic crystals are explicable in terms of transport of particles and excitations through the periodic potential of the atom cores, and their structure can be elucidated using diffraction techniques. Amorphous solids, on the other hand, have no periodicity, indeed no long-range order whatsoever. Quasicrystals are in some ways intermediate between crystals and amorphous materials in that they do have long-range order, but without the imposition of periodicity.

They were discovered serendipitously in 1982 by a young Israeli researcher, Dan Shechtman, who was working during a sabbatical stay at what was then the National Bureau of Standards in Washington D.C. (now the National Institute of Standards and Technology). In his investigations of rapidly quenched aluminium-manganese alloys using electron microscopy, he came across a phase which a selected area diffraction scan revealed had apparent ten-fold rotational symmetry. Every good text-book on crystallography until then carried a simple proof that the only allowed symmetries in crystallographic (i.e. periodic) materials were 1-,2-,3-,4- and 6-fold (see Figure 1). The observation of ten-fold symmetry was a great surprise. Shechtman's paper announcing his discovery was published in 1984 and entitled "Metallic phase with long-range orientational order and no translational symmetry" (Shechtman *et al.*, 1984). The paper was initially met with much scepticism from the crystallographic community. Notably, Linus Pauling, Nobel prize winner in Chemistry in 1954,

Corresponding author: mcgrath@liv.ac.uk



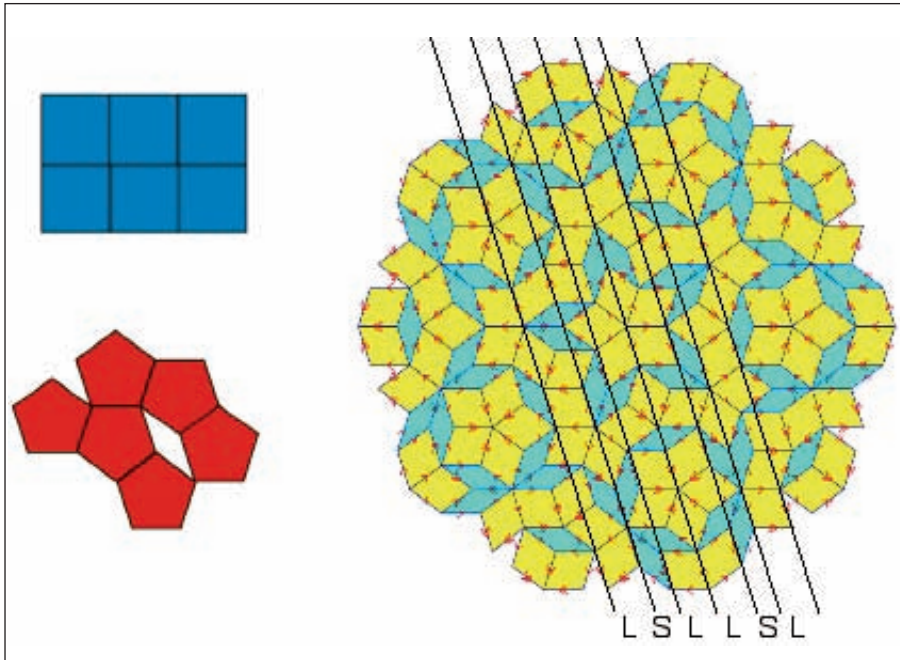


Figure 1. A pattern of identical tiles can cover a plane without overlapping or leaving gaps only if the tiles have certain allowed symmetries. Left: Squares can be arranged periodically to form a tiling, but pentagons cannot; hence 5-fold symmetries are forbidden in periodic crystals. Right: A Penrose tiling is formed when two kinds of four-sided tiles are fitted together according to certain matching rules. This forces the tiling to be quasiperiodic and to possess long-range order. The symmetry of this tiling is 10-fold. Fibonacci spaced lines are drawn by joining identical edges of the tiles.

published a critical assessment of Shechtman's work entitled "Apparent icosahedral symmetry is due to directed multiple twinning of cubic crystals" (Pauling, 1985). However his objections were quickly shown to be invalid, and quasicrystals (an abbreviation of quasiperiodic crystals), as these materials became known, had truly arrived on the materials stage.

