MEETING REPORT

Aperiodic crystals*

Aperiodic crystals, which exhibit the discrete diffraction patterns in spite of absence of long-range periodicity, exist in almost every type of solid, including organic and inorganic compounds, minerals, metals and alloys, and even macromolecules. It is convenient to describe their structures in superspace (higher dimensional space), a conceptual environment, in which aperiodic crystals recover their periodicity. Studies of aperiodic structures have greatly contributed to a better understanding of the new perspectives for correlating the structures with the physical properties of complex materials. After the landmark discovery of quasicrystals (QCs) in 1982 by D. Shechtman, the International Union of Crystallography (IUCr) changed the definition of crystals and thus coined the term 'aperiodic crystals' in 1991 (*Acta Crystallogr. A*, 1992, **48**, 922–946). The official definition of IUCr says that 'by "crystal" we mean any solid having an essentially discrete diffraction diagram, and by "aperiodic crystal" we mean any crystal in which three-dimensional lattice periodicity can be considered absent'. The terminology of 'aperiodic crystal' was in vogue to encompass the QCs and incommensurate crystals and incommensurate composite crystals. The incommensurate crystals are basically the modulated structure of periodic crystals, whereas QCs are a completely new type of crystals without having any fundamental periodic lattice in three dimensions. The triennial conference series was initiated under the auspices of the commission of 'Aperiodic Crystals' of IUCr. It was first held as 'Aperiodic-94' at Les Diablerets, Switzerland and subsequently at various other venues. It is pertinent to point out that in 1988, this conference series in the name of MOSPOQ was held at Banaras Hindu University, Varanasi.

The seventh conference in the series was held under the chairmanship of R. L. Wither and S. Schmid (co-chairs) from Australian National University, Canberra. There were 111 participants who attended from all over the world from various disciplines. The technical programme consisted of 3 tutorials, 9 invited talks, 48 contributed talks and 2 poster sessions totalling 106 papers. There were lively discussions on the following topics: Crystallographic and structural studies of QCs; Metallurgy, synthesis, growth and stability of QCs and related complex metallic alloys; Frustration, defects, partial order, correlated disorder and structured diffuse scattering in incommensurate crystals; Electronic, magnetic and other physical properties of aperiodic crystals; Dynamics of aperiodic crystals; Aperiodic surfaces, thin films and adsorbents; Quasiperiodic soft matter and biomolecular aperiodic ordering; Applications of aperiodic crystals, including metamaterials and photonic QCs. Details of the conference and abstracts of the papers presented can be found at: http://rsc.anu.edu.au/Aperiodic2012. In the following sections some interesting issues that were discussed intensely during the conference are highlighted.

Nobel lecture on discovery of quasi-periodic crystals

In this conference, there was a festive celebration on the award of the 2011 Nobel Prize in Chemistry to Dan Shechtman (*Phys. Rev. Lett.*, 1984, **53**, 1951) for the discovery of QCs. On this occasion, a special 'Nobel lecture' was delivered by Dan Shechtman under the chairmanship of A. P. Tsai (Japan). The lecture highlighted the history related to the discovery of QCs in 1982, which led to the paradigm shift in crystallography. The forbidden rotational symmetry ($m35$) in the electron diffraction patterns obtained from rapidly solidified Al–14% Mn alloys was elegantly recorded on 8 April 1982 by Shechtman in his well-circulated notebook (Figure 1). However, at that time, the crystallographers were not ready to accept the new structural order without any long-range translational order (periodicity) in solid state which can exhibit the discrete diffraction patterns, as it was defying the conventional wisdom that the crystals must have long-range periodicity in order to have sharp diffraction patterns and consequently the allowed rotational symmetry. Thus, this landmark discovery of QCs should be recognized as the evolution of a new and another perfect order in solid state instead of the demise of perfect order (*Curr. Sci.*, 2011, **101**, 981). At the end of this historical and interesting presentation, he predicted that still there are many more discoveries waiting to be made in the area of QCs and thus inspired the young delegates to pursue work with full conviction and enthusiasm.

