

Quasicrystals: Rules of the Game

Two camps are trying to explain how these odd materials form. One emphasizes rules, the other randomness. Both sides have recently reported data that seem to support their point of view

IN A REMARKABLY SHORT TIME the debate over quasicrystals has come down to a simple—albeit philosophically resonant—choice: rules or randomness? Only 6 years ago it was thought that this odd form of matter, which is intermediate between orderly crystal and disorderly glass, could not exist. Since then, physicists have observed a myriad of quasicrystalline materials and, after intense debate, forged a rough consensus on their structure.

But one battle continues to rage—over how quasicrystals form. There are two camps. One favors a model in which quasicrystals form according to subtle rules; the other emphasizes the role of chance. In the past few months results have come thick and fast, and each side claims to have new findings that support its point of view. Results reported late last year seemed to support the random-model camp. But now supporters of the rule-based model claim that the very latest data—from AT&T Bell Laboratories and only weeks old—tips the balance in their favor. This tussle doesn't have any immediate practical applications, but it does provide a window onto how rapidly major scientific controversies can move.

Even before quasicrystals were actually observed, two maverick physicists at the University of Pennsylvania—Dov Levine and Paul J. Steinhardt—had suggested that these law-breaking structures might exist. The reason other physicists had dismissed this possibility is that quasicrystals display a fivefold symmetry, violating the rules of traditional crystallography.

Crystals are formed from unit cells stacked in periodic (repeating) patterns, and one can no more form a crystal out of unit cells with fivefold symmetry than one can cover a plane using only pentagons (give it a try). But Steinhardt

and Levine, drawing their inspiration from work done by British mathematician Roger Penrose in the early 1970s, thought they saw a way that “quasiperiodic” materials with fivefold symmetry might provide a loophole.

Penrose had shown that, using only two types of tiles (a fat diamond and a skinny one), it is possible to cover an infinite plane without settling into any repeating pattern. Although Penrose tiling patterns are technically nonperiodic, they bristle with forms that show fivefold symmetry, such as decagons and five-pointed stars. Steinhardt and Levine therefore proposed that the three-dimensional analogs of Penrose tiles, shrunk to the atomic level, could provide the basis for a material with fivefold symmetry.

The proposal by Steinhardt and Levine

was purely theoretical. Startlingly, it was only a brief period before a corresponding form of matter was actually observed. The place was the National Bureau of Standards (NBS); the evidence consisted of electron-diffraction images of an alloy of aluminum and manganese. The most surprising thing about the images was that they appeared the same when they were rotated by one-fifth of a circle (72 degrees)—the very pattern prohibited by the traditional crystallography scheme.

On the basis of the NBS observations, Steinhardt and Levine declared that their theory had been vindicated. Steinhardt even proposed the name that stuck: quasicrystals. But the debate over what the new form of matter was and how it got to be that way was far from over.

