# CURRENT SCIENCE

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**EDITORIAL**

# Seeing is Believing: Quasicrystals and the Demise of Perfect Order

The Nobel prize in Chemistry is often awarded to scientists who are formally viewed as practitioners of other disciplines. Ernest Rutherford, who professed a considerable disdain for subjects other than physics, was anointed a laureate in chemistry in 1908. Since then, biologists, physicists and even barely disguised mathematicians have been inducted into chemistry's hall of fame; a tribute to the richness of a field, which shares its borders with many other disciplines of science. This year's Nobel award to Dan Schechtman for his discovery of quasicrystals once again recognized a major scientific advance that, at first glance, appeared to be far removed from the concerns of traditional chemistry. Shortly after the announcement a physicist colleague exclaimed: 'Ah, this is a physics prize'. Not to be outdone, a colleague in materials engineering, classically metallurgy, proclaimed: 'This is a prize for materials.' Curiously, my chemistry colleagues seemed subdued, although the study of materials might legitimately be classified under chemistry. Indeed, the vast majority of the practitioners of science, in the years before disciplinary boundaries crystallized sharply, were engaged in understanding the nature of matter, living and non-living, organic and inorganic, gaseous, liquid and solid. Alloys are the province of the metallurgist; materials whose utility has been immense. The serendipitous observation of a remarkable electron diffraction pattern in a manganese–aluminium alloy by Schechtman in 1982, led to the discovery of quasicrystals, eventually transforming our understanding of the crystalline state of matter. In a lecture at Schechtman's seventieth birthday celebration at the Technion in Haifa, chemical historian and structural chemist Istvan Hargittai reflects on 'the lessons of a discovery' (*Struct. Chem.*, 2011, **22**, 745). Crystallography has its roots firmly embedded in the mid-19th century in the work of Bravais on periodic lattices. By the turn of the century it was clear that periodic, long range order imposed restrictions on the observable symmetries in crystals. The 20th century was marked by the remarkable growth of X-ray diffraction beginning with the work of Lane and the Braggs. Chemistry and biology have been propelled along by the spectacular successes of X-ray crystallography, to an extent that X-rays and crystals seem inextricably linked. Schechtman's observation of 'impossible' symmetries under the electron microscope appeared to fly in face of established principles. Five-fold and ten-fold symmetries that he observed seemed easier to dismiss as artefacts of twinning of crystals. Hargittai enumerates several lessons that might be learnt from Schechtman's discovery. Amongst the most important pieces of advice he gives are: 'Do not discard the unexpected' and expose your findings 'to wide scrutiny'. In Hargittai's assessment published earlier this year: 'The discovery caused a paradigm change in physics, chemistry, crystallography and materials science. It deserves the highest recognition.' That has now happened.

In a prelude to Schechtman's experimental discovery, Alan Mackay visited the relationship between 'crystallography and the Penrose pattern', noting that 'equivalence is replaced by quasi-equivalence' in Penrose tiling schemes. He considered the possibility of 'tiling of two-, three- (and perhaps four-) dimensional space by tiles of two kinds in a unique non-periodic pattern'. In reviewing the field nearly two decades after the initial discovery, J. W. Cahn, a coauthor on the seminal 1984 paper (Schechtman *et al.*, *Phys. Rev. Lett*., 1984, **53**, 1951), writes that 'the study of quasicrystals benefited greatly from prior research in the mathematical subjects of quasiperiodic functions, aperiodic tilings and hyperspace crystallography'. He notes that the discovery has 'led to much interdisciplinary activity involving mainly materials science, physics, mathematics and crystallography' (*J. Res. Natl. Inst. Stand. Technol*., 2001, **106**, 975). Materials science and crystallography today are really under the broad umbrella of chemistry.

Are quasicrystals of great practical utility? In 1999, an overview of the area listed a number of potentially useful applications for the hundreds of alloys with quasicrystalline structures, that appeared in the wake of Schechtman's finding (Jacoby, M., *Chem. Engg. News*, 1999, **77**, 44). New cooking surfaces and hardening steels are hardly applications likely to excite the Nobel committee. Two previous awards for work done in the 1980s, that might broadly be classified as 'materials science', come to mind when thinking about quasicrystals. The discovery of high temperature superconductivity in 1985 in the perovskite type oxides was announced in a modestly entitled publication: 'Possible high $T_c$ superconductivity in the Ba–La–Cu–O system' (Bednorz, J. G. and Muller, K. A., *Zeit. Phys.*, 1986, **B64**, 189). The perovskite structures were well known in this class of materials. There was little glamour associated with their structures or their chemistry. Their promise as materials that would make superconductors widely accessible touched off a frenzy of activity, propelling the discoverers to a Nobel Prize in 1987, a remarkably short time after the first publication.