Quasicrystals

During the tutorial session, Tsai discussed how the discovery of stable QCs

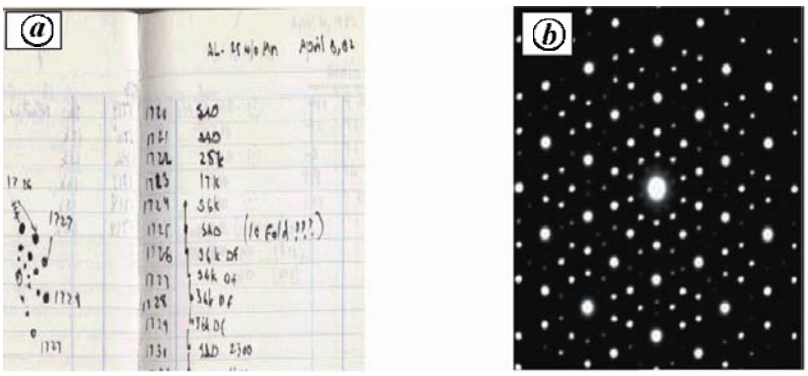

Figure 1. ***a***, Note book record showing the observation of 10-fold pattern from quasicrystal. ***b***, 10-fold Electron diffraction pattern. Later, it has been found to conform to 5-fold symmetry of icosahedral group ($m\bar{3}\bar{5}$). (Courtsey: D. Shechtman).

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(in 1987) was made and helped understand the structure and the possibility of applications. T. Janssen (The Netherlands) described that the superspace concept advocated in early seventies is helpful to determine the structures of incommensurate crystals, QCs and incommensurate composites. The various features for different classes of aperiodic crystals have been addressed. P. A. Thiel (USA) dealt with our latest understanding of solid surfaces on the QCs. It was mentioned that Al-based QCs exhibit resistance to surface oxidation, promising catalytic properties (i.e. steam forming of methanol) and low friction coefficient due to their aperiodicity. The correlations of these properties with atomic structure of the surface were discussed. The statistical description of aperiodic structures using the concept of average unit cell (AUC) was presented by J. Wolny (Poland). Structure factor for different aperiodic structures was determined using this concept. The structure refinement of three decagonal phases in Al–Cu–Me (Me = Co, Rh, Ir) was worked out by P. Kuczera (Poland) using the SUPERFLIP program based on charge flipping algorithm with reasonable *R*-values. The structure refinement was performed in real space using the AUC approach. T. Ors (Switzerland) presented the structural analysis of decagonal ZnMgDy QCs. The results were discussed with a cluster-covering model. The reconstructed electron density shows structural motifs similar to HRTEM studies reported in the literature. H. Takakura (Japan) presented the work on structure refinement using the single-crystal X-ray data of a ternary $Mg_{41}Cd_{41}Yb_{18}$ QC. The 6D model is composed of three non-equivalent occupation domains (ODs) disposed at (000000), (111111)/2 and (100000)/2. The structure refinement suggested that Mg atom preferentially occupies OD at (000000). This means that Mg replaces Cd in threefold and fivefold vertices of the outermost shell of the rhombic tricontahedron (RTH) cluster and at the vertices of the dodecahedron shell inside the cluster. These preferential sites of Mg atoms are intimately linked to each other by the connection scheme of RTH clusters in QC.

R. Al Aijouni (USA) studied the octagon-based quasicrystalline formation in Islamic architecture. A global multi-level structural model derived from these drawings is presented. This model is able to describe the global long-range translational and orientational order of 8-fold and 16-fold quasilattice symmetries in Islamic architecture. A new method has been advocated to construct infinite patches of octagon-based quasicrystalline tiling, including Amman–Beenker tiling, without the need for local strategies (matching, scaling, etc.) or complicated mathematics. H. R. Trebin (Germany) presented evidence that QCs confirm all predictions of the random tiling hypothesis in a fully atomistic model. The free energy calculations confirm the phase transition from an entropically stabilized decagonal random tiling phase to an energetically stabilized periodic crystal. It is important to observe that at the transition one of the phason elastic constants changes sign. J. Yuhara (Japan) studied the composition of decagonal Al–Co–Cu surface by Auger electron spectroscopy (AES) and low energy ion scattering (LEIS). Two types of characteristic clusters were observed by scanning tunnelling microscopy (STM). Structural optimization using *ab-initio* calculations based on density functional theory was performed on several compositional models. It was found that the topmost layer was composed of Al and Cu atoms and the compositional ratio was consistent with AES and LEIS results. R. Mcgrath (UK) studied the growth of thin films of various elements and molecules on the surface of icosahedral Ag–In–Yb QCs using the surface science techniques. It has been shown that quasicrystalline molecular thin film has been formed on the surface substrate. The observed model structures of single element quasicrystalline thin films can be used to study the influence of atomic order in physical space.

