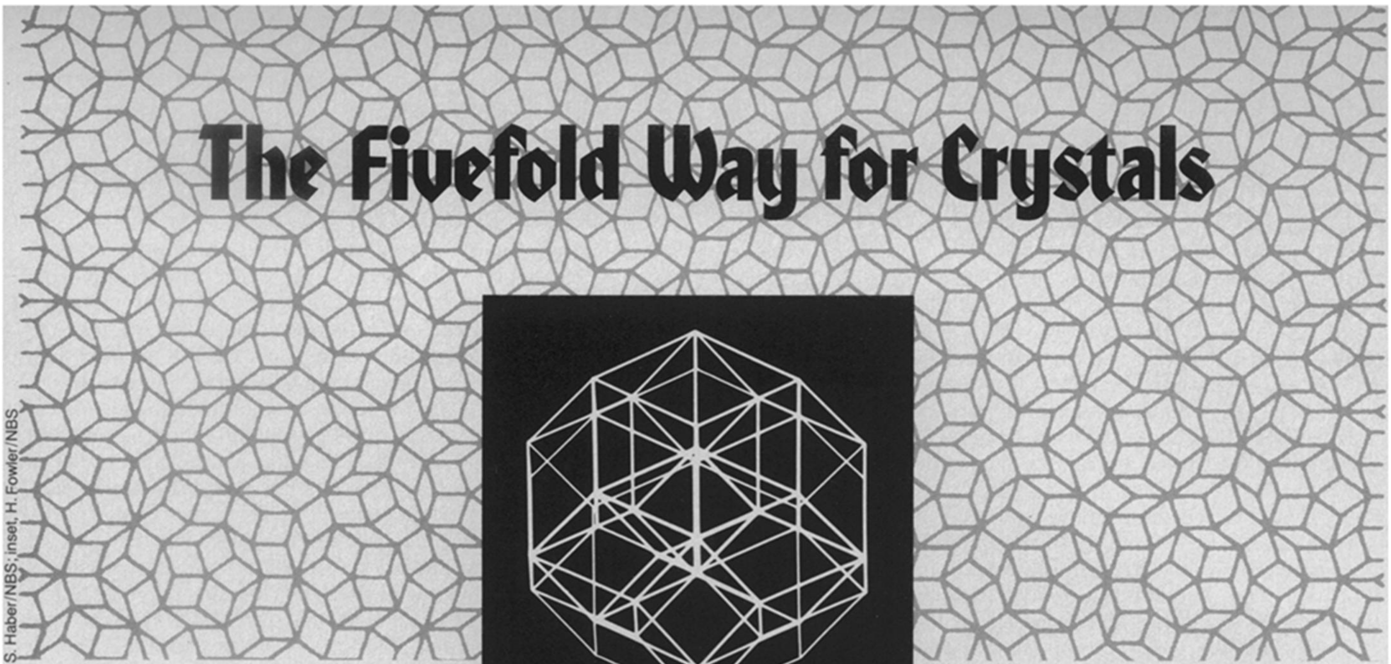
The Fivefold Way for Crystals



S. Haber/NBS; inset, H. Fowler/NBS

The triacontahedron (shown above against the backdrop of a Penrose tiling), with its 30 faces, is the building block for a three-dimensional Penrose pattern. The structure itself is constructed from two types of rhombohedra: One type is acute or "sharp," the other is obtuse or "flat."

By IVARS PETERSON

Roger Penrose didn't have anything practical in mind for the remarkable tiling patterns he created when he started drawing his diamond tapestries about 10 years ago. The exercise was simply a challenging mathematical game that tickled his fancy.

This game has turned into a serious mathematical pursuit with the recent discovery (SN: 1/19/85, p. 37) of tiny metallic crystals, wrapped in aluminum cocoons, that have a form as startling and unexpected as five-pointed snowflakes. X-rays or electrons reflected from these crystals trace out patterns that, according to the long-standing rules of crystallography, shouldn't even exist.

The discovery not only strikes at some well-entrenched assumptions in crystallography but also opens up a new kind of solid-state physics and raises the possibility of finding such crystals in nature. Penrose's special tiling patterns point the way toward understanding this new crystal structure.

In its simplest form, a tiling problem is not unlike the task of completely covering a bathroom floor with tiles. Tiles in the shape of equilateral triangles, squares, parallelograms or hexagons do the job nicely. But when the tiles are regular pentagons, with five sides of equal length, embarrassing gaps punctuate the pattern.

Penrose, a physicist then at Oxford University in England and now at Rice University in Houston, solved the pentagon problem by devising a pattern that has a pentagon's fivefold symmetry but covers a flat surface completely. The trick is to use a pair of diamond-shaped figures, one fat and one thin, rather than just a single shape. But, whereas a tiling pattern made up of, say, squares repeats itself at regular intervals, this pattern does not. It is nonperiodic. Tiles don't line up to form neat rows with lattice distances defined by whole numbers. Instead, the irrational number, $(1+\sqrt{5})/2$, pervades the pattern.