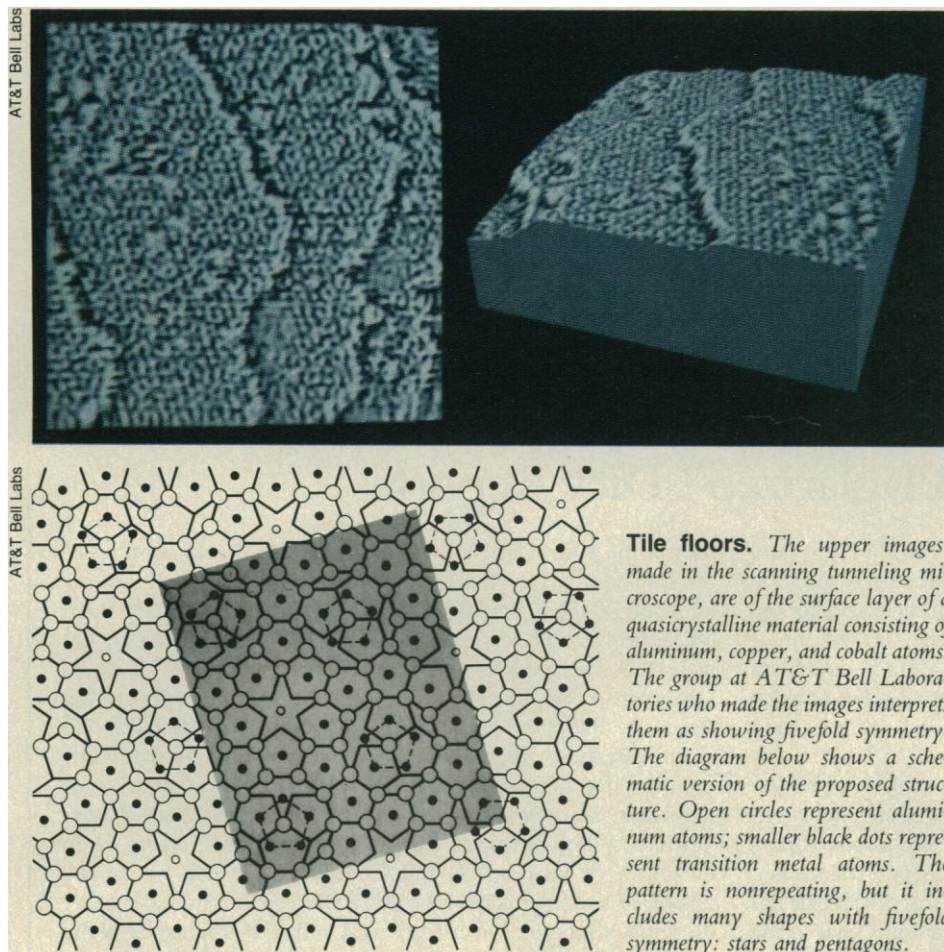
Initially there were several competing hypotheses about quasicrystal structure. Steinhardt was tirelessly promoting a model based on the Penrose tiling model, and there were a number of other, more conventional hypotheses. But as experimenters created and analyzed new quasicrystals, and as Steinhardt and others refined the Penrose tiling model, that possibility began to shoulder aside the others.

Yet the tiling model posed at least one major theoretical problem. To ensure proper formation of a tiling pattern, Penrose had devised “matching rules” that stipulated which tile goes where. But correct placement often required knowledge of the positions of very distant tiles. To physicists, this smacked of nonlocality—events in one place simultaneously affecting events in another—which is prohibited by the laws of physics.

To overcome this objection, Steinhardt and other theorists—including George Y. Onoda and David P. DiVincenzo of IBM—devised a set



Fearful symmetry. Model of a quasicrystalline material in which the silver balls represent aluminum atoms, the blue cobalt atoms, and the red copper atoms.



Tile floors. The upper images, made in the scanning tunneling microscope, are of the surface layer of a quasicrystalline material consisting of aluminum, copper, and cobalt atoms. The group at AT&T Bell Laboratories who made the images interprets them as showing fivefold symmetry. The diagram below shows a schematic version of the proposed structure. Open circles represent aluminum atoms; smaller black dots represent transition metal atoms. The pattern is nonrepeating, but it includes many shapes with fivefold symmetry: stars and pentagons.

of rules that made Penrose tiling possible without any nonlocal interactions. The new rules called for variations in the "stickiness" of the tiles' edges. In real quasicrystals, such stickiness might correspond to the binding energy that causes the unit cells to adhere to one another. Recently Steinhardt has been advocating a variation on this theme that he thinks is even more plausible: an initial "defect" (an arrangement of the unit cells violating the matching rules) serves to seed the growth of the quasicrystal.

In spite of Steinhardt's pirouettes, some physicists still find it hard to imagine how matching rules would be enforced in nature. As a result, many prefer a theory that dispenses with rules altogether. That theory was proposed 2 years ago by Michael Widom of Carnegie Mellon University and Katherine J. Strandburg of Argonne National Laboratory, who noted that if Penrose tiles are positioned at random, in most cases they will still form quasiperiodic patterns. The only requirements are that the tiles cover the plane and occur in a certain proportion. The patterns formed in this way are less orderly than those formed by following matching rules—but they still display the quasicrystalline hallmark: fivefold symmetry.

The advantage of this model, Widom

says, is that it has the backing of the second law of thermodynamics, which states that nature favors systems with greater entropy, or randomness.

That justification is theoretical, but the entropy model has recently received its strongest experimental support to date. In the 18 December issue of *Physical Review Letters*, Peter A. Bancel of the IBM Watson Research Center reports that x-ray images of an aluminum-copper-iron quasicrystal exhibited fivefold symmetry most clearly at 670°C; as the sample was progressively cooled, the diffraction peaks grew dim and blurry. According to Widom this is in accord with the entropy model, because the entropy of a system decreases with temperature. In a rule-bound system, on the other hand, cooling a sample should in theory lead to stronger diffraction patterns, because the binding energies that enforce the rules would have less competition from random thermal energy.

