CHEMISTRY

BIMAN BASU

The Magic of Quasicrystals

THE *Oxford Dictionary of English* defines a crystal as "a piece of a homogeneous solid substance having a natural geometrically regular form with symmetrically arranged plane faces". Inside a crystal, atoms are ordered in repeating patterns, and depending on the chemical composition, they have different symmetries. It may be a three-fold symmetry where if the image is rotated 120 degrees the same pattern will appear.

The same principle applies to four-fold symmetries, where the same pattern repeats itself if the image is rotated 90 degrees; and to six-fold symmetries where the pattern repeats itself when the image is rotated 60 degrees. But the same is not true with five-fold symmetry, as distances between certain atoms will be shorter than between others. The pattern does not repeat itself, which was proof enough to scientists that it was not possible to obtain five-fold symmetries in crystals.

It was thus taken for granted that a five-fold symmetry was incompatible with translational symmetry, and hence with crystallinity. But this year's Nobel laureate in chemistry, Dan Shechtman of the Technion-Israel Institute of Technology in Haifa thought otherwise. He showed that it was indeed possible to have crystalline material with five-fold symmetry. The significance of the discovery can be judged by the fact that the chemistry prize has been awarded to a single scientist this year when most Nobel prizes in recent years have generally split credit for scientific advances among two or three people.

The unusual materials that Shechtman observed were not real crystals; they were named "quasicrystals" or "crystal-like" – materials with a mosaic-like atomic array that never quite repeats, thus flouting the established rules of crystal structure. (This is similar to "quasi-stellar objects" or quasars, which are not stars but "star-like" objects.) Quasicrystals represent a new state of matter that was not expected to be found with some properties of crystals and others of non-crystalline matter, such as glass. Quasicrystals are curious solids whose atomic structures are very regular but which never quite repeat.

Scientists study crystals using electron microscopes or X-ray diffraction. By measuring how the X-rays or electrons are diffracted, scientists can determine the patterns in which atoms are arranged inside the crystals. Electron diffraction basically involves firing electrons at a sample, usually in an electron microscope, when an interference pattern is produced. The pattern consists of dots of various sizes arranged in regular arrays depending on the arrangement of atoms in the crystal. By analysing the arrangement of dots in the diffraction pattern, scientists are able to determine the atomic structure of a crystal.

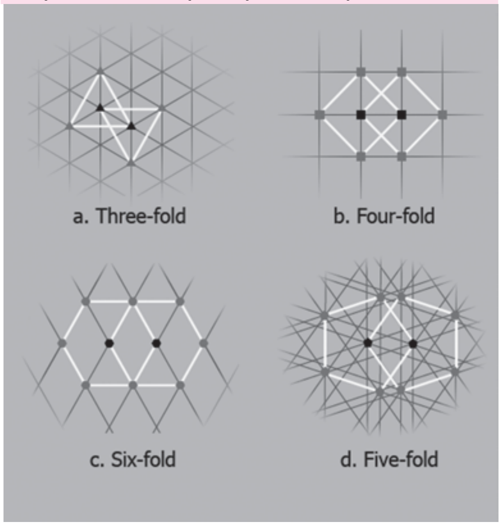
Shechtman discovered quasicrystal in course of routine study of metal alloys in his lab using electron diffraction. During a sabbatical in Maryland at the National Bureau of Standards, now known as the National Institute of Standards and Technology (NIST), he took a molten glob of the metals and chilled it rapidly. Then, on the morning of 8 April 1982 he was studying an aluminium-manganese alloy (Al_6Mn) using an electron microscope, when he found a strange pattern that defied all logic. He saw concentric circles, each made of ten bright dots at the same distance from each other. Startled by his observation, Shechtman is said to have commented, "There can be no such creature" in Hebrew. But he did not reject his observation outright, as many others would have probably done.