So what is the structure of these mysterious materials which appear to defy the conventional wisdom of crystallography? Fortunately there is a simple two-dimensional paradigm which serves to illustrate their geometry. The right-hand side of Figure 1 shows a Penrose tiling. These tilings, discovered by Sir Roger Penrose in 1974, consist of two kinds of four-sided tiles that are fitted together according to certain "matching" rules (indicated by arrows). This forces the tiling to be quasiperiodic and to possess long-range order.

The mathematics necessary to describe such tilings is simple yet elegant. An important element is the ability to describe non-periodic sequences of two objects which have a well-defined structural relationship. We can generate such

a sequence by considering two simple substitutional rules; starting with two entities, denoted L and S, successive terms are obtained by obeying the rules $L \rightarrow LS$ and $S \rightarrow L$. The first few terms are thus S, L, LS, LSL, LSLLS, LSLLSLSL.... The sum of L and S entities in each generation gives the Fibonacci numbers 1,1,2,3,5,8,13,.... The ratio of successive terms approaches an irrational number known as the golden mean τ (approximately equal to 1.618) as the sequence grows to infinity. Figure 1 shows a Fibonacci sequence of lines drawn on a Penrose tiling by joining matching edges of the tiles.

We can extend this concept by considering three-dimensional Penrose tiles. If a three-dimensional Penrose tiling is decorated by the addition of suitable clusters of atoms to give the material the appropriate chemical stoichiometry, we have a model of a quasicrystal which will exhibit an appropriate 5- or 10-fold diffraction (Figure 2). This rather simple description, while avoiding the geometrical complexities of more realistic models, nevertheless serves to illustrate the essential elements involved in quasicrystal structure.

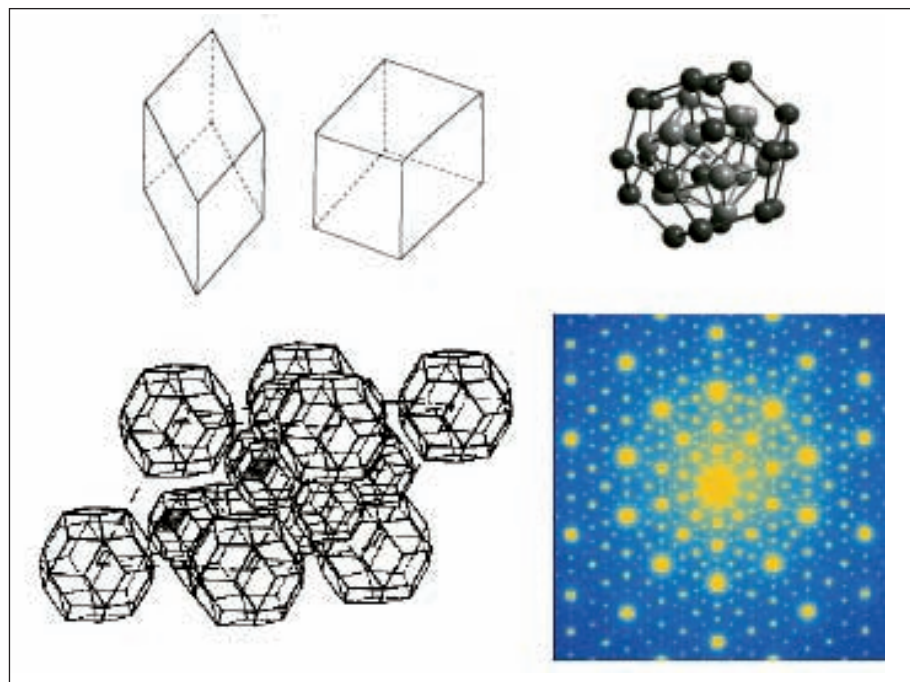


Figure 2. Top left: 3-dimensional Penrose tiles; Top right: An example of the atomic clusters which decorate the vertices of the 3-dimensional Penrose tiling in the model; Bottom left: Schematic of the resulting 3-dimensional cluster structure of the quasicrystal; Bottom right: an electron diffraction pattern from an icosahedral quasicrystal which has 10-fold rotational symmetry. The presence of sharp spots reveals the material has long-range order.

