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QUASICRYSTAL: DISCOVERY TO NOBEL PRIZE

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Quasicrystals are orientationally-ordered structures with classically forbidden rotation symmetries (e.g. five and ten fold rotation axes) which are incompatible with the periodic translational ordering. The discovery of quasicrystals has completely changed the understanding of crystallography.

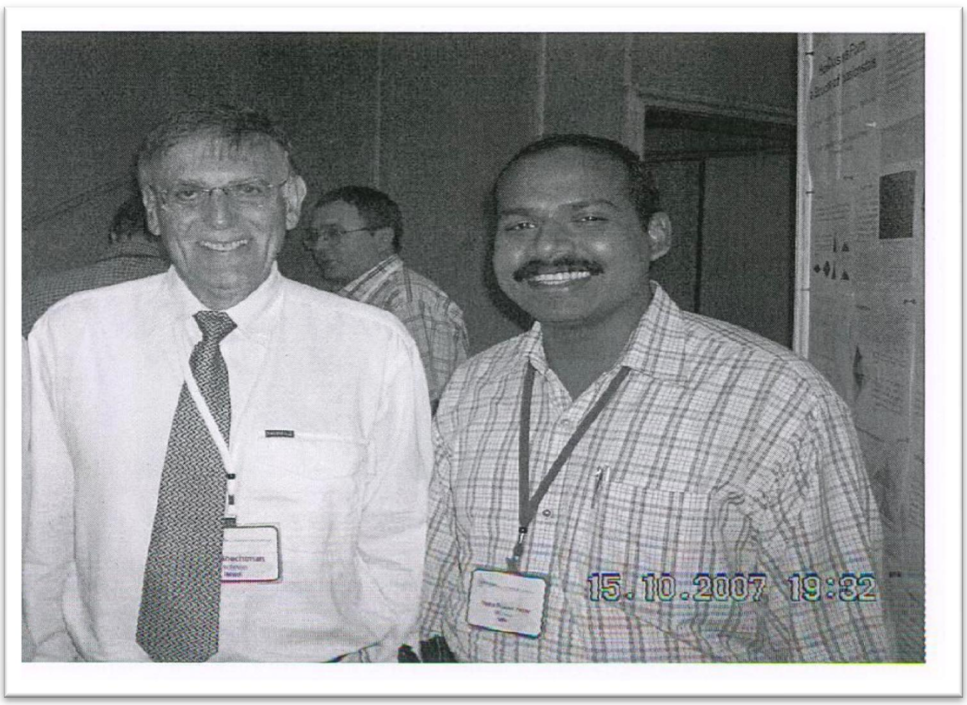

Fig.1

Professor Danny Shectman (Technion-Israel Institute of Technology: Left) with Dr. T. P. Yadav in 2009 marking the 25th (the silver jubilee) year of Quasicrystals-Israel.

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For this discovery, the 2011 Nobel Prize for Chemistry has been awarded to Professor Danny Shectman [1]. Prof. Shechtman himself on observing diffraction patterns exhibiting five fold symmetry is said to have cried "Eyn chaya kazoo", which translates from Hebrew as "there can be no such creature".

Dr. Shechtman had to fight a fierce battle against established crystallographers to convince them of what he had first seen in his laboratory at the National Institute of Standards and Technology in Washington-formerly called the National Bureau of Standards – on an April morning in 1982. His discovery was first published in 1984, with co-authors Blech, Gratias, and Cahn. [1]. The breakthrough experiments by Shechtman on rapidly solidified Al-14% Mn alloys have created a new concept of ordered but nonperiodic atomic arrangements which exhibit sharp diffraction peaks (spots) with icoshahedral symmetry (m35). Using transmission electron microscopy and associated high-energy electron diffraction, Shechtman made the key observation that rapidly-quenched $Al_{86}Mn_{14}$ alloy forms small crystallites in which the nature and relative orientations of the rotational axes could only be explained with icosahedral symmetry. Furthermore, it was found that these crystallites did not exhibit twinning, an effect which may give rise to diffraction patterns which can be erroneously taken to correspond to icosahedral symmetry.

