

preliminary test of wearability: They maintained functionality through 1000 cycles of stretching to 25% strain. The researchers used the transistors to build a primitive wearable device: a small patch, shown in figure 3, that drives the on-off switching of an LED.

To Simone Napolitano, a polymer physicist at the Université libre de Bruxelles, the achievement is an impressive application of basic research. “You always see in the introductions of papers that this fundamental work on confinement effects will bring marvelous applications, but when I actually asked around, no one could give an example of a real success story,” he says. “Bao’s group has been able to apply these ideas in a very direct way and arrive at excellent results.”

The body electric?

Last year Bao and her colleagues reported a different method for imparting stretchability to semiconducting polymers.³ The resulting films exhibited lower carrier mobilities than the new composite films do, but they had one trait that the new materials lack: Due to their hydrogen-bonding chemistry, they



FIGURE 3. FINGER FILMS. A stretchable, polymer-based thin-film transistor (TFT) worn on the knuckle of an index finger is used to control an LED on the middle finger. The transistor switches on when a sufficiently large gate voltage V_G is applied, remains on as the finger flexes, and switches off when the gate voltage is turned off. (Photo credit: Jie Xu and Sihong Wang of Zhenan Bao's group at Stanford University.)

could heal themselves. Bao thinks that by incorporating similar chemistry into the new semiconductors, she and her coworkers may be able to make them self-healing too.

But other matters will also demand the group's attention: The stretchable transistors' operating voltages, around 40 V, are still relatively high; their carrier

mobilities remain far lower than those of crystalline silicon; and techniques for patterning them into circuits will have to be developed essentially from scratch. Those patterning techniques are unlikely to rival the exquisitely honed methods developed for silicon. “In terms of cost per transistor,” says Bao, “I don’t think we’ll be able to beat silicon. The feature size is so small and the design is so sophisticated.”

Still, says Bao, polymer-based electronics will have significant advantages in applications that demand sensors distributed over large areas or that call for electronics in close contact with skin or soft tissue. “They can be used to make simple circuits that amplify and condition sensor signals, which could then be wirelessly transmitted and processed using silicon chips,” she explains. “We could imagine potentially having a whole bodysuit made of stretchable electronics.”

Ashley G. Smart

References

1. J. Xu et al., *Science* **355**, 59 (2017).
2. D.-Y. Khang et al., *Science* **311**, 208 (2006); Y. Sun et al., *Nat. Nanotechnol.* **1**, 201 (2006).
3. J. Y. Oh et al., *Nature* **539**, 411 (2016).

Electron diffraction sees hydrogen atoms

The detection of the small, light atoms heralds the emergence of the technique as a powerful crystallographic tool.

For finding the atomic structures of new molecules and materials, x-ray crystallography remains the reigning technique of choice. But it's hampered by a major limitation: Its simplest and most powerful form requires a crystalline specimen tens of microns on a side—a size that's beyond crystal growers' reach for many substances. The size requirement results from two factors: the relatively weak scattering of x rays off atoms in the crystal and the impracticality of focusing x rays onto a submicron spot.