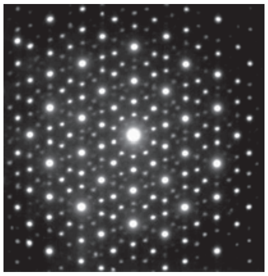
Shechtman had prepared the alloy sample by rapidly chilling the glowing molten metal, and the sudden change in temperature should have created complete disorder among the atoms, producing a non-crystalline mass. But the pattern he observed told a completely different story: the atoms were arranged in a manner that was contrary to the then accepted laws of nature. The diffraction pattern showed that the atoms inside the metal were packed into an ordered crystal, but a ten-fold symmetry was unknown in nature. Science plainly stipulated that a diffraction pattern with ten dots in a circle was impossible. Further experiments showed that the crystal itself did not have ten-fold symmetry like the diffraction pattern, but was instead based on an equally impossible five-fold symmetry. Shechtman concluded that the scientific community must be mistaken in its assumptions.

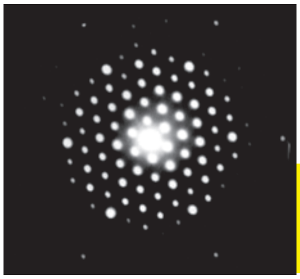
Revolutionary though the discovery was, Shechtman had a tough time convincing his colleagues and peers. At first the chemistry community refused to believe Shechtman's discovery – crystals could not have this strange structure. Shechtman was ridiculed for having made a foolish error. The head of the laboratory gave him a textbook of crystallography and suggested he should read it. Shechtman, of course, already knew what it said, but he preferred to trust his experiments more than the textbook. All the commotion finally led his boss to ask him to leave the research group, as his research had become an embarrassment. There could be no worse ignominy for a scientist.

But Shechtman had full confidence in his own findings. In 1984, he along with a colleague Ilan Blech wrote a paper attempting to interpret the observed diffraction pattern and translate it to the atomic pattern of a crystal and sent it to

Different kinds of symmetries in crystals. The pattern within the crystal with five-fold symmetry will never repeat itself.

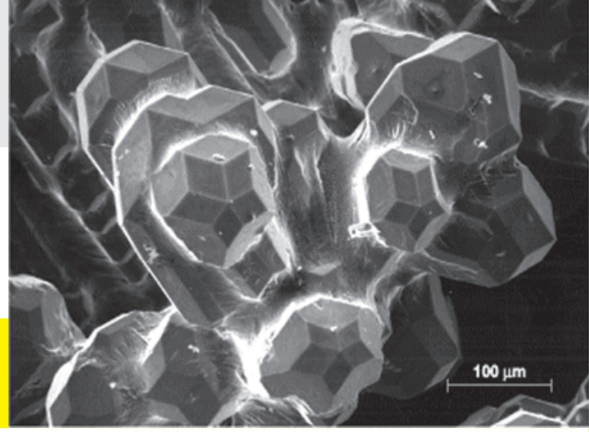






Shechtman's diffraction pattern was ten-fold: turning the picture a tenth of a full circle (36 degrees) results in the same pattern (far left) Electron diffraction pattern of a crystal showing six-fold symmetry (left).

Quasicrystals of an alloy of aluminium, copper, and iron, displaying an external form consistent with their icosahedral symmetry (right)

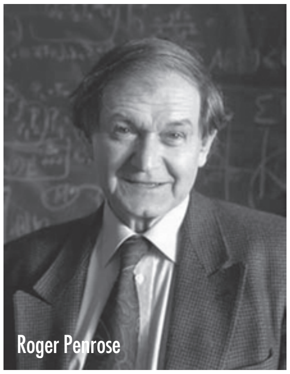


the *Journal of Applied Physics* for publication, but it was promptly returned. Then, in November 1984, together with Blech and two other physicists John Cahn and Denis Gratias, Shechtman finally got to publish his data in *Physical Review Letters*. The article "went off like a bomb among crystallographers". It questioned the most fundamental truth of their science: that all crystals consist of repeating, periodic patterns. Shechtman had proved his point.

On Christmas Eve, 1984, only five weeks after Shechtman's article appeared in print, physicists Paul Steinhardt and Dov Levine published an article where they described quasicrystals and their aperiodic mosaics. The term 'quasicrystals' appeared for the first time in this article.

