IMPOSSIBLE CRYSTALS

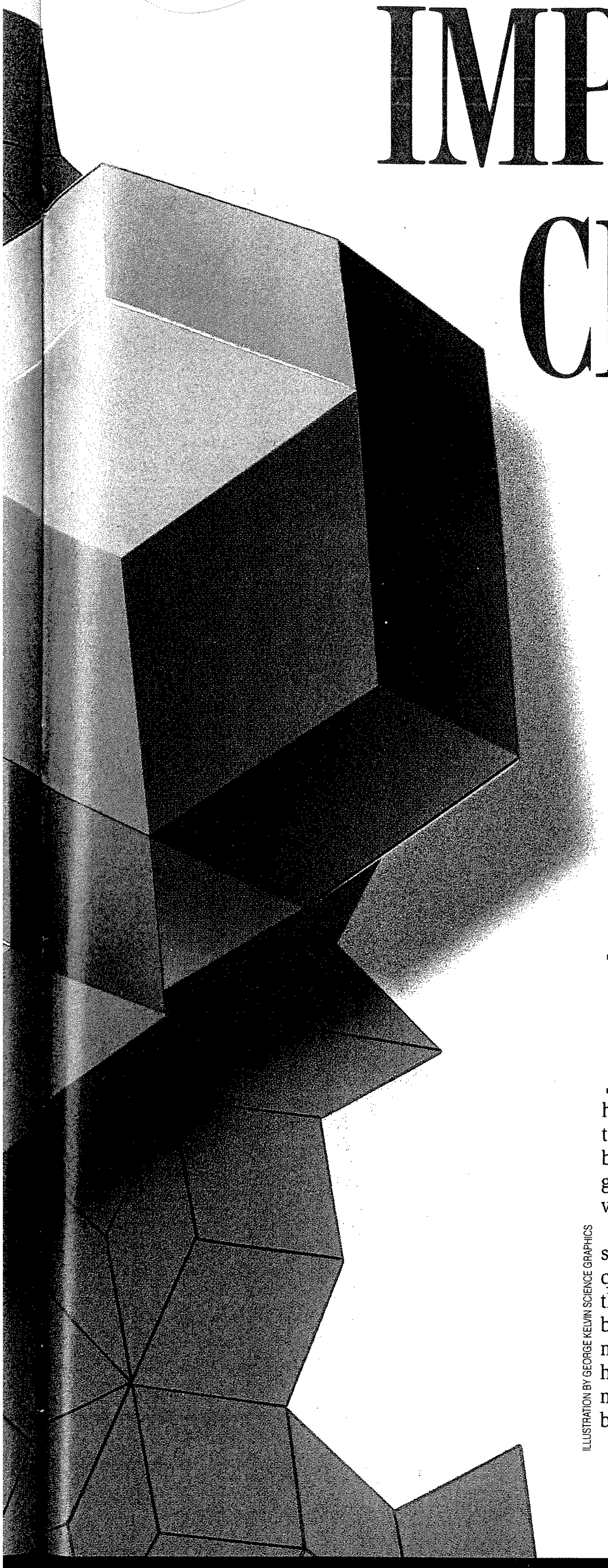


ILLUSTRATION BY GEORGE KELVIN SCIENCE GRAPHICS

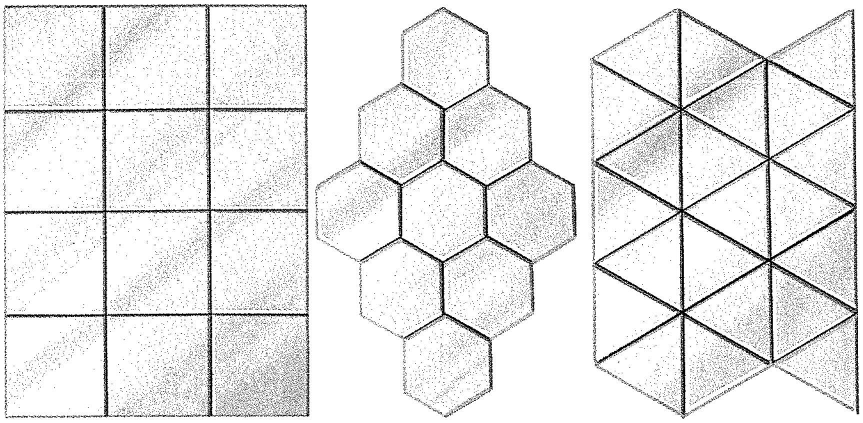
Quasicrystals started out as a mathematical game. But one day the game became real.

BY HANS C. VON BAEYER

I do not know what I may appear to the world; but to myself I seem to have been only like a boy, playing on the seashore." Thus Sir Isaac Newton, the patriarch of modern physics, defined his life's work. And in so doing he revealed a truth about his vocation that is rarely apparent to nonscientists. Too often the playful child in the center of the enterprise is hidden by a wall of abstruse theory and an impenetrable welter of technology. But occasionally we see a little face peeking out from behind the mask of profundity, and from such rare glimpses we gain a better insight into the true nature of science than from volumes of erudite explanation.

