Quasicrystals

The well ordered world of solid materials was forced to reassess its rules of order by the spectacular results of D. Shechtman, I. Blech, D. Gratias, and J. W. Cahn [1]. By the year 1801, the fundamental laws of crystal morphology had been well established, and in the last two decades of that century, theories of the internal symmetries of crystals were being discussed [2]. Early in the following century, 1912-1916, the development of x-ray diffraction techniques allowed the periodic arrangement of atoms in a crystal to be established experimentally [3]. By 1984 it was universally accepted that an x-ray diffraction pattern with sharp peaks could only be the result of a periodic arrangement of atoms or molecules occurring in a crystalline solid, and every possible crystal symmetry was known [4].

In general, crystals are classified according to their allowed translational and rotational symmetry operations. Each possible crystal lattice is characterized by having a smallest structural unit, called a unit cell, and when those cells are stacked together face-to-face, an infinite region of space can be filled without leaving a single hole. Quite notable in the mathematics of crystal symmetry is the impossibility of a three dimensional crystal possessing a five-fold axis of rotation.

> "We report herein the existence of a metallic solid which diffracts electrons like a single crystal but has point group symmetry $m\bar{3}\bar{5}$ (icosahedral) which is inconsistent with lattice translations." [1]

That pronouncement appearing in *Physical Review Letters* in 1984 heralded the discovery of a new class of materials, now called quasicrystals, which possessed the heretofore forbidden icosahedral point symmetry!

It is not surprising that there followed immediately several years of raging controversy regarding the origin of the diffraction symmetry, but importantly, sufficient results from electron diffraction experiments were reported in this initial paper to confirm that the icosahedral symmetry was indeed real. The primary point of contention was the well-known experience that disallowed diffraction patterns could be produced artificially as a result of a superposition of multiple allowed, but rotated, patterns. As a crystal is grown, it is not uncommon for the growth direction to change suddenly resulting in a process called twinning. Indeed, John Cahn said [5], "My reaction was, 'Go away, Dany. These are twins and that's not terribly interesting.'"

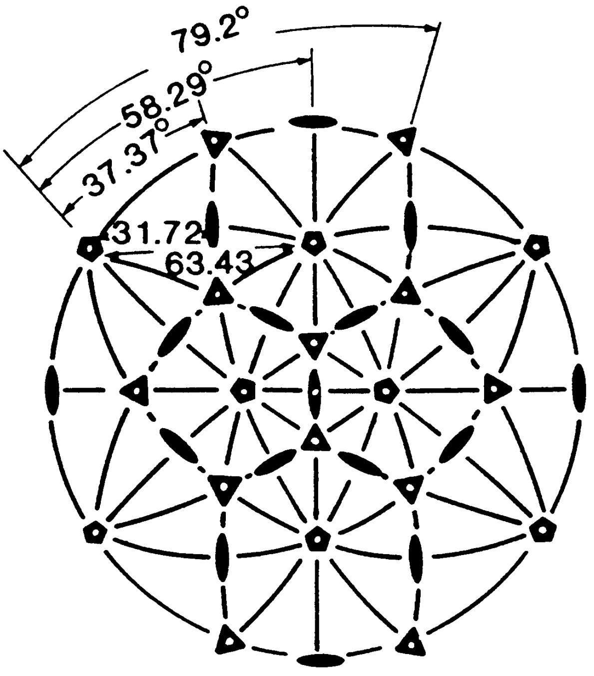

Fig. 1. Stereographic projection of the symmetry elements of the icosahedral group $m\bar{3}\bar{5}$.

However, to produce the five-fold symmetry, twinning would have to occur five times in succession. That hypothesis can be tested experimentally by focusing the diffraction beam on smaller and smaller regions of the specimen. When the size of the diffraction volume becomes too small to enclose all five twins, the five-fold symmetry must disappear. Such was not the case in the work of Shechtman, Blech, Gratias, and Cahn! The five-fold symmetry persisted to the smallest dimension that was examined, about 10 nm, and there was no evidence of twinning.

Rather quickly, a number of models were developed to explain the icosahedral symmetry of the diffraction patterns. The leading contenders were a relatively disordered "icosahedral glass" phase and a highly ordered tiling model.

The icosahedral glass model, initially proposed by Shechtman and Blech [6] and developed by Stephens and Goldman [7], is composed of many interconnected aligned polyhedra of icosahedral symmetry. These glasses possess long range orientational order, but no long range translational symmetry. Although these structures do not form a regular lattice, models indicate

Fig. 2. John Werner Cahn, NIST Senior Fellow, received the 1998 National Medal of Science, conferred by the President of the United States on the recommendation of the National Science Foundation.

that they are able to produce diffraction peaks as sharp as those that were measured in the earliest icosahedral phases. However, the glass models have too great a degree of disorder to be consistent with the extremely sharp diffraction spots of icosahedral phases such as Al-Cu-Fe and Al-Cu-Ru phases that were observed subsequently.

