Quasicrystals: Indian research accomplishments and imperatives

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Within two months of the first report on quasicrystals in PRL in November 1984, Indian research which had a 'premature discovery' in 1978 in this area got under way. In the past nine years these efforts have led to original discoveries relating to new types of quasicrystalline phases as well as extensive investigations involving tiling theory, hyperspace, positron annihilation and electrical properties. These researches have been multi-institutional and multi-disciplinary. Enlightened and generous funding was extended by DST from 1986 by recognizing it as a thrust area in basic research via SERC and US–India Funds. International recognition, subjective though it is, in the form of citation of Indian papers, invited lectures and reviews, books as well as the membership of International Advisory Committee has followed and is among the highest in the fields of condensed matter science covered at the Bangalore meeting. Future directions pertaining to the exploration of mechanical and electronic properties as well as structures beyond the quasicrystalline order will be pointed out.

Icosahedral and associated pentagonal symmetry have been a subject of fascination from the times of Plato. In the first exercise on relating form to internal structure, Kepler associated the six-sided snowflake to its internal atomic arrangement. He tried the packing of pentagons in flat two dimensional space and his failure led him to surmise that pentagonal symmetry was confined to the plant kindgom. The advent of crystallography showed that there are 32 point groups, 230 space groups and 14 Bravais lattices with the conditionality of translational symmetry.

It was Roger Penrose[1] among others who broke this crystallographic restriction and showed that pentagonal symmetry can be achieved in two dimensions when strict translational symmetry is replaced by quasiperiodicity. Alan Mackay[2] showed that these quasiperiodic patterns are capable of giving sharp diffraction patterns.

The mathematical recreations and physicist's dreams gave way to a metallurgical reality, when in 1984 Shechtman and coworkers[3] announced the discovery of a new ordered phase in rapidly solidified aluminum–manganese alloy without translational symmetry. The phase was soon christened as quasicrystal. This paradigmatic shift led to a surge in scientific research in this intriguing field, resulting in 20 books, over 5000 publications and numerous conferences during the past decade.

Indian contributions to this field have been surprisingly large due to propitious circumstances. T. R. Anantharaman had spent a brief stint with Pol Duwez as early as 1965 and established a strong school in rapid solidification processing at the Banaras Hindu University in Varanasi. Indeed, this school came quite close to the discovery of quasicrystals in 1978 but indexed a tenfold pattern as arising from twins[4]. However, the PRL 1984 paper[3] triggered intensive research in Indian laboratories and this led to over 300 publications. It is noteworthy that in March 1985 Ramaseshan[5] spoke about the new architecture of solids during the Golden Jubilee Celebrations of the Indian Academy of Sciences and drew attention to exciting possibilities for research in this area.

Research support

The research on quasicrystals has received generous support from the Department of Science and Technology, Government of India. It was recognized as a thrust area and as many as 12 projects with an outlay of Rs 120 lakhs have been sanctioned during this period at the Departments of Metallurgy and Physics at the Indian Institute of Science (Bangalore), Banaras Hindu University (Varanasi) and the Indian Institute of Technology (Kanpur). These projects have led to over 300 research publications.

In addition, active research has been pursued at the Bhabha Atomic Research Centre (Bombay), the Indira Gandhi Centre for Atomic Research (Kalpakkam) and the Defence Metallurgical Research Laboratory (Hyderabad).

The support provided compares favourably with those provided in France, China and Japan from where major contributions have come. The funding was not so marked in the US and many nations in Western Europe.

Important discoveries

The discovery of the new phase with decagonal symmetry is an impressive achievement of the Indian effort[6,7]. It is comparable in terms of scientific importance to the discovery of the discotic phase in liquid crystals. The decagonal quasicrystal is a two-dimensional quasicrystal, as one of its directions is periodic. It is noteworthy that this discovery was announced in a paper in *Current Science*[7]. Another important contribution was the discovery of variable periodicity in decagonal phases[8].

In a similar fashion the observation that vacancy ordered phases can be visualized as converging to an one-dimensional quasicrystal was an outstanding contribution[9]. While the entire research community was in hot chase after aluminum alloys for unearthing new quasicrystals, Ramachandrarao and Sastry[10] quenched a Mg–Zn–Al alloy and in a brilliant fashion produced a new type of icosahedral quasicrystal and announced it in *Pramana*. The associated crystalline compound, $Mg_{32}(ZnAl)_{49}$ was full of icosahedral symmetry and had been earlier solved by Pauling and coworkers[11].

That quasicrystals could order came as a surprise. Its first intimation in the form of diffuse arcs was detected by Mukhopadhyay *et al.*[12]. Subsequently, well ordered and stable phases were discovered in Al–Cu–Fe and Al–Mn–Pd alloys by Japanese scientists.

Quasicrystals can be synthesized by a variety of techniques. Sekhar and Rajasekharan[13] added solidification under high pressure as a new route.