The vital role of scientific playfulness is vividly illustrated by the story behind the discovery of a new class of materials known as quasicrystals. Quasicrystals are three-dimensional structures, but their antecedents exist in two dimensions, in the plane. The story begins in January 1977, when Martin Gardner devoted his Mathematical Games column in *Scientific American* to the question of how to cover a plane with tiles. It's a problem as ancient as Greek mosaics, yet Gardner's essay sparked a flurry of research that brought tiling to the forefront of modern physics.

The mathematical analysis of tiling begins with the observation



There are only a few basic shapes, such as squares, regular hexagons, and triangles, that can fill a plane completely without leaving gaps.

that a plane—a bathroom floor, for example—can be covered, without gaps, by tiles in the shape of rectangles, triangles, or hexagons, but not by circles or stars or even, significantly, regular pentagons. No matter how you try to join pentagonal tiles, they will always leave gaps. To convince yourself of that, just cut out a pile of identical pentagons and play with them on your desk. You will soon develop a distinct antipathy toward the five-sided monsters.

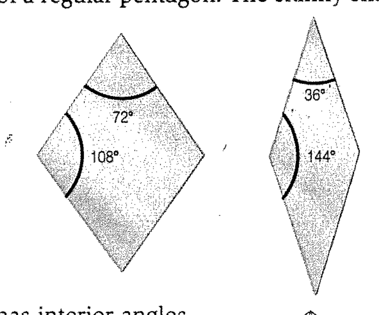
A regular pentagon has fivefold symmetry, which means that if you rotate the pentagon about its center, it looks the same after every one-fifth of a rotation. Similarly a square has fourfold symmetry, a hexagon sixfold, and so on. Any shape that tiles a plane can impart its symmetry to the whole tiling pattern: you can rotate a hexagonal tiling about the center of any hexagon, for example, and see that the whole pattern has sixfold symmetry. If you could use a pentagon to tile a plane, then the tiling could exhibit fivefold symmetry. But, of course, pentagons are prohibited.

Using two tile shapes instead of one, however, Gardner reproduced intriguing tiling patterns that did indeed display fivefold symmetry: whole regions could be rotated so that the arrangement of tiles within looked the same every one-fifth of a rotation. One pattern, for example, contained groups of tiles that looked like five-pointed stars. It was as if pentagons were defining the rules without actually being present.

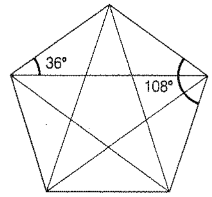
Gardner learned how to construct these puzzling tilings from Roger Penrose, a British mathematical physicist. Penrose has a knack for playing tricks with geometry. In his youth he and his father drew an impossible object, the "Penrose staircase," which spirals round and round without getting higher or lower. The Dutch artist M. C. Escher used their mind-boggling concept in a famous lithograph, *Ascending and Descending,* which shows a line of men going both up and down the stairs simultaneously.

"Penrose tiles" are equally intriguing. Neither of the two basic shapes is a pentagon, and they do not combine to form a pentagon. But the shapes are like mischievous pentagonal offspring: they have angles and proportions that can be found in a pentagon and its diagonals, and when assembled on a plane the two proudly display the fivefold symmetry of their parent.

The simplest Penrose tiling uses two diamond shapes, one fat and the other skinny. The fat shape has interior angles of 72 and 108 degrees, the interior angle of a regular pentagon. The skinny shape



has interior angles of 144 and 36 degrees, an angle formed by the pentagon's diagonals. While all the tile edges are of



equal length, the ratio of the area of the fat tiles to that of the skinny tiles is $(1+\sqrt{5})/2$, which equals approximately 1.618. This happens to be the ratio of the length of a diagonal to that of a side of a regular pentagon. It is also the famous "golden ratio," a measure revered as a standard of harmony by both the ancient Greeks and a legion of Renaissance painters and architects. As we shall see, the golden ratio and pentagonal symmetry are embedded in the design of Penrose tilings in many wondrous ways.

Any Penrose tiling can be constructed in an infinite variety of patterns. Every variation is nonperiodic, and therein lies its allure. Unlike the individual bricks in a wall or the pickets in a fence, no group of one or more tiles can be repeated indefinitely to generate the whole pattern. At first glance Penrose tilings may look periodic. Groups of tiles do form such repeating motifs as five-pointed stars. But a more careful look reveals that the spacing between these motifs is irregular, and some are rotated with respect to others.

Naturally, when researchers saw these patterns balance teasingly between order and chaos, they were drawn to them like children to a brand-new toy. Over the next half-dozen years many Penrose tilings were generalized to three dimensions, using solid polyhedrons that fill space without gaps. Like their counterparts in the plane, the three-dimensional tilings were also nonperiodic.