The enthusiasm for high temperature superconductors, that might revolutionise power transmission and generate a whole world of new applications, is now muted. At around the same time in September 1985, a new form of carbon, $C_{60}$ or Buckminsterfullerene, was discovered by Harold Kroto and his colleagues (*Nature*, 1985, **318**, 162). $C_{60}$ attracted immediate attention; chemists of all hues were seduced by the beauty of its structure. To transform a substance as prosaic as graphite into a molecular object of great symmetry and beauty was an act reminiscent of the elegant swan emerging from the ugly duckling. The beguiling symmetry of the material, fuelled a search for applications which still continue; albeit, with less enthusiasm as newer forms of carbon, nanotubes and graphene, have emerged. Fullerene ($C_{60}$) has the same structure as a soccer ball (football, to the world outside America). Kroto, Curl and Smalley received a Nobel prize in 1996, just over a decade after their discovery. In his Nobel lecture Kroto notes 'that, perhaps, the molecule's most delightful property lies in its inherent charisma which arises from its elegantly simple and highly symmetric structure that is quite unlike any other'. Schechtman's quasicrystal announcement which appeared in 1984 has transformed the way we view the solid state; indeed the beauty of crystals is enhanced by expanding their universe to encompass aperiodic structures.

The criticism of the idea of quasicrystals and forbidden symmetries in crystalline solids by Linus Pauling, soon after publication of the Schechtman paper in 1984, has been widely written about after the Nobel announcement. There is an appealing David and Goliath angle to the early controversies about quasicrystals. Pauling (1901–1994) was 84 years old when he began his criticism of the idea of quasicrystals, advancing instead alternative explanations for the observed symmetries in diffraction patterns. His credibility had eroded in the later years of his long and extraordinary career, especially in his controversial espousal of vitamin C as a universal therapy. He wrote his last paper, clinging to his interpretations, just before he turned 90 (*Proc. Natl. Acad. Sci.*, 1990, **87**, 7849). There were many studies, in laboratories across the world, that quickly followed Schechtman's publication, including work at Bangalore which lent support to the idea of quasicrystals (Chattopadhyay, K. *et al.*, *Curr. Sci.*, 1985, **54**, 895). The theoretical underpinning was strong, with the work of Mackay and Levine and Steinhardt (*Phys. Rev. Lett.*, 1984, **53**, 2477). Pauling's formidable reputation did not deter many critics of his twinning hypothesis (cf. Heiney, P. *et al.*, *Phys. Rev. Lett.*, 1987, **59**, 2119). Hargittai notes that 'Pauling died in 1994 without accepting Schechtman's discovery'. It is not clear whether Pauling by then had many followers. Hargittai quotes Max Planck: 'A new scientific truth does not triumph by convincing its opponents and making them see the light, but rather because its opponents eventually die, and a new generation grows up that is familiar with it.'

Students of the history of chemistry will recall Herman Kolbe's famous attack on van't Hoff's proposal in 1874 of the tetrahedral disposition of the bonds about a saturated carbon atom; an idea that catapulted chemistry into the third dimension: 'A Dr J. H. van't Hoff of the Veterinary School at Utrecht has no liking, apparently for exact chemical investigation. He has considered it more comfortable to mount Pegasus (apparently borrowed from the Veterinary School) and to proclaim in his *La Chimie dans L'espace* how the atoms appear to him to be arranged in space, when he is on the chemical Mt. Parnassus which he has reached by bold flight.' Harshly worded attacks were common in the 19th century when some of the most profound concepts of modern science were born. In van't Hoff's day, chemists used the idea of atoms as a convenient device to picture the bewildering range of molecules being uncovered by organic chemistry. Physicists of the time were impatient with a discipline that seem to be based on tenuous imagery. Von Helmholtz famously said: 'The whole extraordinarily comprehensive system of organic chemistry has developed in the most irrational manner, always linked with sensory images which could not possibly be legitimate in the form in which they are presented' (Riddell, F. G. and Robinson, M. J. T., *Tetrahedron*, 1974, **30**, 2001). I cannot think of past battles over the structure of matter without turning to Boltzmann. In his classic narration of the *Ascent of Man*, Jacob Bronowski stands at Boltzmann's grave and reflects: 'Who would think that only in 1900, people were battling, one might say to the death, over the issue whether atoms are real or not. The great philosopher Ernst Mach in Vienna said, No. The great chemist Wilhelm Ostwald said, No. And yet one man, at the critical turn of the century, stood up for the reality of atoms on fundamental grounds of theory. He was Ludwig Boltzmann…. Did Boltzmann just argue? No. He lived and died that passion. In 1906, at the age of sixty two, feeling isolated and defeated, at the very moment when atomic doctrine was going to win, he thought all was lost, and he committed suicide.' In remembering past battles in an area of science that has seen its share, the duel over the nature of quasicrystals seems mild.

Quasicrystals were uncovered by the electron microscope. Microscopy has come a long way since van Leeuwenhoek discovered a 'world within a world' in the latter half of the 17th century. Electron microscopy promises to provide even more surprises as the power of the method grows with every technical advance. Some years ago Alan Mackay wrote that 'if we can escape from our preconceptions engendered by the immense success of X-ray single-crystal structure analysis', we might expect 'still more varied structures' that 'lie outside the austere domain of classical crystallography' (*Nature*, 1988, **391**, 334). Gautam Desiraju, another perceptive commentator, noted: 'As chemistry moves towards systems of greater complexity and diversity, the meaning and scope of the term "crystal" can only evolve and expand' (*Nature*, 2003, **423**, 485). Schechtman 'saw' quasicrystals in the images produced by an electron microscope. Most often, seeing is believing.

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