Before moving to a description of our work in imaging surfaces of quasicrystals, it is worth noting that the International Union of Crystallography adopted a new definition of what constitutes a crystal in 1992 (International, 1992). The traditional definition of a crystal as a mathematical lattice plus a basis of atoms was replaced by the statement that a crystal is “any solid having an essentially discrete diffraction pattern”. Although this wording may appear vague at first glance, it purposely shifts the definition of what constitutes a crystal from “real space” to “Fourier” or “reciprocal” space and has the effect that both periodic and aperiodic (quasicrystalline) materials are just different classes of crystals. It seems however, that even the latest textbooks on condensed matter physics remain unaware of this development (Singleton, 2001)!

STM imaging and image analysis

In early research on bulk quasicrystals, it was discovered that there are many interesting tribological aspects of quasicrystalline materials, which include their high hardness and resistance to wear, their oxidation resistance, and their low coefficients of friction compared to other metals (Trebin, 2003). These properties are related to the surfaces of these materials and provided the motivation for a programme of surface studies. Such studies became possible when the preparation of single-grain quasicrystals with large enough surface areas (1 cm^2) for conventional surface science techniques was perfected. Research on quasicrystal surfaces in Liverpool began in 1997.

The initial aim of our surface characterisation work was to determine the atomic structure of the surface. Surfaces of materials often exhibit different atomic arrangements than the bulk because the atoms at the surface have lower coordination; in energetic terms the surface will minimize its surface free energy. This often leads to structural effects such as relaxation, where the outermost layers have interlayer spacing different from the bulk, and the more drastic phenomenon of reconstruction, where atoms at the surface rearrange into a structure which is more complex than a simple termination of the bulk structure.

Over the past forty years, many surface science techniques have been developed to provide quantitative information on surface structure. Among the most successful are low energy electron diffraction (LEED) and surface x-ray diffraction (SXRD) where measurements of diffraction spot intensities are compared with calculations based on trial structures. However these tools are not easily applied to solve quasicrystal surface structure because the calculations of diffraction spot intensities are based on periodic unit cell

calculations. Scanning tunnelling microscopy, however, being an imaging technique, provides real space information which can be analysed and interpreted without recourse to a periodic formalism.

We start by presenting data for $\text{Al}_{70}\text{Pd}_{21}\text{Mn}_9$. This material is a three-dimensional quasicrystalline alloy, and can be grown using conventional methods such as the Bridgman or Czochralski techniques. It is the most widely available and hence the most studied of the quasicrystalline alloys, and it possesses icosahedral symmetry, meaning that the bulk structure has five-fold, two-fold and three-fold axes of symmetry. In what follows we will concentrate on the surface polished perpendicular to the five-fold symmetry axis, i.e. a “five-fold” surface.

Our surface preparation methodology, developed over the course of a number of years, involves careful alignment and cutting of the samples in the correct orientation followed by manual polishing of the surface to be studied using successively finer grades of diamond paste. After insertion into an ultra high vacuum chamber, the sample surface is first cleaned by a process of bombarding the surface with argon ions accelerated through a potential of about 1 keV. This removes the topmost surface layers, including any oxide and contaminants. However it also means that the topmost region of the sample is left disordered and depleted of the lighter elements. Hence prolonged annealing at temperatures of order 940 K is necessary to restore the quasicrystalline composition and long-range order at the surface by diffusion from the bulk.

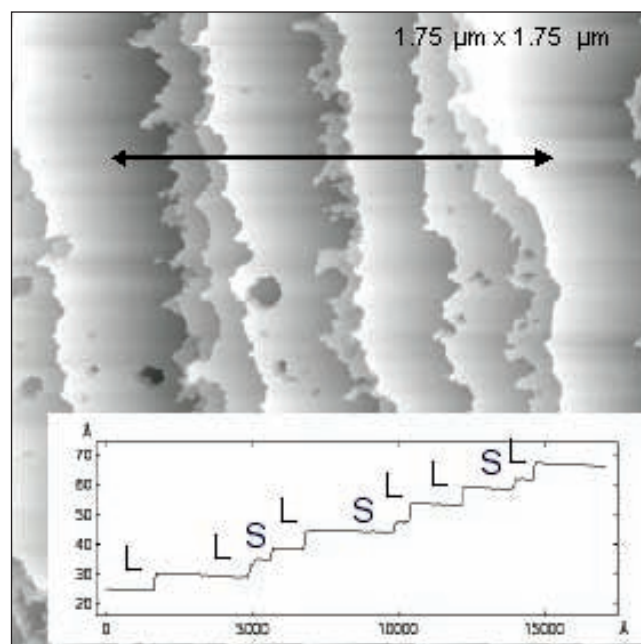


Figure 3: $1.75 \mu\text{m} \times 1.75 \mu\text{m}$ image of the five-fold surface of icosahedral AlPdMn . Inset: a line profile along the direction indicated by the arrow. Two step heights are observed, $L=6.6 \text{ \AA}$ and $S=4.1 \text{ \AA}$, and the sequence of these steps is consistent with the Fibonacci sequence.