But this new evidence has hardly quieted the fray. At least two groups—one led by Alan I. Goldman at Iowa State University and the other by Mark Audier and Pierre Guyot of the Laboratory of Thermodynamics and Physical-Chemical Metallurgy at Grenoble—have reported data that seem to corroborate Bancel's. Two others, howev-

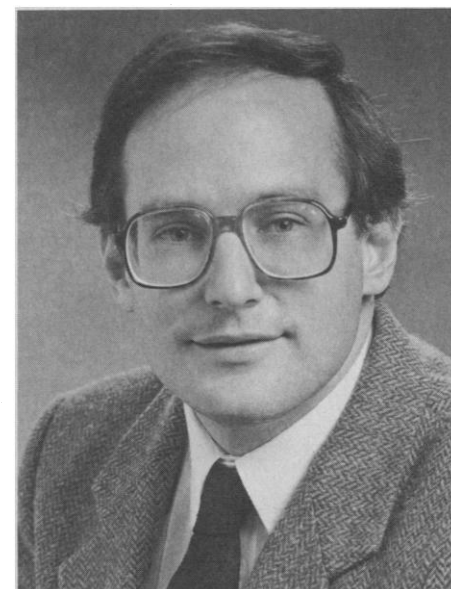
er—one led by Denis Gratias at the Center for Studies of Chemical Metallurgy in Vitry, France, and the other by A. Inouye at Tohoku University in Japan—have been unable to replicate the IBM results. Bancel and Gratias have recently swapped samples to determine whether it is differences in their analytical methods, rather than in the structure of the materials, that account for the observed discrepancies.

Meanwhile, the matching-rule model has received a big boost from a group of researchers at AT&T Bell Laboratories led by A. Refik Kortan. In the 8 January issue of *Physical Review Letters*, they report that their examination of an aluminum-cobalt-copper quasicrystal with a scanning tunneling microscope (STM) provides "strong evidence" for the rule-based hypothesis.

The material Kortan works with is well suited for surface analysis. Although most quasicrystals have a three-dimensional structure, the AT&T sample consists of quasicrystalline sheets that stack one atop the other. Under the STM, that material yields images exhibiting fivefold symmetry. One can (with some difficulty) observe that the atoms form rows in five directions separated from each other by 72 degrees or multiples thereof. According to Kortan, in an entropy-driven system those rows would be jagged or undetectable.

It probably isn't surprising that Steinhardt agrees: "I could find ways to make this result consistent with the entropy model, but I'd really have to stand on my head."

Defenders of the entropy model are certainly not throwing in the towel. Even Kortan's images, they argue, don't necessarily contradict their theory. Goldman argues that the disorder predicted by an entropy



Paterfamilias. Paul J. Steinhardt of Penn gave quasicrystals their name.

model may only show up in a sample considerably broader than the one Kortan analyzed. Widom adds that he has found signs of such disorder in unpublished STM data that were sent to him by Kortan. "I still think the evidence leans in favor of the entropy model," he says.

And some continue to hold a third position: somewhere above the fray. One of them is DiVincenzo of IBM, who argues that until further data have been gathered the question of whether the rules model or the entropy model is correct must remain

"an article of religion." Indeed, the true nature of quasicrystals might even combine aspects of both theories, DiVincenzo suggests. If that is the case, he says, the field could become mired in a protracted "semantic turf battle" as advocates argue over which model provides the closest match.

In such a conflict, the rules model would have one distinct advantage. Even if researchers find 1000 materials that conform to the entropy model and only a single sample that unambiguously fits the rule model, the rule model would become the

focus of the most excitement, according to Peter W. Stephens of the State University of New York at Stony Brook. The reason is that the notion of "matching rules" is so bizarre in terms of current theory that it would be the much more interesting research prospect.

"That's the model that is the most surprising," Stephens says, adding slyly: "That's why I find it so hard to accept."

■ JOHN HORGAN

John Horgan writes for Scientific American.

Academy Sued on "Plagiarized" Diet Report

Victor Herbert, a nutritionist and lawyer who rattles (and sometimes wields) his legal expertise like a saber, has sued the National Academy of Sciences for plagiarism and violation of the copyright laws. At issue is the authorship of the 10th edition of the *Recommended Dietary Allowances* (RDA), a guide to human vitamin and food requirements, published by the Academy in November 1989. RDA data are widely used by the food industry—commonly on cereal boxes.