When Shechtman published his discovery, he still had no clear grasp of what the strange crystal actually looked like on the inside. Evidently its symmetry was five-fold, but there was no clue as to how the atoms were packed in the crystal. That understanding came later, from a combination of mathematics and art.

Mathematical puzzles and logic problems are quite common and also popular. During the 1960s, mathematicians began to ponder whether a mosaic could be laid with a limited number of tiles so that the pattern never repeated itself, to create a so-called 'aperiodic' mosaic. Then, in the mid-1970s, a British professor of mathematics, Roger Penrose, provided a most elegant solution to the problem. He created aperiodic mosaics with just two different tiles, for example, a fat and a thin rhombus. In fact, understanding the structure of quasicrystals was only possible thanks to Roger Penrose's discovery of that beautiful set of aperiodic tiles. What had started out as a mathematical idea, explored by Penrose "just for fun", unexpectedly provided the answer to a question from a very different, and very applied, area of study.



He created aperiodic mosaics with just two different tiles, for example, a fat and a thin rhombus. Thanks to Roger Penrose's discovery of that beautiful set of aperiodic tiles.

In mathematics and the arts, two quantities are in the golden ratio if the ratio of the sum of the quantities to the larger quantity is equal to the ratio of the larger quantity to the smaller one. The golden ratio can also be obtained from the Fibonacci sequence in which each number is the sum of the two preceding numbers: 1, 1, 2, 3, 5, 8, 13, 21, 34, 55, 89, 144, etc. If one of the higher numbers in the Fibonacci sequence is divided with the preceding number – for instance, 144/89 – one gets the golden ratio.

A fascinating aspect of both quasicrystals and aperiodic mosaics is that the golden ratio, which is also designated by the Greek symbol tau (ô) and has a value of approx. 1.61803399, occurs over and over again. For instance, the ratio between the numbers of fat and thin rhombi in Penrose's mosaic is ô. Similarly, the ratio of various distances between atoms in quasicrystals is always related to ô.

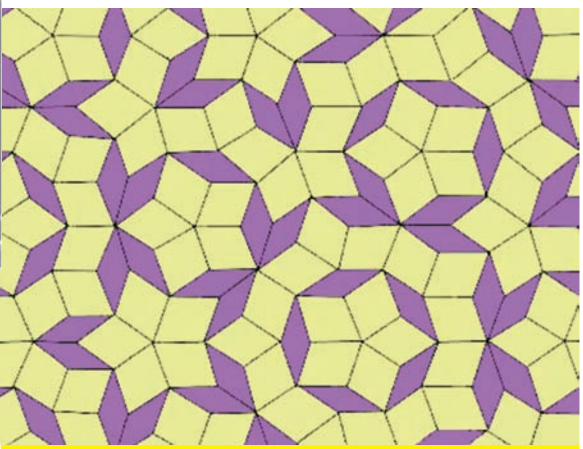
Both the Fibonacci sequence and the golden ratio are important to scientists when they want to use a diffraction pattern to describe quasicrystals at the atomic level. The Fibonacci sequence can also explain how the discovery of quasicrystals has altered chemists' conception of regularity in crystals.

Subsequent to Shechtman's work, in 1992, even the definition of crystal had to be changed. The International Union of Crystallography had to alter its definition of what a crystal is. Previously a crystal had been defined as "a substance in which the constituent atoms, molecules, or ions are packed in a regularly ordered, repeating three-dimensional pattern". The new definition became "any solid having an essentially discrete diffraction diagram". This definition is broader and allows for possible future discoveries of other kinds of crystals.

Shechtman's discovery indeed revolutionised chemistry. Since the day he dared to stand firm against established science, ridicule and mockery from colleagues, scientists have succeeded in producing other kinds of quasicrystals in the lab. Quasicrystals have also been found in many other materials, including a naturally occurring mineral from a Russian river. Materials scientists have been exploring quasicrystals because of their distinct properties – they are hard, brittle, slippery and, unlike most metals, poor conductors of electricity.