One of the enchanted players was Paul Steinhardt, a physicist at the University of Pennsylvania who is well aware of the research value of playthings. Steinhardt's office is filled with toys. Scattered among the books and computers that are the standard trappings of the scholar's craft is every conceivable kind of model, from the crudest cardboard cutouts untidily held together with tape to expensive computer graphics. Anything at hand is pressed into service: coat hangers, foam balls, dice from the game Dungeons and Dragons, acetate sheets, Tinkertoy pieces, toothpicks, construction paper. Steinhardt is a natural victim for the kind of game that can be played with three-dimensional nonperiodic tilings.

Indeed, in 1984, he and one of his graduate students, Dov Levine, became so caught up in the game that they took the analysis one step further: they programmed their computer to calculate the diffraction patterns these theoretical

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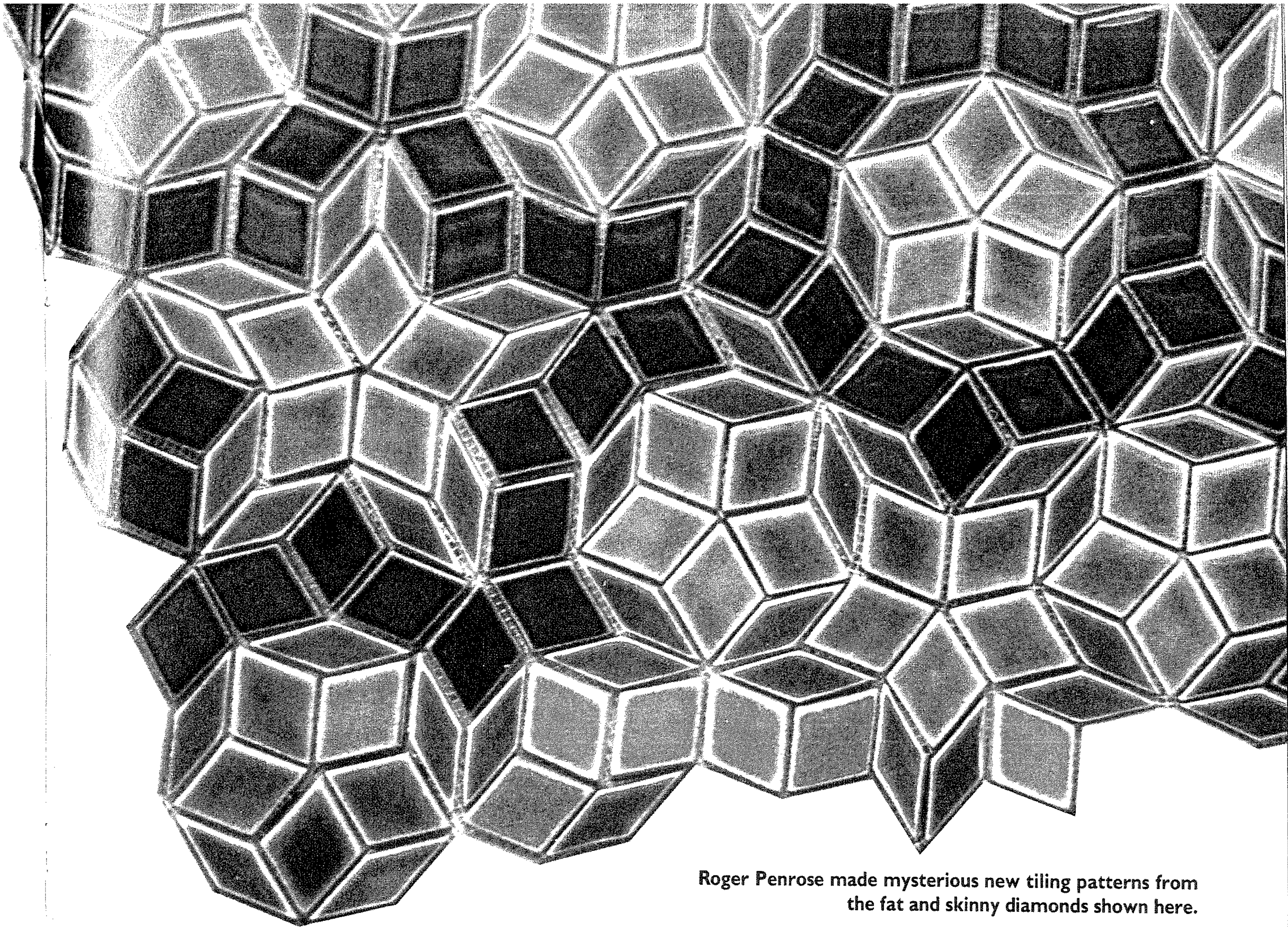


Roger Penrose made mysterious new tiling patterns from the fat and skinny diamonds shown here.

structures would produce if the building blocks were real atoms instead of imaginary tiles.

Diffraction patterns are the windows physicists use to peer inside materials. When beams of electrons or X-rays pass through a solid material, they are diffracted, or scattered, by the atoms inside. The diffracted beams can be photographed head-on, and the images they form on the film reflect the atomic architecture of the solid. By themselves diffraction patterns are not much to look at. They consist of mysterious arrangements of dots and streaks that bear little resemblance to the solids they portray. But to the initiated they are as recognizable as family snapshots.