Penrose also played the three-dimensional version of his tiling game — packing space with simple blocks, such as pairs of squashed cubes (rhombohedra), that generate nonperiodic solid structures with fivefold or, in three dimensions, icosahedral symmetry. "It did occur to me that this certainly had implications for crystallography," recalls Penrose. In fact, it was clear to him that some of the things that crystallographers accepted without question were not always strictly true. But, he says, "I suppose I'm used to people not paying attention to me."

Penrose couldn't counter traditional crystallography's weighty authority, rooted in rules that had been developed a century before. These rules rigidly maintained that nonperiodic structures are forbidden because the units of atoms that make up crystals must fall into an orderly, regular arrangement in order to fill space completely. In common salt, for instance, sodium and chloride ions sit at the corners of a cube, and these cubes stack neatly to fill out each salt crystal.

A few people, including crystallographer Alan L. Mackay of Birkbeck College in London, England, actually did take Penrose's ideas seriously. But it took the discovery of a real material showing fivefold symmetry, a metallic solid composed of aluminum and manganese, to get scientists and mathematicians excited.

The discoverer was Dan Shechtman of the Israel Institute of Technology in Haifa. Three years ago, while working at the National Bureau of Standards (NBS) in Gaithersburg, Md., on a project involving the study of aluminum alloys, he found a material that yielded a peculiar diffraction pattern. No one had ever seen such a pattern before. It implied that crystals of this new aluminum-manganese alloy had a fivefold symmetry. So contrary was this to conventional views of crystals that it took Shechtman a long time to persuade others that his discovery was legitimate.

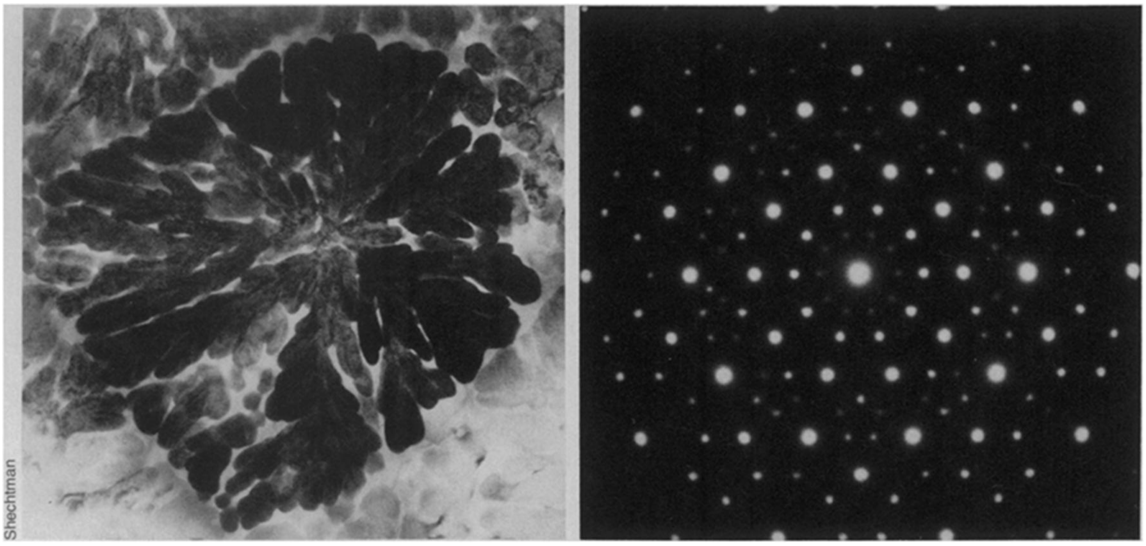
It's the kind of discovery that prompts friends and colleagues to call you up "to find out whether you've gone crazy," says NBS materials scientist John W. Cahn. Because so many scientists at first couldn't believe that such a crystal structure existed, the first paper describing the alloy, which Cahn playfully calls "shechtmanite," didn't appear until last November.

"Shechtman was the key person in this work," Cahn says. "He was persistent, pushing ahead in the face of ridicule." Now, several NBS researchers (including Cahn) and other scientists throughout the world are starting to look at these new crystals more closely, both theoretically and experimentally.

The crystal-growing process begins with a hot, liquid mixture of aluminum and manganese, iron or chromium. Squirted onto a spinning, water-cooled, copper wheel, the molten metal freezes rapidly to produce a thin, metallic ribbon (SN: 12/12/81, p. 380). Within this ribbon, icosahedral crystals form as clusters of nodules, only a few microns in size.

The cooling rate is very important. "If we cool it too fast, we make a metallic glass," says Cahn. "If we give it too much time, we get the equilibrium crystal." In the latter case, the crystal's atoms settle into an orderly, periodic pattern consistent with crystallographic rules. However, if the metal crystallizes into its icosahedral form, this unusual structure is stable for hours even at temperatures as high as 350°C before it rearranges itself into its regular, equilibrium form.