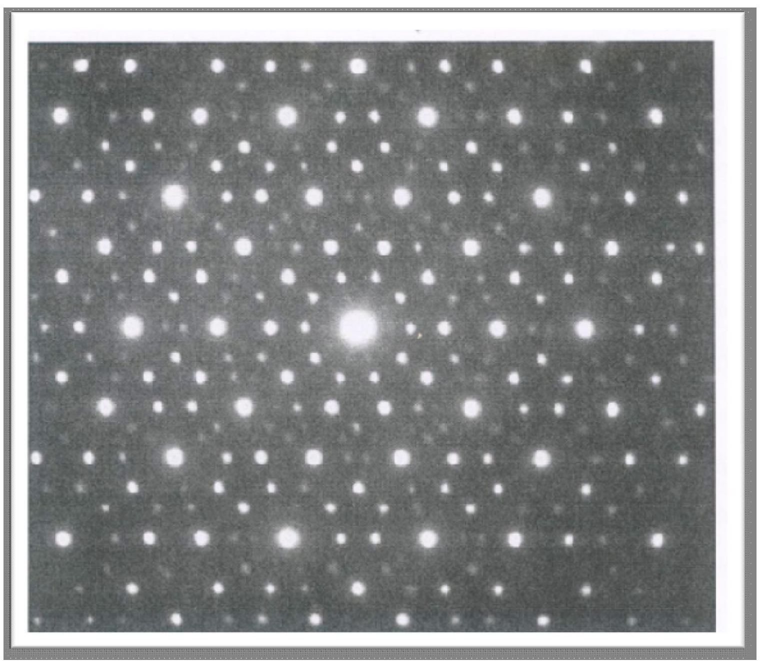

Fig. 2

The five fold "forbidden symmetry" was first seen in (1982) leading to the birth of a new class of materials: The quasicrystals.

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The icosahedral point group is incompatible with translational periodicity. The sharpness of the diffraction peaks had been explained until this time on the basis of the periodicity of the crystalline materials. This problem can be sorted out by constructing an aperiodic lattice with icosahedral bond orientational order. The diffraction patterns simulated from these structures are startlingly close to those observed for the icosahedral phase. They also showed that the appearance of sharp diffraction peaks do not necessarily require periodicity. Of course this was discussed by Mackay (1982) long before the discovery of quasicrystals [2]. Mackay extended the idea of Penrose (1979) who had developed a scheme of filling space aperiodically by a finite number of tiles [3]. Mackay constructed the three dimensional analogue tiles and stressed their importance in the context of crystallography. It may be pointed out that diffraction patterns indicative of existence of pseudo pentagonal symmetry was observed in (1978) at B.H.U. by Sastry *et al*. [4], but detailed analysis and point group symmetry was not determined.

Soon after the discovery of icosahedral quasicrystals, Chattopadhyay *et al*. (1985) and Bendersky (1985) independently found the decagonal quasicrystals in Al-Mn alloys [5-6]. The octagonal quasicrystals with eight fold symmetry and dodecagonal quasicrystals with twelve fold symmetry were reported by Wang *et al*. (1987) and Ishimasa *et al*. (1985) respectively [6-7]. The first known quasicrystals were all metastable, they could be prepared only by rapid quenching. As a result, single-grain samples were limited to a few micron in size. It was rather quite difficult to test physical properties or obtain detailed structural models. Indeed, it was postulated at that time that quasicrystals might be inherently metastable. The situation changed in 1987, when Tsai et al. reported the first stable quasicrystals in the Al-Cu-Fe (1987) system. Later on other stable quasicrystals in Al-Co-Ni and Al-Cu-Co (1987), Al-Cu-Ru, Al-Cu-Os (1988) and Al-Pd-Mn (1990) system were reported [8-12].