The most distinct diffraction patterns contain sharp, isolated dots. These are the portraits of crystals, and they owe their clearly defined spots to the periodicity of the underlying structure. When the beams hit the atoms in a crystal, they scatter in all directions; but in a few preferred directions, depending on the arrangement of atoms, the diffracted beams reinforce one another, producing bright spots on the film. A crystal is a little like an orchard planted in a rigid geometric grid. Most lines of sight are blocked by trees, but you can see right through to the other side in a few directions.

In another class of diffraction patterns the dots are either spread out into fuzzy rings or altogether absent. These are the images formed by glassy materials. Glasses, in contrast to crystals, are made of atoms or molecules stuck together randomly; they're more like random forests than well-planned orchards. Because they offer no preferred directions for diffraction, the patterns they produce contain no sharp dots.

Until the discovery of quasicrystals, it was thought that there were only these two classes of solid materials, corresponding to these two types of diffraction patterns. If the pattern contained sharp dots, the material was a crystal; if the dots were fuzzy or absent, the material was a glass. Every pure solid in nature, from gemstones to metals to DNA, was either crystalline or glassy.

Levine and Steinhardt called that neat scheme into question when they aimed a simulated X-ray beam at one of their imaginary solids. The computed diffraction pattern contained a surprise: unmistakable sharp points. Since the atomic arrangement of their solid was nonperiodic, it should have produced the fuzzy diffraction pattern characteristic of glassy substances.

This contradictory result required an explanation, of course, and to understand what was going on the two physicists went back to the source of their computer model: the two-dimensional Penrose tiling. They also consulted Robert Ammann, a recreational mathematician. Ammann's work led them to the discovery that the spacing between the tiles was neither periodic nor random but something in between, an order called quasiperiodic.

This is a subtle kind of order, which

is revealed, Ammann found, only by reference to a pentagonal grid. In this grid the rulings are not perpendicular, like those of normal graph paper, but parallel to the five sides of a pentagon. The five sets of intersecting lines, each set rotated 72 degrees from the next, produce a graph paper with fivefold symmetry.

The tricky part of Ammann's procedure was to draw one of these fivefold grids over a Penrose tiling so that a line from each of the five sets passed through each and every tile; it's a tough thing to do on a nonperiodic tiling. But Ammann figured out how to draw such a grid by adjusting the spacing between parallel lines to correspond to an order with an old mathematical pedigree: The distance between "Ammann lines" is one of two lengths, either a longer length, *a*, or a shorter length, *b*. The ratio of the longer to the shorter is the golden ratio. And the two lengths succeed each other in a predictable, fixed order—an infinite series known as the Fibonacci sequence.

Just as a Penrose tiling contains no group of tiles that can be repeated to generate the entire pattern, the Fibonacci sequence contains no shorter string of *a*'s and *b*'s that can be repeated to generate the whole. Yet the sequence can be produced by following two simple rules. Leonardo Fibonacci, a thirteenth-century mathematician, defined those rules when he considered the idealized propagation of rabbits. The first rule: Start with one adult rabbit, *a*, and assume that at the end of every year each adult has a baby, *b*, which you record right after its parent. Second rule: Every baby grows into an adult the year after it is born. (Fibonacci, a realist, made each letter stand for a *pair* of rabbits. Steinhardt and many others simplify by pretending that a single parent can have a baby, and we follow the simpler description here.)

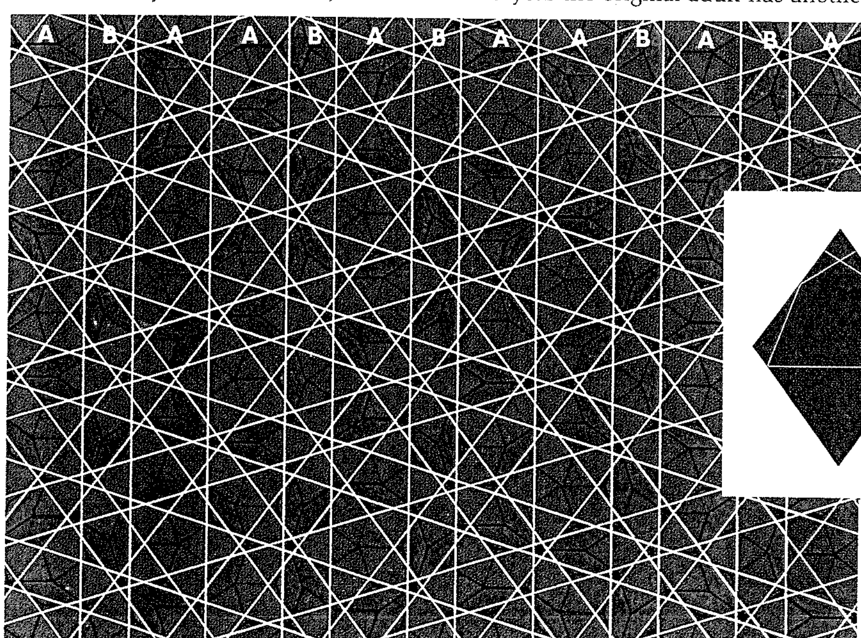
Thanks to the recreational mathematics of the Middle Ages, Steinhardt and Levine finally had an explanation for their imaginary solid.