However, quasicrystals have so far had a modest impact in the everyday world, although a few of their applications are significant. For example, one kind of highly resilient steel, consisting of hard steel quasicrystals embedded within softer steel, is now used in razor blades and thin needles for eye surgery. A Swedish company has also found quasicrystals in a certain form of steel, where the crystals reinforce the material like armour. Scientists are currently experimenting with using quasicrystals in different products such as frying pans and diesel engines.

Daniel Shechtman was born in Tel Aviv in 1941 and was educated in Israel. He received his Bachelor's degree in 1966, Master's degree in 1968, and a Doctorate in 1972, all from Technion-Israel Institute of Technology in Haifa. After receiving his doctorate, Shechtman was an NRC fellow at the Aerospace Research Laboratories at Wright Patterson AFB, Ohio, where he studied for three years the microstructure and physical metallurgy of titanium aluminides. In 1975, he joined the department of materials engineering at Technion. In 1981-I983 he was on Sabbatical at the Johns Hopkins University, where he studied rapidly solidified



Mosaic made of fat and thin Penrose tiles

aluminium transition metal alloys (joint program with NBS). It was during this study that he discovered the icosahedral phase, which opened the new field of quasicrystals.

In 1992-1994 he was on Sabbatical at NIST, where he studied the effect of the defect structure of chemical vapour deposited (CVD) diamond on its growth and properties. Shechtman's research at Technion is conducted in the Louis Edelstein Centre, and in the Wolfson Centre, which is headed by him.

Daniel Shechtman

Shechtman is the recipient of several prestigious awards, which include Weizmann Science Award (1993), Israel Prize in Physics (1998), Wolf Prize in Physics (1999), Gregori Aminoff Prize of the Royal Swedish Academy of Sciences (2000), Muriel & David Jacknow Technion Award for Excellence in Teaching (2000), EMET Prize in Chemistry (2002), and European Materials Research Society 25th Anniversary Award (2008), among others. He has also served on several Technion Senate Committees and headed one of them.

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PHYSICS

K. SMILES MASCARENHAS

"The Universe will End in Ice"

ACCORDING to the 2011 Nobel laureates in physics, the Universe will end in ice!

It all started with theories regarding the nature of the Universe. As early as in 1917, Albert Einstein came to know that the Universe was not static but expanding when he solved the gravitational field equations arising in the General Theory of Relativity. It was Einstein's firm belief at that time that the Universe will remain the same at whatever epoch we make our observation (the steady state theory as it is called is still being advocated by some astrophysicists).

For the first time in his life he gave way to a "common sense" approach to physics, rather than his normal "revolutionary" approach. He made use of a technique that university science students adopt when they do not get the desired result in the Lab – a technique commonly called "cooking"! He introduced a "cosmological constant **l**" and arrived at a "modified field equation" that made the Universe static.

Later, in 1929, Edwin Hubble (a former lawyer by profession) and Milton Humason (a former mule driver by profession), through their observation of distant galaxies at the Mount Wilson Observatory, concluded that the Universe is indeed expanding. Einstein later regretted that introduction of the Cosmological constant was the "greatest blunder" in his life. Had he predicted the expansion of the Universe in advance, he could have added one more feather in his cap (though it is debatable if we could find space for one more feather in his cap!). It is remarkable that he rated this blunder above his blunder of getting married twice!

However, observations made by two groups of physicists in 1997 and published in 1998 (for which this year's Nobel Prize in Physics is being awarded), have shown that Einstein's cosmological constant, introduced for the wrong reason, is actually right! One of the two research groups was headed by Saul Perlmutter of Lawrence Berkeley National Laboratory, Berkeley, CA, USA and the other by Brian P. Schmidt of Australian National University, Weston Creek, Australia. One half of the 2011 Nobel Prize in Physics will go to Saul Perlmutter, and the other half will be shared by Brian P. Schmidt and Adam G. Riess of Johns Hopkins University, Baltimore, MD, USA.