The evidence in favor of the existence of crystals with an icosahedral symmetry is



Shechtman

The feathery needles of a rapidly cooled aluminum and iron alloy reveal the material's icosahedral crystal form (left). The diffraction pattern obtained by firing electrons at a small area of the crystal (right) shows concentric rings of 10 spots, consistent with a fivefold symmetry.

steadily becoming more persuasive. Perhaps the most dramatic instance is seen in the five-branched, leafy crystals of a recently produced aluminum-iron alloy. As materials scientists learn to grow purer and larger crystals, says Cahn, they may eventually find single crystals in the shape of icosahedra—20-sided solids with triangular faces.

Cahn suspects that some mineral crystals in nature may also show an icosahedral symmetry. He now has a sample of pyrite, an iron sulfide mineral, that has the shape of a dodecahedron, a solid with 12 pentagonal faces and 20 corners. But a small triangular section is missing from each corner, indicating that the crystal could have grown as an icosahedron.

This type of pyrite may have been formed deep within the earth at pressures and temperatures at which the icosahedral crystalline form is stable, says Cahn. However, he speculates, when the mineral reached the earth's surface, its atoms gradually rearranged themselves into a more regular pattern, while the mineral's outward form remained unchanged.

Cahn's theory may clear up a long-standing mineralogical mystery that has surrounded this particular form of pyrite. Such an explanation, he says, would have been unthinkable just a short time ago. But, adds Cahn, "This is enough information to convince me that the icosahedral phase can be stable under some range of pressures and temperatures and that we will be able to grow large crystals. Nature has probably already done so.

"We are trying to expand the window of growth conditions [between the glass and equilibrium crystal phases] so that we can grow bigger and better crystals," he says. So far, samples of the new crystal form have been too small and too impure to allow the measurement of properties like density. But already there are hints that these new materials may show remarkable structural and electronic qualities.

This possibility excites Shechtman, who is beginning a systematic study of the electrical, magnetic, mechanical and chemical properties of the various alloys that have been and continue to be discovered. These new materials are interesting, says Shechtman, because they have the highest possible degree of symmetry, yet despite being very structured, they are isotropic.

Generally, periodic crystals are anisotropic: They have different properties in different directions. Stated simply, this means that a path through a periodic crystal's lattice, depending on the direction chosen, may be cluttered with atoms or, if it happens to fall between the evenly spaced rows, completely free of obstacles. On the other hand, in a lattice with an icosahedral symmetry, every path is essentially identical. Hence, many of its properties will be the same in all directions.

"This is the first truly isotropic crystalline material that we have found," says Shechtman. Out of this may come some unique uses for the new alloys.

"All my training has been with the assumption that crystals are strictly periodic," says Cahn. "Now, almost everything has to be reexamined. The axiom of periodicity is so deeply embedded in solid-state physics that we've been going through elementary textbooks to see which properties are going to be different."

"Theoretically, we've opened up a whole realm of condensed-matter physics," says Paul J. Steinhardt of the University of Pennsylvania in Philadelphia. Steinhardt and graduate student Dov Levine introduced the idea of a "quasiperiodic" lattice to describe these new crystals. Their concept is based on a three-dimensional version of Penrose's tiling patterns.

"We have to ask all of the same questions that one asks for crystals all over again for these quasicrystals," says Steinhardt. Using his mathematical model, Steinhardt has started to work out the theoretical electronic and thermal properties of quasicrystals. He is also looking at quasicrystalline analogs of the types of defects, such as cracks, misalignments or dislocations, that weave through ordinary, periodic crystals.

"These are all things that we have made some progress on," says Steinhardt, but much more needs to be done. Theoretical values for these properties will be important, he says, for checking out how good an approximation the "real" material is to a "true" quasicrystal.

Says Cahn, "There are still a lot of things that need to be explained." One important instance is the location of individual atoms within the icosahedral crystal lattice. Diffraction patterns and current mathematical models give only the basic overall arrangement or lattice. "When you decorate the lattice with actual atoms, you get a whole variety of different structures," he says. All such lattices generate the same diffraction pattern, although the relative intensities of the pattern's spots vary, depending on the location of individual atoms within a lattice.

"The way in which atoms are arranged seems to be best understood by the new science of tiling," says Shechtman. This is the best way — the only way — to fill an n-dimensional space with the minimum number of units so that they fall in a nonperiodic sequence, he says.

"We've needed a lot of help from mathematics," says Cahn. "A number of crystallographers have said to me: 'We've had blinders on. The [conventional] mathematical theory was so perfect, so complete, so much without exception that after a while we stopped looking for exceptions. It became part of the basic axioms and we proceeded from there. If there was an exception, we said it was not an exception — it was just a complication, and we were still within the framework.'"

Now, crystallographers need to learn some new mathematics. And theorists have a strange new structure to ponder. □