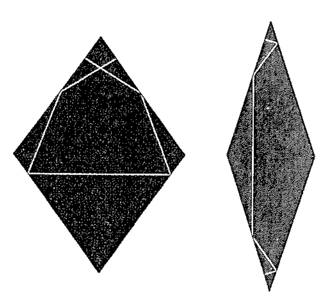
To get the first term of the sequence, you start with one adult: *a*. In the second year the adult has a baby, and the sequence goes to two terms: *ab*. In the third year the original adult has another baby, which is recorded after the adult, and the first baby grows up, to give you *aba*. In the fourth year you add a baby after each adult, and change the baby that was already there to an adult, getting *abaab*. If you keep going year after year, you get *abaababa, abaababaabaab,* and so forth. Another way to generate the sequence is to add the sequences of the two previous years, writing last year's sequence first. And so the sequence does not change from year to year; it just grows longer. If you write down the total number of rabbits in each year (1 in year one, 2 in year two, 3 in year three, 5 in year four, and so on), you get a string of integers that make up the famous Fibonacci sequence (1, 2, 3, 5, 8, 13, 21, 34, 55, 89 . . .), in which each term is the sum of the previous two. And again the golden ratio rears its beautiful head. As the series progresses the ratio of any two successive terms approaches 1.618.

Obviously Fibonacci was onto something. Nearly eight centuries ago he invented a sort of one-dimensional Penrose pattern, a sequence that while not periodic is not random either. There is a perfectly rigorous prescription for predicting what the next member of the sequence will be. Thanks to the recreational mathematics of the Middle Ages, Steinhardt and Levine were onto something, too. They finally had an explanation for the diffraction pattern of their imaginary solid. Their discovery amounted to the demonstration that, contrary to established belief, periodicity in three dimensions was not necessary for producing diffraction spots—quasiperiodicity was quite sufficient.

But their quasiperiodic solid had an awkward feature: the dots in the diffraction pattern were arranged with fivefold symmetry. To traditional crystallographers, such a pattern is simply unacceptable. It is a fundamental tenet of their science. Crystals cannot produce diffraction patterns with fivefold symmetry because the underlying arrangement of atoms cannot have pentagonal symmetry, any more than bathroom floors can be tiled with pentagons.

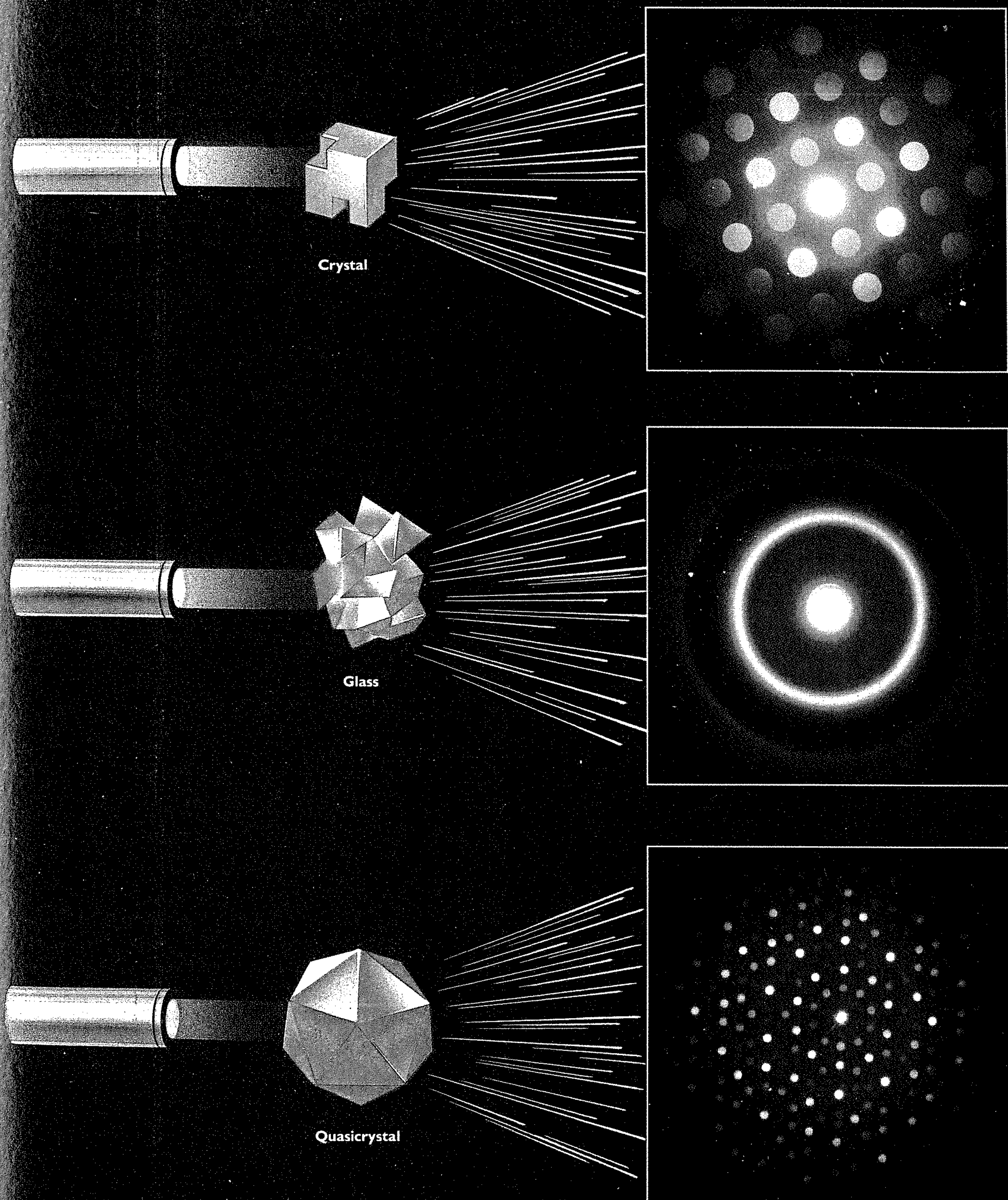
So whatever Steinhardt's imaginary solids were, they were not crystals. But