Even without the Cosmological constant, it was a million dollar question whether the Universe was "open" (that is, keeps on expanding for ever, probably at an accelerated pace) or "closed" (slows down in its expansion, ultimately collapsing into a "big crunch" where all matter will end in a singularity). The first would happen if "dark energy" (energy that could not be detected by conventional equipments) dominated the Universe and the latter would happen if the so-called "dark matter" (matter that does not emit radiation at observable wavelengths) filled up the Universe, causing a gravitational collapse. Most astronomers (including the Nobel Laureates) believed in the latter scenario and they were in for a great surprise when observations proved the contrary.

The teams reached the conclusion by observing supernova explosions at about one-third the distance to the observable limit of the Universe (modern estimates put the limit of the observable Universe at about 46 to 47 billion light years away!). Supernovae are stars that undergo a cataclysmic explosion during the end of their lives. Normally, very heavy stars (more than ten times massive than the Sun) would rapidly use their nuclear fuel and end up in an explosion that outshines the parent galaxy.

Supernovae can be used as "standard candles" to estimate their distance from us provided they all have the same luminosity. The dimmer supernova would indicate a larger distance from us and the brighter will indicate a relatively closer one. But this was not to be the case, since supernovae can have a wide range of luminosity according to their types. Initially, supernovae were classified as Type I or Type II, but the classification became more and more diversified as more and more supernovae were observed! The light curve of the supernova (intensity variation with time) formed the basis for classification.

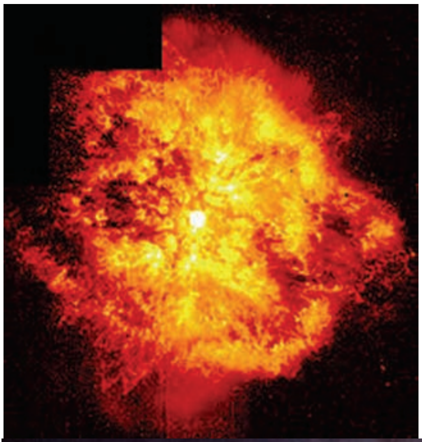
Adem

Brian

Saul

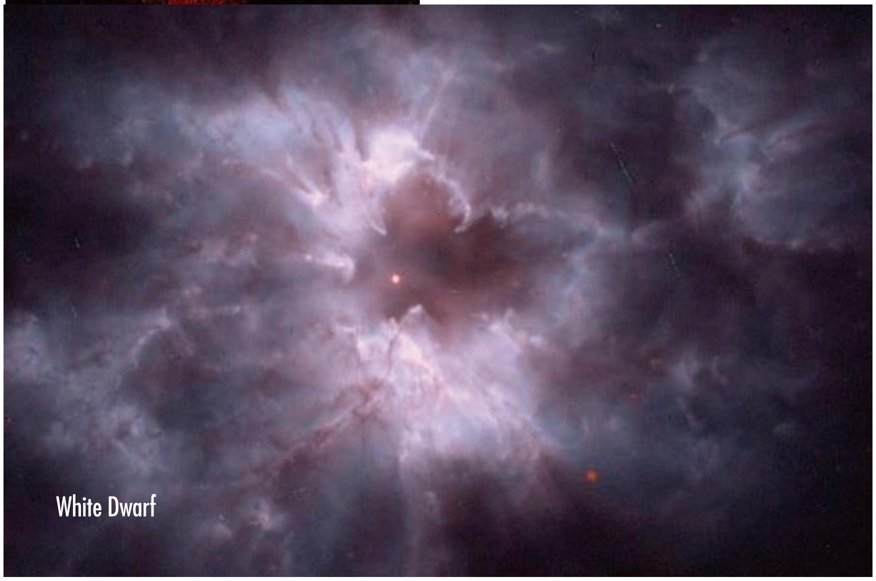
They needed high quality telescopes around the world at the crucial time when the supernova flared, something that cannot be guaranteed with hosts of other astronomers vying for time for their own observations. They needed to act fast because a supernova fades quickly. Thus, the potential problems they faced were numerous, which made the researchers worthy of a Nobel Prize!