Electrons, because of their charge, scatter orders of magnitude more strongly

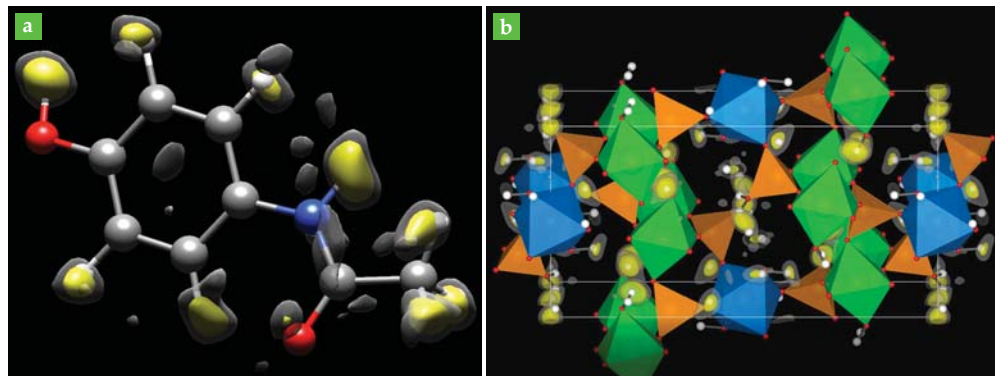


FIGURE 1. STRUCTURAL MODELS of (a) paracetamol and (b) framework cobalt aluminophosphate, derived from electron-diffraction data. Non-hydrogen atoms are shown explicitly, and the hydrogen-atom positions are established from electrostatic potential peaks. Large peaks are shown in yellow and smaller ones in gray; in each case, the largest peaks agree well with the known or expected locations of H atoms. (Adapted from ref. 1.)

than x rays do, and they can be focused much more tightly. Electron diffraction, therefore, has the potential to solve the

structures of submicron crystals, which are much easier to grow than larger ones. But the strong scattering has also been

electron diffraction's drawback: Electrons typically change direction many times on their way through even a thin crystal, and their diffraction patterns are extremely difficult to interpret quantitatively.

For more than 20 years, researchers have been working, with increasing success, toward antidotes to that multiple scattering. Now Lukáš Palatinus (Czech Academy of Sciences in Prague), Philippe Boullay (CRISMAT Laboratory, CNRS, Caen, France), and their colleagues have reached a milestone: using electron diffraction to derive structures that explicitly include the positions of hydrogen atoms.¹

Shown in figure 1 are their proof-of-concept structures of two materials: the organic drug paracetamol (also known as acetaminophen) and a form of cobalt aluminophosphate whose structure was previously unknown. To obtain them, the researchers used a combination of experimental and theoretical approaches to minimize and account for the effects of multiple scattering. Their success is a sign that electron diffraction is approaching x-ray diffraction in its structure-resolving power.

Humble hydrogen

In any form of crystallography except special neutron-based methods, hydrogen atoms are difficult to see: Their low scattering power and large vibrational amplitudes combine to produce broad, weak signals that are easily overwhelmed by noise. Crystallographers typically have to guess at the H-atom positions once they've solved for the positions of all the heavier atoms. Much of the time, that approach works well. Organic molecules, for example, have characteristic bond lengths and angles that don't usually change much from molecule to molecule.

But H-atom positions can sometimes offer important insights into a material's chemistry. When an H atom breaks away from its molecule, for example, it often does so as a bare proton, leaving a negatively charged ion behind. So the positions of H atoms—and how closely they're bound to the surrounding heavier atoms—can be intimately related to a molecule's electric charge distribution, which in turn is related to its solubility in water and other solvents. And solubility is an important property to know for many substances, not least for newly discovered drugs to be administered in solid form.

That said, locating H atoms wasn't the Prague–Caen researchers' explicit or immediate goal. "It was more like a dream come true than the initial motivation for the experiment," says Boullay. Rather, he and his collaborators sought to continue the steady march of electron diffraction progress.

Off-axis tilt

An early milestone on that march was reached in 1994, when Roger Vincent

and Paul Midgley introduced precession electron diffraction (PED).² In x-ray diffraction, aligning the beam with one of the crystal's major axes yields a diffraction pattern with a multitude of peaks, each directly related to the intensity of scattering off a single crystal plane. But in electron diffraction, the strength of multiple scattering means that the one-to-one relationship between peaks and planes no longer holds. Furthermore, electron diffraction patterns

Kurt J. Lesker
Company

Enabling Technology for a BETTER WORLD



We help our customers compete and succeed on the leading edge of technology, utilizing our range of quality products and vast experience providing solutions to the vacuum community.