Herbert is a researcher at the Bronx Veterans Administration Medical Center and also, as a hobby, a scourge of anyone whom he judges to be a quack. The Academy asked him to serve on its dietary panels because it valued his expertise in iron, vitamin B₁₂, and folate vitamin research. However, for the past 5 years, he has been waging a quiet war with the Academy, arguing that in the area of nutrition, it has been led astray by its staff.

On 16 February, the war broke into the open when Herbert filed suit in the District of Columbia, charging that the Academy wrongly listed as authors of its 10th RDA a group of experts whom he claims merely edited the work of an earlier panel on which he sat.

The earlier panel was commissioned by the Academy to write the 9th RDA, scheduled for release in 1985. But the Academy rejected the draft and canceled publication (*Science*, 25 October 1985, p. 420). Herbert argues that the Academy made this

decision for arbitrary policy reasons, but kept his draft chapters—which he later copyrighted—only to publish them without his permission in its 10th RDA.

The Academy cannot have been surprised by Herbert's decision to file suit last week because it has been negotiating with him and his attorney since November. In a letter dated 6 February, Herbert's attorney demands for his client recognition as an au-

thor of the 10th RDA, a payment of \$300,000, and royalties of 5% of sales. The Academy's lawyers were unready to say anything of substance last week. They referred queries to press officer Gail Porter, who said, "We believe that the Academy has not acted improperly in any way."

Herbert agrees, in a sense. He says, "My quarrel isn't with the Academy. But there were a few rotten apples on its staff." He claims that the group that had been asked to write the 9th RDA ran into faddish prejudices among NAS staff members. In particular, Herbert claims that former staffer Sushma Palmer favored a "pop nutrition" theory—namely, that eating large quantities of vitamins A and C reduces the risk of cancer. However, the scientists on the 9th RDA panel went in the other direction, voting for lower levels of A and C. Palmer is out of the country and could not be reached for comment.

Herbert claims that the panel refused to "knuckle under" to the staff's demand that the report be rewritten, and specifically, that the numbers for vitamins A and C be increased. The disagreement eventually went to the Academy's Food and Nutrition Board for review, and finally to Academy president Frank Press. When it became clear that the two camps could not reach an agreement, Press decided to cancel publication.

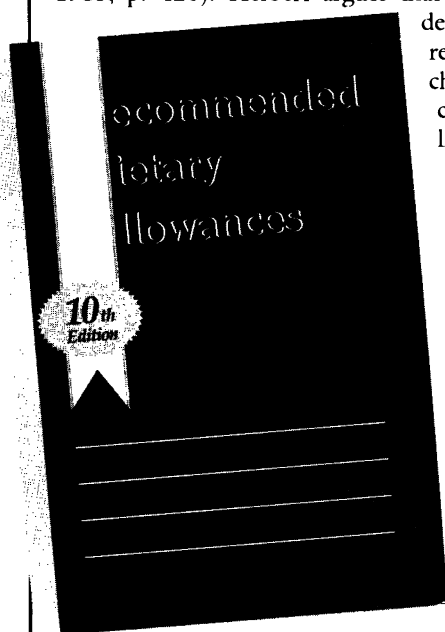
After the report had been rejected, Herbert and his fellow committee members copyrighted what they had written and refused to let the Academy make any further use of it. Herbert also wrote to Congress and to the National Institutes of Health, which had given the Academy \$600,000 to produce the 9th RDA, asking what the taxpayers had received for all this money. Under pressure to make good on the original investment, NIH contracted anew with the Academy, this time for about \$160,000, to bring out a new, 10th RDA.

Herbert argues that the Academy created the 10th RDA simply by editing and updating the old 9th RDA manuscripts. He claims that the sections dealing with vitamin B₁₂, folate, and iron are his own work. "Most of my three chapters were used verbatim or paraphrased," Herbert says.

Likewise, James Olson of Iowa State University, the member of the 9th RDA panel who wrote the sections on vitamins A and C, has complained to the NIH and asked for an investigation. In a letter dated 6 February, he claims that 30 to 70% of the 10th RDA is taken verbatim from the copyrighted draft reports of 1985 and that another 10 to 30% is paraphrased.

As for the bottom line, the new, updated RDA endorses high levels for A and C—just as the 8th edition did a decade ago, before any of this trouble began.

■ ELIOT MARSHALL



Legal fodder. A 5-year-old fight over nutrition guidelines ends up in court.