Both the teams chose to observe a class of supernova called the Type Ia supernova (this suggests that their research was free from the rat race that many research teams adopt!). Type Ia supernovae are totally different from the rest of the massive supernovae. A Type Ia supernova is a sub-category of cataclysmic variable stars that result from the violent explosion of a white dwarf star.



A white dwarf is the remnant of a star that has completed its normal life cycle and has ceased to produce energy by nuclear fusion. They are as heavy as the Sun but as small as the Earth. However, white dwarfs of the common carbon-oxygen variety (on the border of the Chandrashekar limit) are capable of further fusion reactions that release a great deal of energy if their core temperatures rise high enough. This can happen when the white dwarf accretes extra mass from a binary companion star.

This category of supernovae produces consistent peak luminosity because of the uniform mass of white dwarfs that explode via the accretion mechanism. The stability of this value allows these explosions to be used as standard candles. But the enormous distance the astronomers were looking at (about fifteen billion light years away), the light received from them was extremely weak and could be studied only by using CCD cameras (the discoverer of which received the 2009 Nobel Prize in Physics!). The two research teams found over 50 distant supernovae whose light was weaker than expected – a signature that proved that the expansion of the Universe was accelerating. Ultimately, everything in the Universe will cool down into a frozen graveyard.



White Dwarf

The researchers had many other problems to deal with. Type Ia supernovae are not quite as reliable as they initially appeared – the brightest explosions fade more slowly. Furthermore, the light emitted by the supernovae was to be extracted from the background light of their host galaxies. Another important task was to obtain the correct brightness. The intergalactic dust between us and the stars changes the intensity of the starlight. This affects the results when calculating the maximum brightness of the supernova.

The light curve had to be analyzed over time in order to be able to compare it with other supernovae of the same type at known distances. This required a network of scientists that could decide quickly whether a particular star was a worthy candidate for observation. They needed high quality telescopes around the world at the crucial time when the supernova flared, something that cannot be guaranteed with hosts of other astronomers vying for time for their own observations. They needed to act fast because a supernova fades quickly. Thus, the potential problems they faced were numerous, which made the researchers worthy of a Nobel Prize!

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PHYSIOLOGY OR MEDICINE

A Nobel for a Noble Cause

BIJU DHARMAPALAN

ON October 3rd it was announced that this year's Nobel Prize was being awarded to Bruce A. Beutler at the Scripps Research Institute in California and Jules A. Hoffmann at the French National Center for Scientific Research for their discoveries concerning the activation of innate immunity and the other half to Ralph M. Steinman at Rockefeller University in New York City for his discovery of the dendritic cell and its role in adaptive immunity. The prize money would be divided between Bruce Beutler and Jules Hoffmann, who jointly shared half the 10 million-kronor ($1.5 million) award, and Ralph Steinman would receive the other half.

Unfortunatly, in the rarest of events and the first in the history of the Nobel Prize, a dead person was named the laureate. The Nobel Assembly didn't know Steinman was dead when it chose him as a winner. The events that have occurred are unique and are unprecedented in the history of the Nobel Prize. After a series of quick deliberations the committee confirmed that the award still stands.

Diseases have always been a prime area of concern for humanity since ages. In every stage of time scale humans have been afflicted with different diseases caused due to different pathogens present in the environment or due to genetic or physiological reasons. Be it the occurrence of small pox or polio or AIDS or cancers, human beings are always afflicted by one disease or another. There rarely occurs a person who hasn't caught cold or developed fever.

Our body harbors millions of microorganisms, some of which are beneficial and have become an integral part of our system. But there are equal numbers of microbes in our surroundings waiting to invade our cells. All may not be successful, but some indeed gain entry crossing the natural barrier created by our system. Scientists were always fascinated enough to explore the mechanism behind the emergence of diseases. The trio who were awarded this year's Nobel Prize in Physiology or Medicine tried to unravel the secrets behind our immune process.