Over a Penrose tiling it is possible to draw five sets of parallel lines so that one line from each set passes through each and every tile. These lines reveal a hidden order, which is discussed in the text above.

COMPUTER IMAGE COURTESY PAUL STEINHARDT, UNIVERSITY OF PENNSYLVANIA



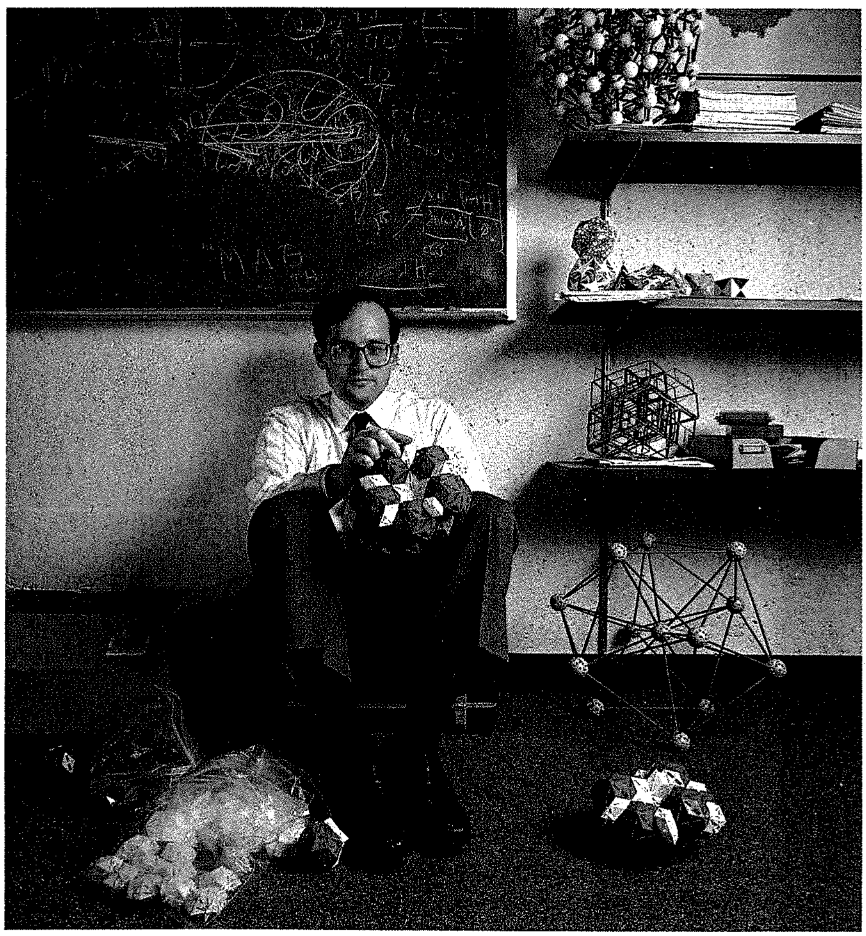
Electron beams or X-rays paint the recognizable portraits of solid matter. As the beams pass through the solid they are scattered by the atoms within and emerge in a pattern characteristic of the material. Crystals divide the beams into clean, geometric patterns of sharp dots. Glasses produce patterns with fuzzy dots or rings. Quasicrystals produce an astonishing amalgam: dots arranged in a pattern that no crystal on Earth could produce. The pattern shown here, from a real metallic alloy, is the one that tipped off physicist Paul Steinhardt that quasicrystals may actually exist.