- Research & Development
- Aerospace
- UHV/Synchrotron
- Electronics
- Wear/Decorative Coatings
- Optics
- LED

Visit Us

APS March Mtg. - Booth 125

www.lesker.com

16-137

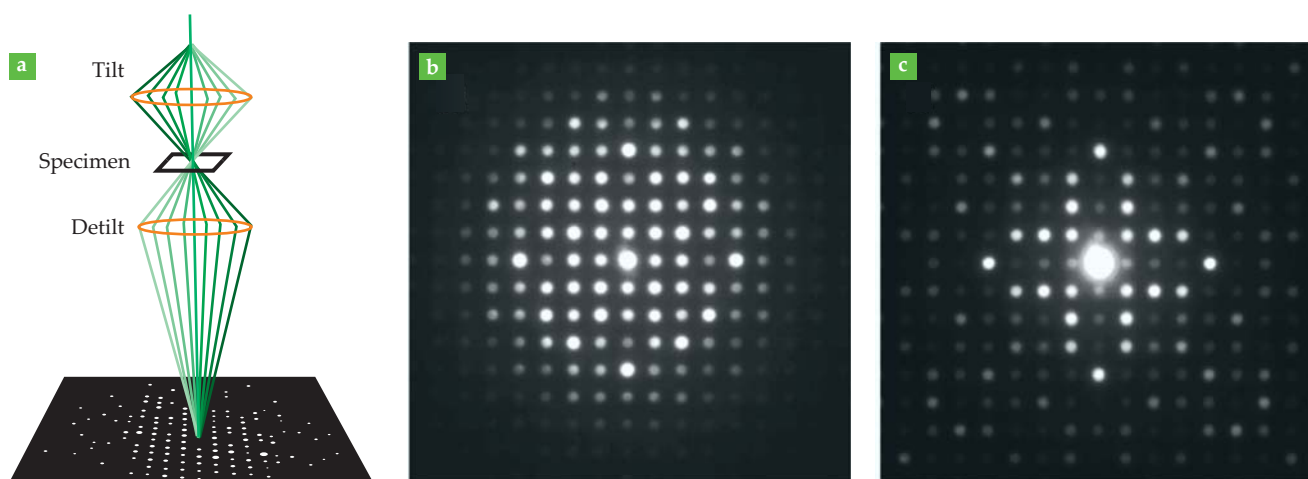


FIGURE 2. (a) IN PRECESSION ELECTRON DIFFRACTION (PED), the electron beam is tilted and precessed about a desired beam axis; the diffracted beams are recombined and their intensities are integrated to produce a diffraction pattern. (Omitting the detilting step would yield overlapping circles instead of discrete diffraction peaks.) **(b)** Without PED, multiple scattering muddies the relationship between peak intensity and crystal structure, and diffraction patterns are difficult to interpret. **(c)** With PED, the brightest peaks correspond to the strongest crystal reflections. (Panels b and c adapted from P. A. Midgley, A. S. Eggeman, *IUCrJ* **2**, 126, 2015.)

are extremely sensitive to sample thickness, small crystal imperfections, and slight misalignments of the beam.

In PED, the electron beam is tilted by a degree or two—the angle is exaggerated in figure 2 for illustrative purposes—and precessed at that fixed angle around the desired axis. The scattering signal is integrated over the entire precession to give a single diffraction pattern. That integration serves to average the signal and dramatically lessen the effects of imperfections and misalignments. And curiously, although multiple scattering is still prevalent, PED diffraction patterns are qualitatively similar to what one would expect in the absence of multiple scattering: The brightest peaks correspond to the most strongly reflecting crystal planes. The similarity is close enough to give some rough structural information.