The tiling models are based on a concept devised by Roger Penrose in 1974 for tiling the plane quasiperiodically using two tile shapes rather than a single unit cell [8]. In 1981 Alan Mackay generalized the Penrose tiling to three dimensions using two types of rhombohedra [9]. In the following year, Mackay designated the two- and three-dimensional patterns as “quasi-lattices” and speculated on possible structures where atoms sit on the quasi-lattice points of the 2-D structure. He showed that these structures give rise to optical diffraction patterns with ten-fold symmetry! In 1984 Peter Kramer and Reinhardt Neri of Tubingen [10] and Dov Levine and Paul Steinhardt [11] of the University of Pennsylvania independently developed a three-dimensional generalization of Penrose tilings by projecting a three dimensional cut through a higher-dimensional periodic lattice. These three-dimensional tilings filled space using two or more rhombohedra and the calculated diffraction patterns were quite similar to the 3-fold and 5-fold patterns published by Shechtman, *et al.* Other models using the 6-D projection approach were developed and shown to be capable of matching the diffraction patterns quite well.

By rotating tiles or clusters of tiles in a Penrose pattern, structures intermediate to the perfectly ordered Penrose tiling models and the icosahedral glass models can be obtained. This additional disorder generates a strain which is consistent with the experimentally observed systematic broadening of diffraction spots. The disordered tiling model thus can account for the varying degrees of strain observed for various alloy systems. It has been suggested that the presence of disorder even contributes to the stability of the structures through an increase in entropy.

The physical realization of quasicrystals and the intellectual understanding of their formation thus has been achieved. At the foundation of this discovery is the work of Shechtman, Blech, Gratias, and Cahn, which has spawned an entirely new branch of materials science. Already, papers numbering in the thousands have been published on this subject in the disciplines of physics, crystallography, and mathematics. It may be noted that Shechtman and Cahn have continued to lead, stimulate, and encourage much of this work.

Dan Shechtman is the Philip Tobias Professor of Materials Science at the Israel Institute of Technology (Technion, Haifa, Israel). His work on both the theoretical and experimental aspects of quasi-periodic structures has earned him numerous awards. He received the Physics Award from the Friedenberg Fund for the Advancement of Science and Education in 1986; the International Award for New Materials from the American Physical Society in 1987; the New England Academic Award of the Technion for Academic Excellence in 1988; the Rothchild Prize in Engineering in 1990; and the Weizmann Prize in Science in 1993. While quasicrystals remain a major focus of his work, he is also pursuing research on chemical vapor deposited (CVD) diamond wafers, metallic multilayers, and rapidly solidified metallic alloys.

John Cahn has had a remarkably prolific career as scientist and teacher. He has published approximately 250 papers and delivered approximately 400 invited lectures to technical audiences worldwide. The excellence of his work has been recognized in more than thirty national and international awards, including the

Nation’s highest scientific award, the National Medal of Science (1998). He was conferred with membership in both the National Academy of Sciences (1973) and the National Academy of Engineering (1998). He has received gold medals from organizations as diverse as the U.S. Department of Commerce, the Japan Institute of Metals, and Acta Metallurgica. He has been accorded the status of Fellow at NIST, the American Academy of Arts and Sciences, the Japan Society for the Promotion of Science, the American Institute of Metallurgical Engineers, and the ASM International. He has been honored no less than eleven times as a Distinguished Lecturer and has received honorary doctorates from Universit d’Evry (France, 1996) and Northwestern University (1990), and an honorary professorship from Jiao Tong University (Shanghai, China, 1980). His awards for distinguished work include the Harvey Prize (Israel Institute of Technology, 1995), the Rockwell Medal (International Technology Institute, 1994), the Hume-Rothery Award (AIME, 1993), the Michelson and Morley Prize (Case Western University, 1991), the Sauveur Award (ASM International, 1989), the Stratton Award (NBS, 1986), the von Hippel Award, (Materials Research Society, 1985), the Dickson Prize (Carnegie-Mellon University, 1981), and the S. B. Meyer Award (American Ceramic Society, 1966). He is currently Senior Fellow in the NIST Materials Science and Engineering Laboratory where he is continuing his pioneering work on the thermodynamics and kinetics of phase transitions, diffusion, and interface phenomena.

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