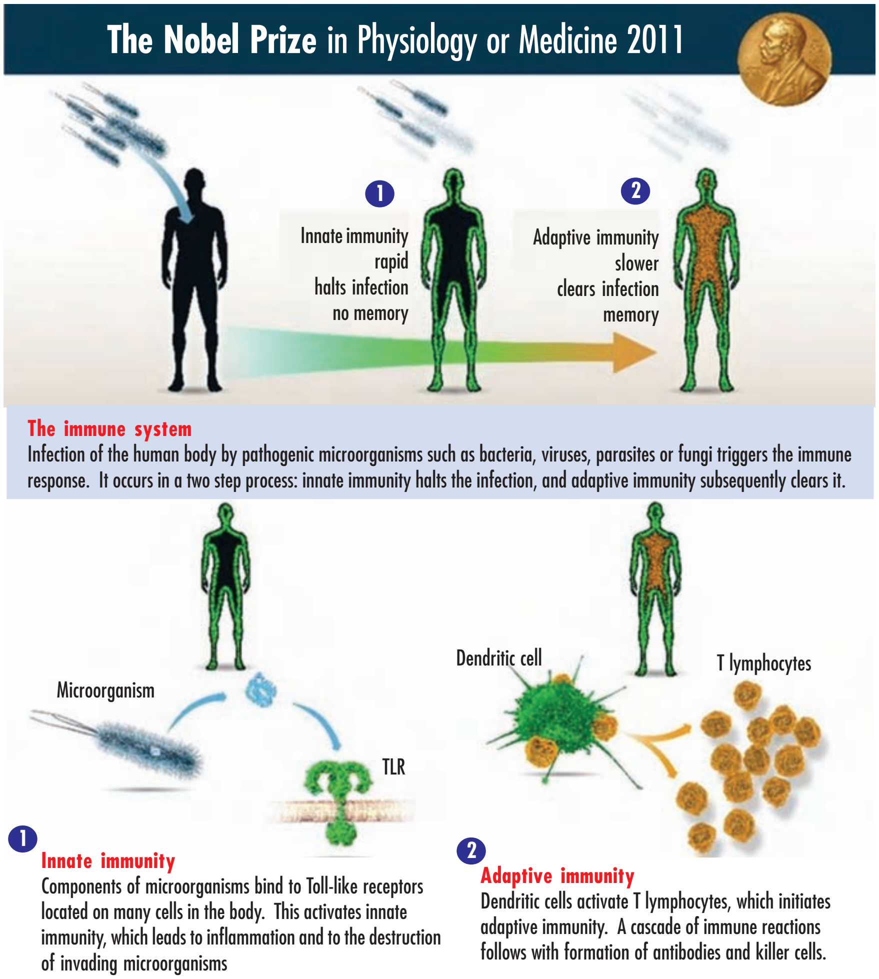
There are two lines of defense mechanism in humans—innate and adaptive immunity. The first line of defense, innate immunity, can destroy invading microorganisms and trigger inflammation thus blocking their assault. If microorganisms break through this defense line, adaptive immunity is called into action. With its T and B cells, it produces antibodies and killer cells that destroy infected cells.

After successfully combating the infectious assault, our adaptive immune system maintains an immunologic memory that allows a more rapid and powerful mobilization of defense forces the next time the same microorganism attacks. These two defense lines of the immune system provide good protection against infections but they also pose a risk. If the activation threshold is too low, or if endogenous molecules can activate the system, inflammatory disease may follow.

The discoveries of the three Nobel Laureates have revealed how the innate and adaptive phases of the immune response are activated and thereby provided novel insights into disease mechanisms. Their work has opened up new avenues for the development of prevention and therapy against infections, cancer, and inflammatory diseases.