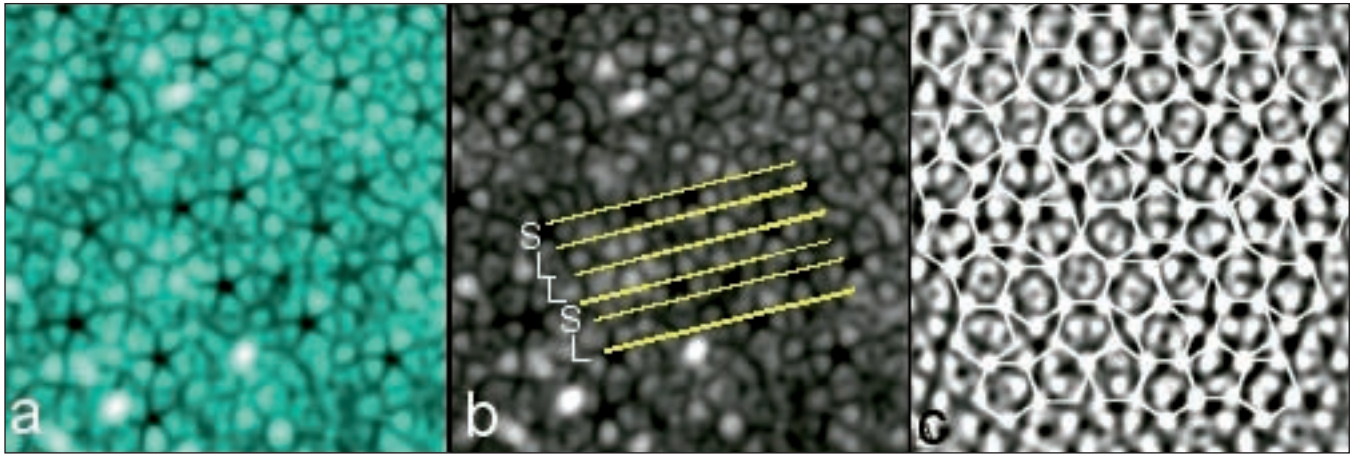


Figure 4: (a) 100 Å x 100 Å image of the clean five-fold surface of AlPdMn. (b) The same image as (a), with lines superimposed by joining identical points of the characteristic “dark star” motifs. The sequence of spacings LSLLS (from bottom to top) is consistent with the Fibonacci sequence. (c) A 100 Å x 100 Å image after Fourier filtering. A Penrose P1 tiling has been formed by inserting pentagons whose vertices coincide with high contrast points of the image.

Following such procedures, surfaces such as those shown in Figure 3 are generated. This image shows a 1.75 μm x 1.75 μm image of a quasicrystal surface. The flat regions or terraces, are separated by steps with heights measured at 4.1 ± 0.2 and 6.5 ± 0.2 Å. The inset to this figure is a height profile along the line indicated in the image. The sequence of step heights observed is LLSLSLLSL, which is consistent with the Fibonacci sequence. Furthermore, the ratio of L to S step heights = 1.61, which within experimental error is equal to the golden mean τ . This simple analysis provides immediate evidence for the 3-dimensional Fibonacci/Penrose structure of this material.

Figure 4(a) shows a higher resolution scan of the surface over a 100 Å x 100 Å section of the surface. This scan is at the best resolution that can be achieved. What can we learn about the atomic structure of the surface from such scans? Although the surface is not periodic, there are certain striking arrangements of motifs which recur at many locations. These include the “dark star” and the “white flower” motifs which have proved extremely useful in comparisons with models of terminations of the bulk structure. However, bearing in mind that what the scanning tunnelling microscope actually measures is the electronic joint density of states between the tip and the sample, it is dangerous to ascribe the protrusions and asperities observed to atoms. Furthermore, as the material is quasiperiodic, it is impossible to assign a unique unit cell to the surface which could be used as a basis for further analysis. Progress can be made however using other strategies.

