Solving a crystal's structure when you've only got powder

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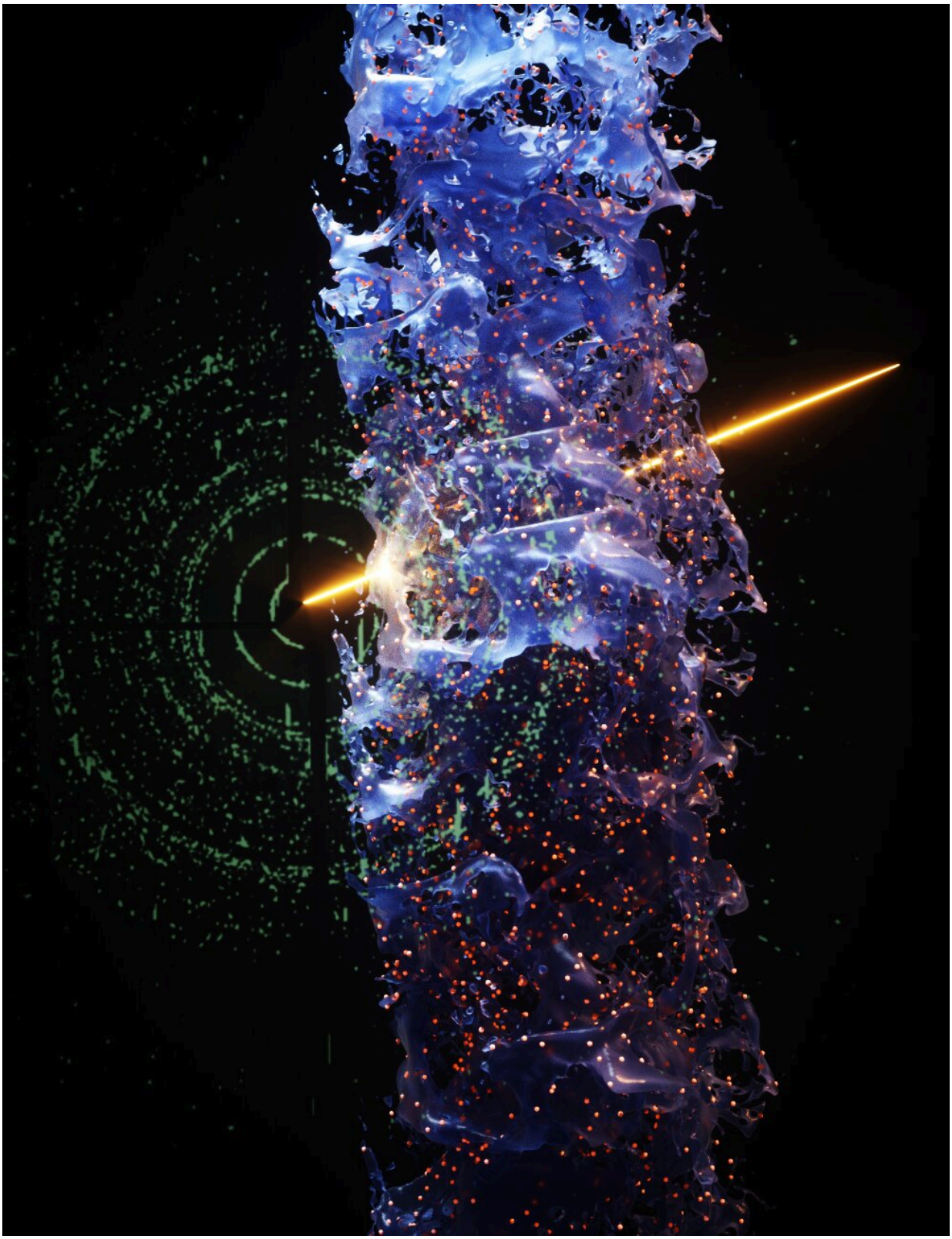

Artist's rendition of X-ray beam illuminating a solution of powdered crystalline

chalcogenates. Credit: Ella Maru Studios

Crystals reveal the hidden geometry of molecules to the naked eye. Scientists use crystals to figure out the atomic structure of new materials, but many can't be grown large enough. Now, a team of researchers report a new technique in the January 19 issue of Nature that can discover the crystalline structure of any material.

To truly understand a chemical, a scientist needs to know how its atoms are arranged. Sometimes that's easy: for example, both diamond and gold are made of a single kind of atom (carbon or gold, respectively) arranged in a cubic grid. But often it's harder to figure out more complicated ones.