ILLUSTRATIONS BY GEORGE KELVIN/SCIENCE GRAPHICS; DIFFRACTION IMAGES COURTESY H. CHEN, G. J. SHIFLET, HE AND S. J. POON, UNIVERSITY OF VIRGINIA the discrete spots in the diffraction patterns showed they were not glasses either. Their underlying structure combined properties of crystals with those of glasses; the theoretical substances were like mammals that lay eggs, the platypuses of physics. Steinhardt decided to call them quasicrystals, and added them to the growing list of amusing ideas that sprang from Penrose's mathematical recreation.

But then the incredible happened. In the fall of 1984 Steinhardt was on leave at the IBM research center in Yorktown Heights, New York. One day a colleague, Harvard physicist David Nelson, came into the office with exciting news. He put on the table a small copy of a diffraction image made with a real alloy of aluminum and manganese. Nelson explained that a team of researchers at the National Bureau of Standards had made the picture, and he pointed out the unusual appearance of the pattern of dots: an obvious fivefold symmetry.

In the closet lurked a skeleton: no one could think of a way that millions of real atoms could arrange themselves in the intricate patterns of quasiperiodicity.

Steinhardt's pulse quickened. The picture looked amazingly similar to a computer simulation he and Levine had produced and not yet published. Levine happened to be visiting from Philadelphia that day. Immediately the three scientists, as excited as boys playing on the seashore, set to work measuring the spacing between dots on an enlargement of the real photograph and comparing the results with the computer printout. Steinhardt recalls that he knew what the answer would be even before the measurements confirmed it. The two pictures agreed with each other.



In his office at the University of Pennsylvania, Steinhardt builds a three-dimensional cousin to the mischievous Penrose tiles.

PHOTOGRAPH BY BILL REDIC

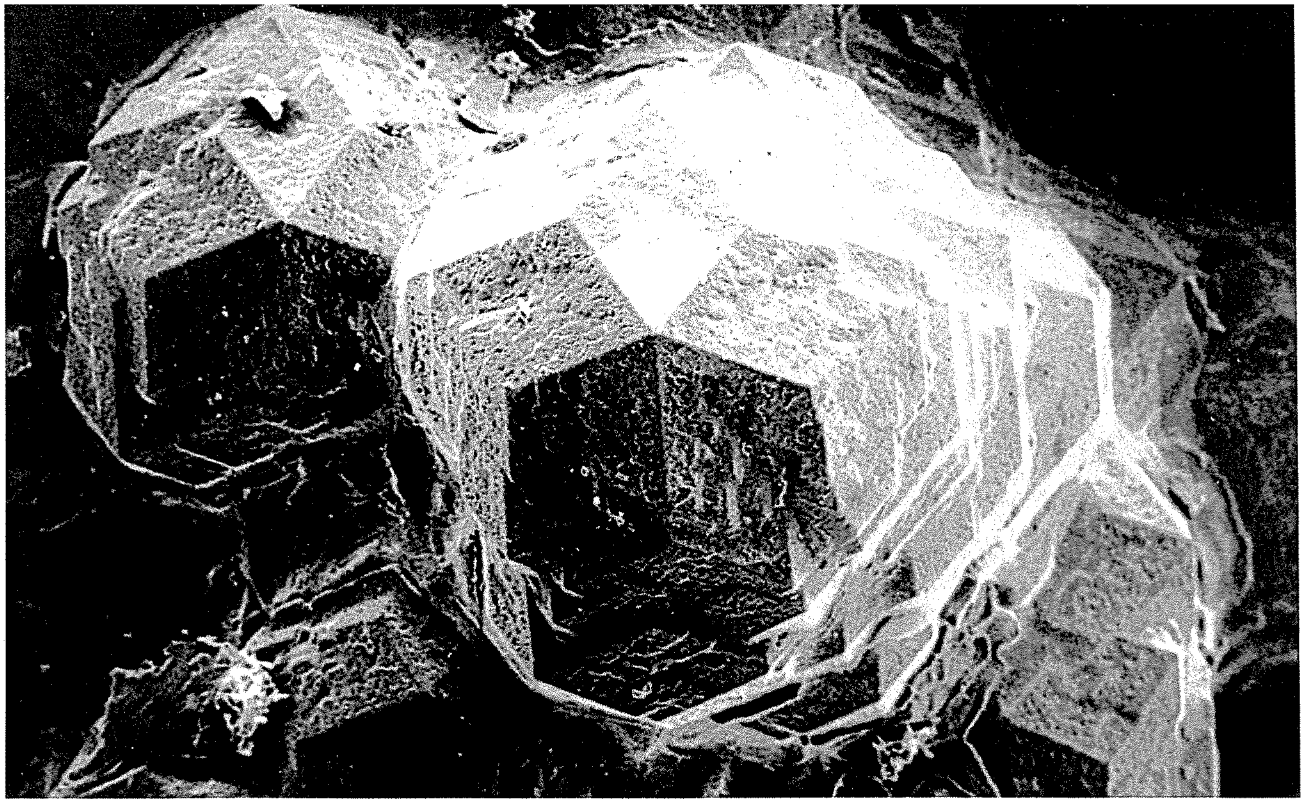
The moment of truth, in science, comes when theory confronts experimental evidence. Agreement between the two is the ultimate arbiter of validity. Nothing else matters. The comparison of data with calculations usually proceeds in bits and pieces, and truth emerges gradually from the confusion that surrounds all creative effort. But when the moment of truth arrives in an unexpected flash, as it did that day at IBM, it illuminates and energizes the scientific enterprise for years to come.