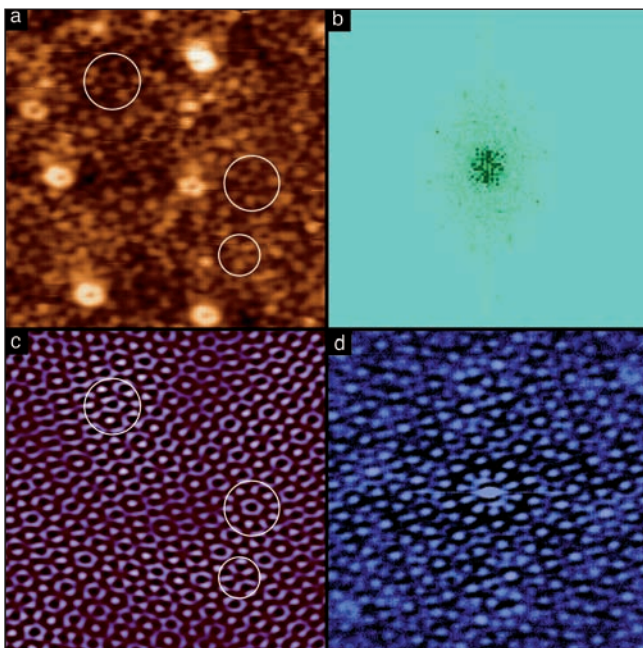


Figure 5: (a) 200 Å x 200 Å image of the ten-fold surface of the decagonal quasicrystal Al₇₀Ni₁₃Co₁₇. (b) Fourier transform of the image in (a), showing two ten-fold rings of spots where the distances between the rings are related by powers of the golden mean. (c) Inverse Fourier transform of (b) after applying a mask to suppress those spatial frequencies that are not related to the 10-fold symmetry of the surface structure. (d) Two-dimensional autocorrelation function derived from the Fourier transform (b) of the image (a).

Figure 4(b) shows the same image but with the superposition of several lines, which are drawn parallel to each other and aligned and positioned along major axes of the “dark stars”. The lines naturally have two separations, of $L=7.4$ and $S=4.6$ Å. The sequences of these spacings, LSLLS, is consistent with the Fibonacci sequence, and the ratio of the spacings is 1.6, again consistent with the quasiperiodic geometry of the material. This image can be actually tiled by filling the surface with pentagons whose vertices join high intensity protrusions on the surface. Figure 4(c) shows a part of a tiling derived in this way; it is in fact a portion of a Penrose P1 tiling, where the tiles have edge length 8.0 Å. We have in collaboration with theorists, been able to derive such tilings from slices through the bulk geometric models; the edge-length of the tiling derived from the model is 7.8 Å, in good agreement with the experimentally derived value.

Through comparisons such as this, much progress has been made in determining the atomic structure of the surface. A detailed understanding of the atomic

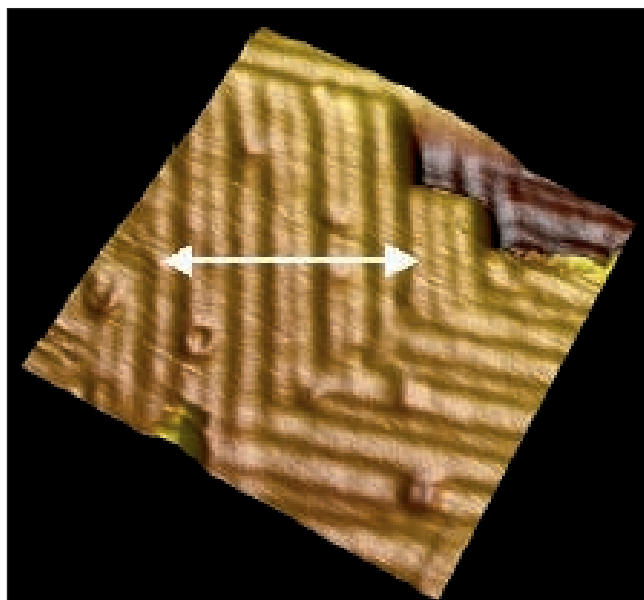


Figure 6: 100 Å x 100 Å scanning tunnelling microscopy image of 5.5 monolayers of copper deposited on the five-fold surface of Al-Pd-Mn. The sequence of the row spacings along the arrow is LSLLSLSLL where $S=4.5 \pm 0.2$ Å and $L=7.3 \pm 0.3$ Å. The ratio of these numbers equals the golden mean τ within experimental error.

composition of the “dark stars” and “white flowers” has been achieved, and indeed this information has allowed us to propose some general rules for what terminations of the bulk structure are to be expected when a surface is formed (Papadopolos *et al.*, 2004).