"Every single one of these is a special snowflake—growing them is really difficult," says UConn chemical physicist Nate Hohman. Hohman studies metal organic chacogenolates. They're made of a metal combined with an organic polymer and an element from column 16 of the periodic table (sulfur, selenium, tellurium or polonium.) Some are brightly colored pigments; others become more electrically conductive when light is shined on them; others make good solid lubricants that don't burn up in the high temperatures of oil refineries or mines.

It's a large, useful family of chemicals. But the ones Hohman studies—hybrid chalcogenolates—are really difficult to crystallize. Hohman's lab couldn't solve the atomic structures, because they couldn't grow large perfect crystals. Even the tiny powdered crystals they could get were imperfect and messy.

X-ray crystallography is the standard way to figure out the atomic arrangements of more complicated materials. A famous, early example

was how Rosalind Franklin used it to figure out the structure of DNA. She isolated large, perfect pieces of DNA in crystalline form, and then illuminated them with X-rays. X-rays are so small they diffract through the spaces between atoms, the same way visible light diffracts through slots in metal. By doing the math on the diffraction pattern, you can figure out the spacing of the slots—or atoms—that made it.

Once you know the atomic structure of a material, a whole new world opens up. Materials scientists use that information to design specific materials to do special things. For example, maybe you have a material that bends light in cool ways, so that it becomes invisible under ultraviolet light. If you understand the atomic structure, you might be able to tweak it—substitute a similar element of a different size in a specific spot, say—and make it do the same thing in visible light. Voila, an invisibility cloak!

Hybrid chalcogenolates, the compounds Hohman studies, won't make you invisible. But they might make excellent new chemical catalysts and semiconductors. Currently he's working with ones based on silver. His favorite, mithrene, is made of silver and selenium and glows a brilliant blue in UV light or "whenever grad students are around," Hohman says.

Elyse Schreiber, a chemistry graduate student in Hohman's lab, convinced Hohman they should try illuminating some of the small, messy hybrid chalcogenolates in a high powered X-ray beam anyway. If they could figure out the math, it would solve all their problems.

While working at the Linac Coherent Light Source at the SLAC linear accelerator in Menlo Park, California, Schreiber met Aaron Brewster, a researcher at Berkeley. Brewster mentioned he'd solved the math required to solve the crystal structure of difficult materials using X-ray crystallography. But he needed something to test it on. Hohman and Schreiber had the material. They provided plenty of tiny, imperfect

chalcogenolate crystals, which they mixed into water emulsified with Dawn dish soap (another indispensable item in Hohman's lab that glows blue) and shot jets of them into the accelerator beam. Each X-ray pulse illuminated the crystals incredibly brightly, allowing Brewster to capture a snapshot of the atomic structures of hundreds of tiny crystals. With enough snapshots, Brewster was able to run the calculations and figure out how the atoms were arranged.

Not only did they solve the crystal structures—they also figured out that the previous best guesses of what those structures were had been wrong. In theory, the technique, called small-molecule serial femtosecond crystallography, or smSFX, can be used for any chemical or material.

Computer scientists Nicolas Sauter and Daniel Paley at Lawrence Berkeley National Laboratory also helped develop smSFX. When you have a true powder, Paley explains, it's like having a million crystals that are all jumbled together, full of imperfections, and scrambled in every possible orientation. Rather than diffracting the whole jumble together and getting a muddied readout of electron densities, like existing powder diffraction techniques, smSFX is so precise that it can diffract individual grains, one at a time. "This gives it a special sharpening effect," he said. "So that is actually the kind of secret sauce of this whole method. Normally you shoot all million at once, but now you shoot 10,000 all in sequence," Paley says.

"There is a huge array of fascinating physical and even chemical dynamics that occur at ultrafast timescales and this technique could help us to understand how these dynamic events affect the structure of microcrystalline materials. In a way, connecting the dots between a material's structure and its function," Schreiber elaborates. Hohman is equally excited about their success.

"Now that we can solve these hard to crystallize structures, we can

design the best" structures for our purposes, Hohman says. Often, a material will come close to having a certain desirable property, but its crystalline structure won't be quite right. Hohman hopes that with the data they can get from X-ray crystallography using Brewster's technique, they can design better materials from the ground up.

Now, Hohman and Brewster are collaborating with Tess Smidt, a machine learning specialist at MIT, to try to teach a computer to design materials with specific properties.

This work involved the use of the SACLA free-electron laser in Japan, the Linac Coherent Light Source at SLAC National Accelerator Laboratory, and the Molecular Foundry and National Energy Research Scientific Computing Centers, U.S. Department of Energy Office of Science user facilities located at Berkeley Lab.

More information: Elyse Schriber, Chemical crystallography by serial femtosecond X-ray diffraction, *Nature* (2022). DOI: 10.1038/s41586-021-04218-3.
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