Indian contributions to the theory of tilings are equally impressive. Sasisekharan[14] has contributed in a enormous measure to the theory of tiling. It was shown that while crystals have restricted symmetries, quasicrystals admit all the symmetries including 2, 3, 4 and 6-fold[15]. One of the remarkable aspects of quasicrystals is that they could be understood as periodic crystals in higher dimensions. Such crystals on projection give rise to quasiperiodic arrangements in real space. Mandal and Lele[16] have derived a variety of quasicrystalline structures and predicted the possibility of a new pentagonal quasicrystal. Kulkarni *et al.*[17] have contributed to this field and shown the derivation of octagonal and dodecagonal quasicrystals.

The possibility that crystal structures with increasing lattice parameters could converge to quasicrystals is a major advance in this field. Kumar *et al.*[18] identified Al_3Fe as a possible rational approximant. Early Indian work was revisited to show that Al–Mn–Ni structure formed an excellent approximant to the decagonal phase[19]. Higher order rational approximants have been discussed in detail by Mukhopadhyay *et al.*[20].

While considerable efforts have been spent in understanding the structure of quasicrystals only a beginning has been made in exploring defects in quasicrystals. The nature of dislocations, grain boundaries and interfaces in quasicrystals poses challenging questions. Some images of these defects by transmission electron microscopy are already available. Hatwalne and Ramaswamy[21] formulated the criterion for the visibility of dislocations. Chattopadhyay *et al.*[7] showed the epitaxial nature of the interface between the icosahedral and decagonal phase. Icosahedral twins have been characterized[22]. The Varanasi school of research had shown that a new type of microstructure known as banded microstructures, can arise in eutectic alloys. Chattopadhyay and Mukhopadhyay[23] showed this to arise in quasicrystalline systems as well.

While the deterministic Penrose tiles are used to model quasicrystals, alternate models involving random tilings and icosahedral glass have been advanced from time to time. A series of measurements, involving positron annihilation, has led Chidambaram and coworkers[24] to support the icosahedral glass model on the basis of vacancy concentrations.

Pauling[25] was strongly resistant to the idea that a new atomic configuration in the solid state had to be invoked. He felt that all existing observations could be explained on the basis of twinning, even though he did not rule out the quasicrystalline arrangement as such. This viewpoint has been shared by Anantharaman[26]. However, a new type of irrational twinning was discovered by Bendersky *et al.*[27] as a spin-off of research on quasicrystals. This is being further extended by us to explain the structure of irrational tilt boundaries as being quasiperiodic.

Almost all early work was centred around unravelling the atomic configurations in quasicrystals. They do present possibilities of attractive properties. One of the earliest studies of mechanical properties in Al–Li–Cu quasicrystals is by Bhaduri and Sekhar[28].

Recognitions

Recognition is a subjective matter. However if one uses conventional yardsticks such as number of citations, invited reviews, invitations to international conferences and prizes, the research output on quasicrystals from India has attracted immense recognition, and must figure close to the top in the fields of metallurgy and material science.

Several papers have been cited many times. It is a matter of some pride that two early papers in *Current Science* and *Pramana* continue to be quoted. There is an international conference series on quasicrystals held successively in Les Houches (1985), Beijing (1987), Vista Hermosa (1989) and St. Louis (1992). The fifth one is scheduled to be held in May 1995 at Avignon in France.

Future directions

The foregoing makes it clear that Indian research has been vigorous, multi-institutional and multidisciplinary, addressing both theoretical and experimental aspects. It is to be hoped that this effort, which has been sustained over a decade, will continue to grow to tackle the many challenges that remain in this field.

The expectation that a new type of atomic configuration will automatically lead to new properties is now being realized. This is especially true of electronic properties. In crystals greater purity and perfection lead to improved electrical conductivity. Quasicrystals exhibit just the opposite behaviour. As purity and perfection are improved, they become semiconducting and even insulating! Current Indian research in this direction needs to be intensified.

The deformation of quasicrystals has become an intensive area of research. Japanese work has shown that it is possible to produce quasicrystals in nanometre dimensions embedded in crystalline or amorphous matrices with a vast improvement in mechanical properties over conventional aluminium alloys. Indian expertise is well poised to take advantage of this new breakthrough.

Quasicrystals have proved to be a fertile field of investigation for mathematicians. Papers of great depth and beauty continue to appear exploring the higher dimensional world and beyond the quasicrystalline order. There is a progression from periodic through quasiperiodic to almost periodic structures.

Inevitably an article of this type is not comprehensive either about the richness of the idea of quasiperiodicity or of the extensive Indian contributions. The reader is referred to two reviews for further details[29,30].

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Scanning probe microscopy

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We have discussed the importance of the area of Scanning Probe Microscopy and its likely impact on different types of measurements that can be carried out at nanometer levels. We have talked about the application of STM in the area of nanofabrication and expressed the view that this area needs careful development in the country.

The discovery of Scanning Tunneling Microscope (STM) in 1982 opened up a new area of research. The area is developing and progressing at a rapid rate. Subsequent to the discovery of STM, a number of scanning microscopes have been invented. The most important is the Atomic Force Microscope (AFM). The first question one may ask is why the area has become so important within a few years of its discovery. Definitely the first answer is that it gives atomic level (or nanometer level) resolution at an affordable cost. This is the first require-