In situations where the 5-fold or 10-fold symmetry of the surface structure is not very clear in STM images, there are a number of image analysis techniques that can be applied to enhance the recognition of quasicrystalline symmetry and extract quantitative structural information. $\text{Al}_{70}\text{Ni}_{13}\text{Co}_{17}$ is a decagonal quasicrystal which is quasiperiodic only in the direction perpendicular to a ten-fold axis of symmetry (Ferralis *et al.*, 2004). Flat surfaces of this material are more difficult to prepare and often contain ordered protrusions. This has the effect of degrading the resolution which can be achieved on the underlying surface.

Figure 5 (a) shows an image of a ten-fold $\text{Al}_{70}\text{Ni}_{13}\text{Co}_{17}$ quasicrystalline surface that exhibits quasicrystalline symmetry but lacks the clarity of the images of AlPdMn shown in Figure 4. Figure 5 (b) shows a Fourier transform of this image which displays 2 ten-fold rings of spots where the distances between the rings are related by powers of the golden mean. These spots clearly indicate the presence of a surface structure possessing quasicrystalline symmetry, even though this is difficult to detect by inspection of the original image. Figure 5 (c) is the inverse Fourier transform of Figure 5 (b) after applying a mask to suppress those spatial frequencies that are not related to the 10-fold symmetry of the surface structure. This Fourier filtering preserves the 10-fold (and also 5-

fold) symmetry of the original image and effectively removes all other contributions to the image, including periodic and random noise components. As the filtering removes the zero-frequency and low-frequency components, the filtered image also does not show the large protrusions that are distributed over the original image. Thus, the Fourier filtered image exhibits the quasicrystalline nature of the original image without any of the contributions that prevent that structure from being observed clearly. The spatial correspondence between the original image and the Fourier filtered image can be seen by comparing three features that have been highlighted at the same positions in each of the two images — two decagonal rings and a pentagonal cluster.

Figure 5 (d) is the two-dimensional autocorrelation (AC) function, or AC image, derived from the Fourier transform of Figure 5(b). This again illustrates the extent of quasicrystalline ordering of the surface, as the AC of an image that has only short-range order will exhibit variations in intensity close to the centre of the AC pattern but will be featureless at greater distances. The AC function can be further analysed by calculating radial distribution functions that yield information on nearest-neighbour spacings — such analysis has proved valuable in making further quantitative comparisons with geometric models of the bulk structure.

Current research directions

Although much has been achieved using the techniques and analysis strategies described above, there are limits to the amount and quality of information which can be gleaned in this way. There is a clear route to achieve further progress, which ironically involves calculations based on a periodic formalism. Approximants are periodic systems with large unit cells which are close in composition to quasicrystals and which display similar local structures. Density functional theory calculations of the surface structure of such model systems have become feasible due to increases in computing power. An additional calculation-based procedure can then be followed to simulate STM images, and the comparison of experimental data with these simulations will give further insight into the nature of these complex surfaces.

A major theme which has developed in the past couple of years and which builds on our understanding of clean quasicrystal surfaces is to use them as templates for the formation of novel symmetry nanostructures, monolayers and thin films of other elements. A strong motivation for such studies is the desire to understand the origin of some of the unusual physical properties of quasicrystals such as relatively low electrical and thermal conductivity, negative coefficient of resistivity, low surface energy, and low

coefficient of friction (Trebin, 2003). However quasicrystals display considerable chemical complexity, being for the most part ternary alloys. Thus it is difficult to distinguish whether the origin of these unusual physical properties lies in this chemical complexity or in the quasiperiodic structure. The fabrication of *single-element* quasiperiodic structures through adsorption on quasicrystal surfaces offers a route to explore the implications of quasiperiodicity in a system of considerably reduced complexity.

