Proposing a Flip Side For Crystallography

Periodicity has become a fetish for crystallographers, says a Cornell physicist, and he thinks he has a better idea

IT TOOK 16TH- AND 17TH-CENTURY SKY-watchers many decades to abandon Ptolemaic, Earth-centered astronomy and replace it with a more realistic Copernican universe centered on the sun. In recent decades a new Ptolemaic mindset has emerged, according to Cornell University physicist N. David Mermin, in the esoteric realm of crystal structure analysis. And he aims to restore a more realistic perspective with a "Copernican" proposal—one he hopes will catch on faster than the original did.

Mermin threw down the gauntlet in the 24 February *Physical Review Letters* (*PRL*) under the title "Copernican Crystallography." There, he points out that the discovery over the past few decades of so-called quasiperiodic solids—materials that show some crystalline features but not others—has strained traditional concepts in crystallography. Crystallographers have been resorting to mathematical contortions in efforts to make sense of the new materials, he says, but at the expense of artificially perpetuating a Ptolemaic narrowness at the base of their discipline. Mermin's solution is a classification scheme that puts both standard crystals and their unruly relatives on an equal footing.

"I wrote this article to be downright provocative and almost insulting so that they have to respond," Mermin says. And he is getting a rise from colleagues—though they seem more intrigued than outraged.

One reason may be that many crystallographers agree with Mermin's fundamental complaint—that their field is becoming mathematically messy. Until recently, conventional crystallography provided an elegant framework for key observations, because most of the solid materials that interested scientists were ordinary crystals such as diamond, Mermin says. These are characterized by a simple configuration of atoms, called a unit cell, that is repeated throughout the crystal at exactly regular intervals like oranges in a grocer's stack. Strict periodicity came to be seen as the hallmark of a crystal. But over the past two decades the simple picture has become muddied by materials that show such crystalline features as symmetry and repeating motifs—but lack strict periodicity.

In the early 1970s, for example, crystallographers began grappling with so-called incommensurately modulated crystals: a group of materials (to which some high-temperature superconductors have recently been added) built of structural units whose spacing varies regularly, somewhat like the pitch of a siren. Still more unsettling for conventional crystallography was the discovery in the 1980s of quasicrystals, solids—mostly metallic alloys—that not only lack strict periodicity but also reveal symmetries ruled out in conventional theory.

When researchers probed these quasiperiodic materials with x-rays—a standard technique for determining crystal structure—they obtained sharp diffraction patterns like those produced by normal crystals but could not interpret them according to standard crystallography. So researchers began resorting to various conceptual and mathematical tricks for inferring the possible structures of the odd beasts. But to Mermin, those stratagems smack of the epicycles Ptolemaic astronomers relied on for keeping their calculations matched with actual planetary motion.

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In his *PRL* paper, Mermin takes aim at one particular scheme for bringing incommensurately modulated materials into the fold of traditional crystallography. Over the past two decades Peter M. De Wolff, now retired from the Technical University of Delft, and Aloysio Janner and Ted Janssen of the University of Nijmegen in the Netherlands have argued that when such rogue materials are viewed as three-dimensional "cross sections" of hypothetical periodic structures of four or more dimensions, they become amenable to the same structural analyses as standard periodic crystals. It's like imagining that an apparently irregular arrangement of atoms in a plane is actually an oblique slice through a regular three-dimensional lattice.

But Mermin thinks that such "superspace" methods—efforts to place quasiperiodic solids within a periodic framework—"obscure deeper similarities between the two types of materials." In his paper, he argues that "a simpler and unified scheme... can be formulated and constructed without ever leaving three dimensions."

Mermin's tack is to replace periodicity as the taxonomic basis for crystals with the notion of "indistinguishable densities," which he says gracefully accommodates both periodic and quasiperiodic solids. According to this notion, both kinds of materials contain substructures, such as a unit cell in normal crystals, that are repeated in identical form throughout the solid. In ordinary crystals, these repetitions are periodic (like those in the orange stack). In quasiperiodic solids, the substructural motifs repeat in more intricate though less strictly periodic ways. No need here for nonintuitive concepts like superspace, Mermin says.

Nonintuitive it may be, counters Janssen, but it works; superspace methods now are in wide use because they help make sense of structures that previously could only wrinkle brows. Besides, he adds, Mermin's reformulation risks conflating subtly distinct structural classes.

But Marjorie Senechal, a mathematician at Smith College and a member of the International Union of Crystallography's commission on aperiodic crystals, thinks that Mermin's ideas will give the superspace camp a run for its money, although she adds that "he has more work to do before anyone will have any reason to accept it." Whether solid-state scientists will buy into Mermin's scheme "will come down to whether they can do things [with it] that they couldn't do before," agrees crystallographer Simon Moss of the University of Houston. One convincing feat would be determining the atomic structures of quasicrystals, a puzzle that no superspace scheme yet has helped to unravel.

Paul Steinhardt, a quasicrystal aficionado at the University of Pennsylvania, also suspects that Mermin's reformulation will have an uphill battle, though he cites other reasons. Classical formulations based on periodicity, he points out, are well entrenched in crystallography's instrumental and methodological infrastructure. Like 16th-century navigators who ignored the Copernican view since their familiar Ptolemaic astronomy was serving them well enough, crystallographers may hesitate to adopt Mermin's new formalism even though it offers a more encompassing perspective on the universe of solids. ■ IVAN AMATO