T. Takeuchi (Japan) explored the development of thermal rectifier using Al-based QCs. The characteristic behaviour is caused due to the fact that there is a narrow pseudo-gap of a few hundred meV in width at Fermi energy under the influence of quasiperiodic structure. It was estimated that from the theoretical calculations using the experimentally determined thermal conductivity, the thermal rectifier consisting of Al–Fe–Cu icosahedral QC and polycrystalline Si is capable of possessing thermal rectification ratio (TRR) in excess of 1.5. Indeed the large TRR value exceeding 1.4 was experimentally confirmed for the thermal rectifier consisting of Al–Fe–Cu icosahedral QC and polycrystalline Si placed between two heat reservoirs kept at 300 and 550 K. N. K. Mukhopadhyay (India) studied the indentation hardness behaviour in milled powder of Al–Fe–Cu icosahedral QCs. This nano-QC phase was prepared by spray-forming followed by mechanical milling using high-energy ball mill. The hardness data obtained from micron-sized to nano-sized QC particles were analysed and it was found that QC materials show a new phenomenon like 'inverse Hall–Petch' (IHP) behaviour in nano scale (Figure 2). This has been attributed to the grain-boundary sliding, rotational and grain movement. Mechanistic diffusion during the indentation may also cause the materials to soften. The effect of Ga in Al–Pd–Mn QC was also presented. Ga goes to solid solution of QC alloy to a limited extent and influences the resistivity to a great extent. This alloy system is found to have good property as coating material. In addition, the structural details of nano-spinel prepared from milled QC powder of Al–Fe–Cu system were also analysed using Mössbauer spectroscopy.

Incommensurate crystals

L. Palatinus (Czech Republic) showed *ab-intio* structure solution of incommensurate structures from electron diffraction data. It has been demonstrated that by combining two techniques: precision electron diffraction and electron diffraction tomography, the solution of crystal structure can be achieved on a regular basis. It was further shown by A. A. Stewrt (France) that automated diffraction

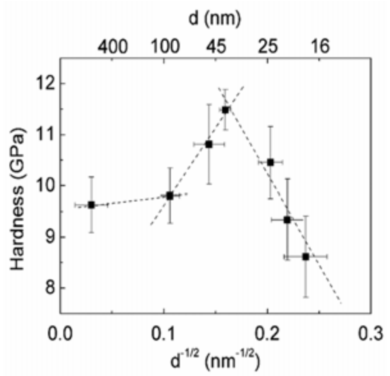

Figure 2. Plot of hardness with the grain size of quasicrystals in Al–Fe–Cu alloys showing the Inverse Hall–Petch (IHP) behaviour in the regime of nanoquasicrystalline grains below 40 nm (courtesy: N. K. Mukhopadhyay).

tomography (ADT) is an innovative approach to electron crystallography and helps identify the disorder, space group easily than zone diffraction pattern alone. G. Chapuis (Switzerland) discussed in detail the superspace approach to understand the properties of the incommensurate phase with some examples. The commensurate composite concept can explain well the electronic properties of the BaV system. P. Rabiller (France) studied the symmetry breakings related to phase transitions in aperiodic composite crystals. It was demonstrated that the new degree of freedom concerns the structural organization, leading to completely unexpected phases. L. Borgeois (Australia) presented structural details of nanochessboard and modulated phases using aberration-corrected transmission electron microscopy and scanning STEM. Perovskites often display complex and highly ordered nanoscale modulations arising from a subtle interplay between structural and chemical factors. Striking examples of such ordering are nanochessboard phases. J. Roth (Germany) has demonstrated that laser potentials which are generated by the superposition of harmonic waves, exhibit local isomorphism classes much like rhombus tilling. While the classes are known for tilling, efforts were made to determine the various classes for *n*-fold symmetric laser fields and show how many free parameters exist.

