Strange-behaving crystals could have impact on research, technology

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Aperiodic, rule-bending crystals are the focus of an article that appears in the Jan. 4 issue of the journal *Science*. Co-authors looked at how these aperiodic crystals behave differently from "normal" periodic crystals. These differences could have implications not only for research but also for technology that relies on crystals, from computer displays to hard drives.

All of us break the rules from time to time -- even crystals.

"There are all sorts of rules about what crystals can do during phase transitions," said Mark D. Hollingsworth, associate professor of chemistry at Kansas State University. "For a long time, scientists have assumed that the norm applied for all sorts of substances.

But aperiodic materials -- those that lack a regularly repeating structure -- don't necessarily work like this, Hollingsworth said.

These aperiodic, rule-bending crystals are the focus of an article co-authored by Hollingsworth that appears in the Jan. 4 issue of the journal *Science*. Building on results from Hollingsworth's collaborator, French researcher Bertrand Toudic, Hollingsworth, Toudic and their co-authors looked at how these aperiodic crystals behave differently from "normal" periodic crystals. These differences could have implications not only for research but also for technology that relies on crystals, from computer displays to hard drives, Hollingsworth said.

For the research featured in the *Science* article, Hollingsworth and colleagues looked at crystals that form a host-guest structure. In this case, urea molecules formed tunnels around nonadecane molecules, making a honeycomb-like structure that takes the form of a double-helix -- the shape of DNA. In periodic host-guest crystals, Hollingsworth said the host molecules forming the tunnels and the guest molecules inside form a regularly repeating structure. But not so with the rule-breaking aperiodic crystals.

"Sometimes the host and guest fit nicely, sometimes they don't," Hollingsworth said. "This can have a huge effect on all sorts of properties. During crystal growth, for example, periodic and aperiodic host-guest crystals can behave very differently."

In aperiodic crystals, in which the host and guest structures don't match, the guest molecules protrude from the ends of the crystals, making the surface rough. This means it's easier to attach new molecules to the end of the crystal. Such crystals, including the ones featured in the Science article, are shaped like long needles.

But it really gets weird when the crystals undergo transitions from one phase to another.

"Bertrand and I have been talking about this for years, trying to find out what's going on in this system," Hollingsworth said. "The idea of studying these systems is to better understand how phase transitions work in aperiodic materials."

To find out what's going on in the phase transitions, the researchers observed the crystals at different temperatures above the phase transition, when the guest molecules are moving rapidly inside their tunnel-like hosts, and also at extremely cold temperatures as molecules are becoming frozen in place. To probe the crystals, the researchers scattered neutrons from them and measured different types of reflections. One class of reflections, called satellite reflections, measures the interaction between the guest and host molecules.

The researchers were surprised by what happened when the crystal was cooled to about -190 degrees Fahrenheit. The satellite reflections showed a change in the interaction between the host and guest structures but no noticeable changes in either the host or guest structures themselves.

"Previously, we thought these materials had homogenous phase transitions and that the normal rules concerning symmetry breaking applied to them," Hollingsworth said. "I don't think anyone would have predicted what happens in this phase transition."

Because these aperiodic materials don't play by the same rules, Hollingsworth said the impact on research is that scientists need to figure out what rules these aperiodic crystals are playing by in phase transitions. In addition to affecting research, these different rules also could have impacts on technology, he said. Crystals like the ones featured in the Science article are ferroelastic. That means that the molecules within the crystals reorient when the crystals are squeezed. The researchers can do this with a small anvil and observe the rotations of large domains in the crystals by viewing the crystal under a microscope. Closely related ferroelectric materials are important to technology because the domains within these materials can be reoriented with electric fields to allow or prohibit polarized light to pass through. This makes them useful in electronic displays.

"The question is whether these phases that we have observed will have unusual properties that are useful," he said.

As research on aperiodic crystals continues, Hollingsworth said that researchers expect this same unusual phase transition behavior in materials other than the urea-nonadecane crystals used in this study.

Source: Kansas State University