Figure 6 shows an example of what may be achieved in this way. In this experiment, monolayers of copper were deposited on the clean five-fold surface of AlPdMn. The structure of the copper overlayer was strongly influenced by the quasicrystal surface. The figure shows an image of the copper layer after the deposition of 5.5 monolayers. The copper self-organises into five domains aligned along the major symmetry axes of the surface. A row structure is seen in the image where the rows have two spacings, L and S, whose sequence from left to right L S L L S L S L L is consistent with terms of the Fibonacci sequence. Subsequent analysis shows that along the rows the structure is that of crystalline copper (Ledieu *et al.*, 2004), (Ledieu *et al.*, 2005).

Conclusions

The activity in this field in the past few years has led to a consensus that quasicrystalline surfaces are in general terminations of the bulk structure, without the presence of significant relaxation and reconstruction (Thiel, 2004). This conclusion is supported not only by evidence from STM measurements but also from a range of other surface techniques such as low energy electron diffraction, medium energy ion scattering and helium atom scattering. The conclusion has been tested for several of the icosahedral quasicrystalline alloys which are structurally similar to AlPdMn, and also for the decagonal quasicrystal AlNiCo. These surfaces are now being used to grow nanostructures and ultrathin films whose structure is strongly influenced by the quasicrystal surface itself.

Acknowledgements

We gratefully acknowledge financial support from the UK Engineering and Physical Sciences Research Council. SDB's Image SXM is available from www.imagesxm.org.uk. We thank the Ames Laboratory at Iowa State University for providing the samples used in the work described in this article. Uwe Grimm is thanked for providing material for Figure 1 and Conradin Beeli for material for Figure 2.

References

- Ferralis, N., Pussi, K., Cox, E. J., Gierer, M., Ledieu, J., Fisher, I. R., Jenks, C. J., Lindroos, M., McGrath, R. & Diehl, R. D. (2004) Structure of the tenfold *d*-Al-Ni-Co quasicrystal surface. *Phys. Rev. B* 69, 153404.
- International, Union of Crystallography (1992) Report of the Executive Committee for 1991. *Acta Crystallographica* 48, 922-946.
- Kittel, C. (1996). *Introduction to Solid State Physics*. 7 edit, John Wiley and Sons, Inc, New York.
- Ledieu, J., Hoeft, J. T., Reid, D., Smerdon, J., Diehl, R. D., Lograsso, T. A., Ross, A. R. & McGrath, R. (2004) Pseudomorphic Growth of a Single Element Quasiperiodic Ultrathin Film on a Quasicrystal Substrate. *Phys. Rev. Lett.* 92, 135507.
- Ledieu, J., Hoeft, J. T., Reid, D., Smerdon, J., Diehl, R. D., Lograsso, T. A., Ross, A. R. & McGrath, R. (2005) Copper adsorption on the five-fold Al₇₀Pd₂₁Mn₉ quasicrystal surface. *Phys. Rev. B* 72, 035420.
- Papadopolos, Z., Pleasants, P., Kasner, G., Fournée, V., Jenks, C. J., Ledieu, J. & McGrath, R. (2004) A maximum density rule for bulk determinations of quasicrystals. *Phys. Rev. B* 69, 224201.
- Pauling, L. (1985) Apparent icosahedral symmetry is due to directed multiple twinning of cubic crystals. *Nature* 317, 512.
- Shechtman, D., Blech, I., Gratias, D. & Cahn, J. W. (1984) Metallic phase with long-range orientational order and no translational symmetry. *Phys. Rev. Lett.* 53, 1951.
- Singleton, J. (2001). *Band Theory and Electronic Properties of Solids*. Oxford Master Series in Condensed Matter Physics, Oxford University Press, Oxford.
- Thiel, P. A., Ed. (2004). Vol. 75. *Prog. Surf. Sci.*
- Trebin, H.-R., Ed. (2003). *Quasicrystals: Structure and Physical Properties*. Berlin: Wiley-VCH.

Surface Investigation Scanning Tunneling Microscopy Image Icosahedral Quasicrystal Convergent Beam Electron Diffraction Pattern Decagonal Quasicrystal. These keywords were added by machine and not by the authors. This process is experimental and the keywords may be updated as the learning algorithm improves.Â Nissen HU., Beeli C. (2002) Electron Microscopy and Surface Investigations of Quasicrystals. In: Suck JB., Schreiber M., HÄussler P. (eds) Quasicrystals. Springer Series in Materials Science, vol 55.