Until the year 2000, most researchers thought that stable icosahedral quasicrystals only formed in ternary systems. But in 2000, the formation of stable quasicrystals in Ca-Cd- and Yb-Cd binary systems were also reported (Tsai and Cuo [13]). This discovery made the 1:6 and 13:58 (in terms of the atomic ratio) phases highly relevant as quasicrystals approximants, because they have compositions very close to those of quasicrystals. Their building blocks contain high-symmetry polyhedral that can be used as possible model for components of the quasicrystalline structures. Also Cu based icosahedral quasicrystals has been reported as an almost single phase in $Cu_{48}Mg_3Ga_{34}Sc_{15}$ alloy annealed at 770^0C for 61 h by Guo *et al*. (2002) [14]. A single phase quasicrystals in $Ag_{42}In_{42}Yb_{16}$ alloy composition was reported by the same group in 2002 [14]. These discoveries of the binary and ternary stable icosahedral quasicrystals have opened the door for research on metallic alloys for the search of more and more quasicrystalline phases. Today, over 100 different compositions are known to form quasicrystalline alloy. Hence, they are by no means rare.

Quasi-periodic materials have certain properties which are unique. Some of these are optical hardness and non-sticking properties. Electrically, they behave in a curious way for example resistivity decreases with increase in temperature. Some of these properties

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have been put to use. The first application of quasicrystals was nonstick coating on frying pans and cooking utensils. It was made by a French company, Sitram. A company in Sweden Sandvik, produces a precipitation-hardened stainless steel that has interesting properties. The steel is strengthened by small quasicrystalline particles and it does not corrode. It is extremely strong steel. It is used for razor blades and surgical tools.

Several groups in India such as Indian Institute of Science Bangalore, Banaras Hindu University Varanasi, Indian Institute of Technology (Delhi, Kanpur, Mumbai, Madras etc) and CSIR labs are investigating quasicrystals.

One such group located at Physics Department, Banaras Hindu University. This group has studied a variety of quasicrystalline phases. Some of these are Al-Cu-Cr, Al-Cu-Fe, Al-Co-Ni Al-Pd-Mn, Zr-Al (Ga)-Cu-Ni, Zr-Al-Cu-Ni-Ti, Ti-Zr-Ni etc. One interesting study made in $Al_{78}Mn_{20}Ge_2$ is that this material exhibited the existence of nearly all the qc variants such as icosahedral (primitive as well as facecentred), decagonal, rational approximant and irrational twins [15]. Fig. 3 shows the electron diffraction patterns from irrational twin and I phase for the said alloy.

Fig. 3

Electron diffraction pattern from irrational twin variants and I-phase grains along equivalent 5-fold [($\bar{3}50$) spots arising from, five different twin variants are indicated by arrows]

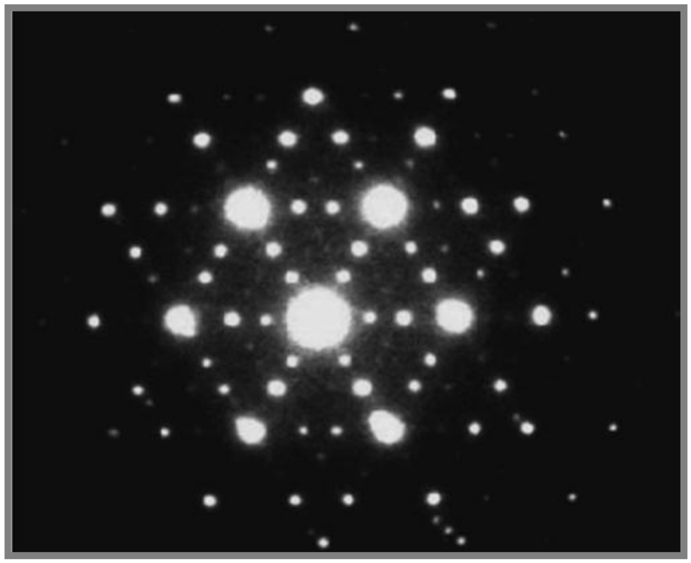

Fig.4

Electron Diffraction pattern of $Al_{65}Ga_5Pd_{17}Mn_{13}$ alloy showing formation of pure (no intervening phase) qc phase.

A recent study on qc alloy by Physics group of BHU is on the synthesis of bulk icosahedral phase of Al (Ga)-Pd-Mn alloy [16-17]. There has been no other study on the synthesis of pure (no other intervening phase) icosahedral phase in this alloy. A typical diffraction pattern from this alloy is shown in Fig. 4. The study of this film version of this qc phase is in progress and results will be forthcoming.

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