Thus a new field of solid-state physics, the science of quasicrystals, was born. It grew up quickly. In short order more than a hundred alloys with fivefold symmetry were discovered; sevenfold, ninefold, elevenfold, and other previously forbidden symmetries proved to be possible; scholarly symposia were convened, and fat monographs were published.

But in the closet there lurked a skeleton—a potentially fatal flaw in the whole scheme. While researchers were beginning to understand the architecture of two- and three-dimensional quasiperiodic tilings, no one could think of a mechanism by which millions upon millions of real atoms could arrange themselves spontaneously in those intricate patterns.

Anyone who tries to assemble Penrose tilings quickly realizes that it's not easy. You have to think ahead, and keep the whole pattern in mind when adding a tile; otherwise there is trouble. If you make a mistake, you have to undo a lot of work that has gone before. The problem is that while there are local rules, or instructions for fitting a tile into a particular niche, these rules are not sufficient to build the entire pattern. It seems necessary to augment them with global rules that force you to plan ahead and check the configuration of tiles at far distant points. And between 1984 and 1988 the conviction grew that perfect quasiperiodic tilings could not be constructed with local rules alone.

Local rules for adding tiles are analogous to forces that attract and hold new atoms to the surface of a growing quasicrystal; they are plausible ingredients in



An alloy of aluminum and lithium, discovered in a search for new aerospace materials, has the familiar diamond-shaped faces of a quasicrystal. Each crystal, among the largest yet made, measures about a quarter-inch across.

the growth mechanism. Global rules are not. The atoms on a growing surface do not plan ahead, and they do not check the orientation of distant surfaces. They respond only to the interatomic sticking force, which is electrical in origin, of their immediate neighbors. If quasiperiodic patterns could be constructed only with the help of global rules, they could not be assembled by real atoms in real alloys, and quasicrystals could not exist in nature.

The problem was so serious that researchers began shifting their attention to more conventional explanations of the observed diffraction patterns. The two-time Nobel laureate Linus Pauling, for example, championed an arrangement of ordinary crystals called twinning. Twinned crystals grow from separate origins and penetrate each other at odd angles, such as 72 degrees. This might produce a diffraction pattern with spurious fivefold symmetry, even though the underlying structure was conventional. Other researchers, including Steinhardt himself, studied glassy structures with tiny embedded crystalline fragments. These fragments, it was thought, might produce a diffraction pattern with spots almost as sharp as the dots from crystals, even though the overall structure was glassy.

But then, in 1988, playfulness paid off once more. George Onoda, an IBM ceramics expert, started toying with about 200 Penrose tiles. Unconvinced by the claims that he wasn't supposed to be able to do it, he learned how to assemble flawless tilings of any size he wished using strictly local rules. "I approached it as a puzzle," he says, "as a challenge to try to prove the naysayers wrong."

Onoda showed Steinhardt his procedures, and the two of them fiddled around with the tiles for a couple of hours. Steinhardt simplified Onoda's insights to a set of rules that force the vertices of the tiles into one of the eight possible combinations found in a perfect Penrose tiling. With the help of two other researchers, he then hammered out a mathematical proof, corroborated by a computer simulation of a million tiles, that quasiperiodic structures can indeed grow naturally—at least in two dimensions.

Following these rules, you can build a Penrose tiling by adding tiles to a growing boundary. The rules specify which type of vacancy to fill first and to choose randomly if there is more than one equivalent vacancy, which of the two tile shapes you should use in every case, and which way it should be turned. You don't have to pay attention to any distant part of the pattern to assemble a tiling, any more than an atom has to know what's going on somewhere else before it decides which way to turn and attach to its neighbors.

For a complete theory of quasicrystals the local rules must be generalized to three dimensions, and they must be shown to correspond to actual atomic forces. Neither of these tasks has been achieved yet, but Steinhardt, for one, believes they will be.

In the meantime, experimentalists have been busy. They continue to report bigger, more perfect quasicrystals and are diligently measuring their physical properties. No one knows what to expect, for none of their vast experience with crystals and glasses permits them to make confident predictions about quasicrystals. Quasicrystalline alloys, because of the intricate interlocking of their constituents, might turn out to be harder than crystals and therefore might be used as replacements for industrial diamonds. Or they might end up at the heart of novel electronic devices as yet undreamed of. Who knows? Researchers are going to have to play around with them a bit and see what they can do. ❑

Hans C. von Baeyer, a professor of physics at the College of William and Mary, won a AAAS-Westinghouse Award for science journalism in 1989.