Jules Hoffmann made his pioneering discovery in 1996, when he and his co-workers investigated how fruit flies combat infections. They had access to flies with mutations in several different genes including Toll, a gene previously found to be involved in embryonal development by Christiane Nüsslein-Volhard (Nobel Prize 1995). When Hoffmann infected his fruit flies with bacteria or fungi, he discovered that Toll mutants died because they could not mount an effective defense. He was also able to conclude that the product of the Toll gene was involved in sensing pathogenic microorganisms and Toll activation was needed for successful defense against them.

Bruce Beutler was searching for a receptor that could bind the bacterial product, lipopolysaccharide (LPS), which can cause septic shock, a life threatening condition that involves overstimulation of the immune system. In 1998, Beutler and his colleagues discovered that mice resistant to LPS had a mutation in a gene that was quite similar to the Toll gene of the fruit fly. This Toll-like receptor (TLR) turned out to be the elusive LPS receptor. When it binds LPS, signals are activated that cause inflammation and, when LPS doses are excessive, septic shock. These findings showed that mammals and fruit flies use similar molecules to activate innate



An overview of immune system in humans (Courtesy: www.nobelprize.org)

immunity when encountering pathogenic microorganisms. The sensors of innate immunity had finally been discovered.

The discoveries of Hoffmann and Beutler triggered an explosion of research in innate immunity. Around a dozen different TLRs have now been identified in humans and mice. Each one of them recognizes certain types of molecules common in microorganisms. Individuals with certain mutations in these receptors carry an increased risk of infections while other genetic variants of TLR are associated with an increased risk for chronic inflammatory diseases.

Ralph Steinman discovered, in 1973, a new cell type that he called the dendritic cell. He speculated that it could be important in the immune system and went on to test whether dendritic cells could activate T cells, a cell type that has a key role in adaptive immunity and develops an immunologic memory against many different substances. In cell culture experiments, he showed that the presence of dendritic cells resulted in vivid responses of T cells to such substances. These findings were initially met with skepticism but subsequent work by Steinman demonstrated that dendritic cells have a unique capacity to activate T cells.

Further studies by Steinman and other scientists went on to address the question of how the adaptive immune system decides whether or not it should be activated when encountering various substances. Signals arising from the innate immune response and sensed by dendritic cells were shown to control T cell activation. This makes it possible for the immune system to react towards pathogenic microorganisms while avoiding an attack on the body's own endogenous molecules.

The work of the three scientists has been pivotal to the development of improved types of vaccines against infectious diseases and novel approaches to fighting cancer. The research has helped lay the foundations for a new wave of "therapeutic vaccines" that stimulate the immune system to attack tumors. They have made possible the development of new methods for preventing and treating disease, for instance with improved vaccines against infections and in attempts to stimulate the immune system to attack tumors. Almost all vaccines against microbes, vaccines against cancer, and vaccines to try to eliminate and down-regulate immunity in inflammatory diseases are based on these discoveries.

Special mention has to be made about Steinman who had set his sights on use of the dendritic cells in vaccines to prevent chronic infections, such as HIV and tuberculosis, and in cancer therapies. For example, understanding dendritic cells led to the launch of the first therapeutic cancer vaccine last year by Dendreon. Its product Provenge (known generically as sipuleucel-T) has been approved by FDA for treating men with advanced prostate cancer.

Steinman also set an example to the scientific fraternity. When he was diagnosed with pancreatic cancer, he volunteered to test the vaccine on his body. Shortly after he was diagnosed he met two former members of his lab Michel Nussenzweig and Mellman, both of whom now run successful immunotherapy research programmes of their own and talked about various possibilities in treatment. It is said that his research with his own body in a way prolonged his life.

Experimenting on his life he showed the way forward in developing a successful immunotherapy for pancreatic cancer. It's sad that a person who showed the value of his discovery through his life and who lived a life for science till his last breath couldn't hear the happy news of him being adorned with the coveted prize. Had the Nobel committee known about the sad demise before announcement of the award they could have been precluded him.

Even though what followed was an unprecedented event in the history of the Nobel Prizes since 1902 where the prizes are not awarded posthumously, the committee made a brave decision not to revoke the award. Even death cannot take away the laurels of hard work and dedication.

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