Complex intermetallics, QC approximants and soft QCs

R. Tamura (Japan) presented a detailed study on structural and magnetic ordering in Cd-based crystalline approximants. It was shown that an occurrence of a low temperature structural transition associated with the dynamical motion of a tetrahedron inside icosahedral clusters in Tsai cluster can be classified into 'non-diffusive order–disorder transition'. In addition, a long-range magnetic order at low temperature was observed. The structural and magnetic ordering in Cd_6M approximants has been discussed. A. I. Goldman (USA) studied the antiferromagnetic order in the Cd_6Tb approximant. It was shown that Tb ions associated with the icosahedral cluster at the corner of the unit cell are antiferromagnetically correlated with Tb ions associated at the body centre of the unit cell. J. Dshemuchadse (Switzerland) elaborated the structural characteristics of complex intermetallics. Many of these compounds were described using cluster approach, superstructures and layered compounds. In the cluster packing, multiple-shell fullerene-like clusters packed closely and blocks of smaller polyhedral (mainly Friauf ployhedra and similar clusters) filled the remaining gaps. The largest unit cell in complex intermetallics family has been found in $Al_{55.4}Cu_{5.4}Ta_{39.1}$ to be a = 71.49 Å (fcc) containing 23,256 atoms. A variety of fcc intermetallics with giant unit cells were reported. The diffraction patterns are often complex due to the subset of diffuse scattering and satellite spots. However, by analysing these subtle patterns one can obtain the building principles responsible for the formation of highly complex intermetallic structures. U. Mizutani (Japan) discussed the importance of Hume–Rothery stabilization mechanism in low-temperature phase Zn_6Sc approximant. It was shown that Hume–Rothery stabilization mechanisms hold good for Al–Mg–Zn, Al–Li–Cu, Al–Mn, Al–Re–Si, Al–Cu–Fe–Si 1/1 approximants and many other phases. The Fermi surface–Brillouin zone (FsBz) interactions involving the set $G^2 = 50$ (where G is the reciprocal lattice vector) are found to be responsible for causing a pseudogap at the Fermi level. He showed that it works also for Tsai type 1/1 approximants. He advocated the universal criterion as electrons per unit cell (e/uc) rather than electron/atom for understanding the Hume–Rothery mechanisms. N. Fujita (Japan) presented structural analysis of a large cubic approximant of F-type icosahedral QCs in Al-based alloys. It appears that this result would provide new insights into the atomic structure of F-type icosahedral QCs and their approximants. M. Kracjci (Slovakia) has studied the catalytic properties of fivefold surfaces of QC approximants. It was shown that local configurations of Al and transition metal (TM) atoms are favourable for selective catalysis of the hydrogenation reactions at the Al–TM surfaces with pentagonal symmetry. S. Hovmooler (Sweden) determined the structure of pseudo-decagonal approximants in Al–Ni–Co systems using electron and X-ray diffraction techniques.

S. C. Glotzer (USA) discussed the design of soft QCs (prepared from soft matter) from computer simulation. The surprising recent discoveries of QCs and their approximants in soft materials – including dendrimers, block copolymers, nanoparticle suspensions and hard colloids pose the intriguing possibility that these structures can be realized in a broad range of nano and micro-scale assemblies conforming QC symmetries. It has been shown that in all these cases the structure is entropically stabilized and it forms in the absence of any explicit attraction. A simple design of assembling QCs and approximants in soft-matter systems can explain QC formation in micellar and related materials. Kobi Barkan (Israel) showed that a large number of soft-matter systems form ordered phases with dodecagonal symmetry. It was suggested that a numerical scheme could be used to provide a platform for the study of the dynamics of these soft QCs.

Concluding remarks

Some major issues have emerged from this conference which are expected to dominate research in aperiodic crystals. These are: (i) structural refinement of QCs by SUPERFLIP using electron diffraction and electron tomography, (ii) structural refinement of aperiodic crystals using the average lattice concept, (iii) growth of quasilattice patterns derived from Islamic architecture, (iv) structurally complex intermetallics, (v) inverse Hall–Petch and nano-QCs, and (vi) soft QCs. It was announced by R. Lifshit (Israel), the present Chairman of the Aperiodic Commission, that the next meeting on Aperiodic-2015 will be organized by L. Palatinus in the Czech Republic in 2015. In addition, International Conference on Quasicrystals (ICQ12) will be held in Krakow, Poland in 2013 and International Congress of Crystallography (IUCr) in Montreal, Canada in 2014 where a symposium related to aperiodic crystals would be organized.

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