Although PED has been around for more than 20 years, it's caught on only in the past decade or so, since the technology has become commercially available to perform the precession with the beam of an electron microscope. Also around 10 years ago, Ute Kolb and her colleagues at Johannes Gutenberg University in Mainz, Germany, began work on the complementary technique of electron diffraction tomography.³ Often combined with PED, EDT mitigates multiple scattering by directing the electron beam far away from the crystal axes. With the beam at an arbitrary off-axis

angle, it can reflect off only a few of the many crystal planes, and the number of available multiple-scattering pathways is greatly reduced.

But EDT has the disadvantage that structures can no longer be solved with just a few diffraction patterns. Instead, data at dozens, hundreds, or even thousands of different beam angles may be necessary, depending on the complexity of the material. “The new electron diffraction methods have benefited greatly from digital cameras replacing photographic film,” says Sven Hovmöller, whose group at Stockholm University also worked on the development of EDT. “Collecting hundreds of diffraction patterns with film would not only have been too expensive, but it would have taken days to collect the exposures and then weeks to scan them all.”

Many structures have been solved with the combination of PED and EDT. “But the accuracy and reliability of the structures was variable and nearly impossible to estimate,” says Palatinus. “The errors on the positions of atoms could be as low as 0.03 angstroms, but it's not exceptional to have errors of up to 0.5 angstroms”—around $\frac{1}{3}$ the length of a chemical bond.

Mapping potential

Better accuracy requires dynamical scattering theory to explicitly model and account for multiple scattering. There are various ways to do that—for example,

the sample can be numerically simulated slice by slice, or the electrons can be treated as quantum mechanical Bloch waves. Palatinus and colleagues' approach uses a Bloch-wave treatment to iteratively refine the structure and check it against diffraction data. They first published their computational method in 2013, and in 2015 they adapted it to accommodate EDT off-axis data.⁴

The latest advance combined PED, EDT, the dynamical scattering codes, and the experimenters' perseverance. Each frame in an EDT series requires the sample to be irradiated by the beam for several seconds; most materials, especially organic ones, can't survive the exposure necessary for a full data series. What's more, it's not always clear when the beam is starting to damage the crystal. In their work on cobalt aluminophosphate, the Prague–Caen researchers collected a whole EDT series before realizing that the sample was showing signs of deterioration. They started over with a new sample and lower beam intensity; they eventually solved the structure using 578 diffraction patterns from six separate crystals. For paracetamol, which can tolerate just 30 seconds in the electron beam before breaking down, they manually shifted the sample between frames so that different parts of the crystal were being irradiated over the 52-frame series.

The structures in figure 1 show the positions of the non-hydrogen atoms

and the local peaks in the electrostatic potential not accounted for by those atoms: Yellow blotches represent large potential peaks, and gray blotches represent smaller ones. With a less accurate method, there would have been no correlation between the largest potential peaks and the expected H locations—the H signal would have been overwhelmed by noise. Here, though, the yellow peaks agree well with the known H positions in paracetamol and the expected H positions in cobalt aluminophosphate.

The new results show that when x-ray diffraction fails due to crystal size, electron diffraction has the potential to stand in for it. But Palatinus and Boullay don't expect x-ray diffraction to give up its position as the favored technique for structural analysis anytime soon. The lower risk of radiation damage to the sample makes x-ray diffraction far less technically challenging. And although the dynamical scattering theory calculations can be performed on an ordinary desktop computer, they can take up to

several hours to complete; computing structures from x-ray diffraction data is 100 to 1000 times faster.

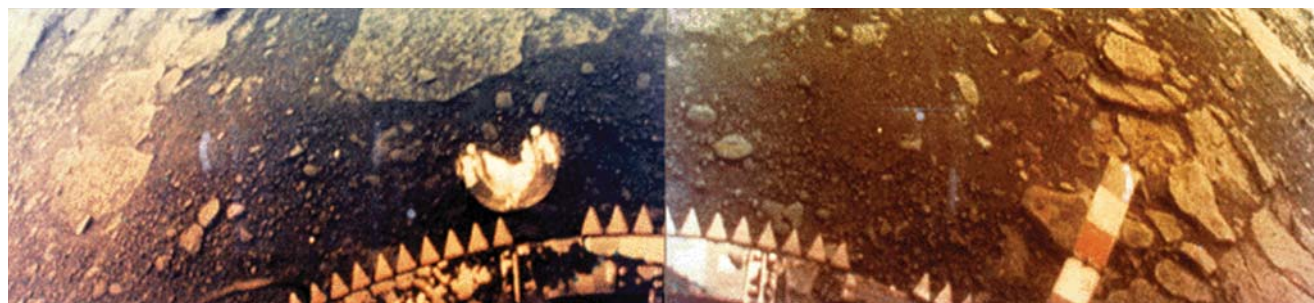
Johanna Miller

References

1. L. Palatinus et al., *Science* **355**, 166 (2017).
2. R. Vincent, P. A. Midgley, *Ultramicroscopy* **53**, 271 (1994).
3. U. Kolb et al., *Ultramicroscopy* **107**, 507 (2007).
4. L. Palatinus et al., *Acta Crystallogr. A* **69**, 171 (2013); L. Palatinus, V. Petříček, C. A. Corrêa, *Acta Crystallogr. A* **71**, 235 (2015).

Circuitry made robust enough for Venus

Silicon carbide devices lasted more than three weeks in a laboratory simulation of the corrosive conditions that prevail on the planet's surface.



Day or night, the temperature on Venus varies little from its mean of about 460 °C. That's hot enough to melt lead and an extreme demonstration of the runaway greenhouse effect of carbon dioxide, which makes up most of the planet's thick atmosphere. With the planet's crushing surface pressure of 9.4 MPa—93 times that on Earth—the gas exists in a supercritical state and behaves as a solvent. (On Earth, supercritical CO₂ is used to decaffeinate coffee beans.) Overhead, sulfuric acid clouds tens of kilometers thick are blown around the planet by hurricane-force winds.

Of the 26 spacecraft sent to Venus since 1961, only a handful have even attempted to land on its harsh surface. In 1982 the Soviet *Venera 13* lander sent the image shown in figure 1 before its instruments stopped working after a mere two hours on the surface, despite being housed in a protective pressurized vessel filled with heat-absorbing lithium salt. The quick demise is unsurprising: Silicon electronics start to fail at temper-

atures above 250 °C because too many electrons are thermally excited across the bandgap.

In the ensuing decades, silicon carbide technology has matured enough to make the semiconductor a more suitable choice for high-temperature applications.¹ Its strong, short Si–C bonds help protect the material from radiation damage by protons and gamma rays, and its wide bandgap allows for transistor action even at temperatures as high as 1000 °C. For the past several years, a team of engineers and materials scientists led by Philip Neudeck of NASA's Glenn Research Center in Cleveland, Ohio, has pursued the goal of developing durable SiC electronics sophisticated enough to reliably monitor the combustion conditions inside an aircraft engine, say, or the stability of an industrial drill bit deep underground.

To that end, the researchers have steadily toughened the various pieces of a SiC-based integrated circuit (IC). Those pieces include the metallic interconnects that run between field-effect

FIGURE 1. THE SURFACE OF VENUS, as captured in true color by the *Venera 13* lander during the 127 minutes its instruments remained functional on the planet's surface. The base of the spacecraft appears surrounded by flat rock slabs and soil, and the entire scene appears orange because the planet's thick atmosphere efficiently filters blue light from incident solar radiation. (Adapted from ref. 7.)

transistors; the insulating dielectric layers that protect everything from oxidation, which can be particularly insidious in hot environments; the gold-capped contacts that help link the IC chip to an external circuit board; and the board's gold- and platinum-embedded glass traces that connect the IC to other circuits. The effort has involved, among other things, choosing pure and relatively inert electronic materials that are stable at high temperature and whose thermal expansion coefficients are well matched to each other.²

Now Neudeck and colleagues have demonstrated that the robust ICs can