An all-in-one device creates and characterizes high-pressure superconductors

Diamond has the ability to squeeze materials to immense pressures and to measure their magnetic properties. Now it can do both at the same time.

The quest for a room-temperature superconductor has grabbed more headlines in recent months for scandal than it has for science. To a packed room at last year's American Physical Society March Meeting, the University of Rochester's Ranga Dias presented findings of "near-ambient" superconductivity in nitrogen-doped lutetium hydride; the results were published in *Nature* at the same time. But by November, the *Nature* paper was retracted—the third high-profile retraction for Dias's group—and in March of this year, the university concluded that Dias had engaged in research misconduct.

The field has made some confirmed progress. Pressurized sulfur hydride and lanthanum hydride, for example, both appear to superconduct at relatively high temperatures. (See PHYSICS TODAY, July 2016, page 21, and "Pressurized superconductors approach room-temperature realm," PHYSICS TODAY online, 23 August 2018.) But Dias's results are not the only ones that the controversy-stricken community has had trouble reproducing.

Part of the problem is that the experiments are genuinely difficult. Most of the candidate materials don't even exist unless compressed to hundreds of gigapascals—millions of atmospheres—so they must be synthesized under pressure, a speck at a time, between the tiny tips of two diamonds in what's known as a diamond anvil cell (DAC). Even Dias's supposed near-ambient material, so called because of its relatively gentle 1 GPa pressure, still required a DAC.

And the small sample size and constraints of the DAC make the purported superconductors extremely hard to characterize. Two key properties identify a material as a superconductor: Its electrical resistance drops to zero, and it expels magnetic fields from its bulk. For technical reasons, reliably making just one of those measurements on a microscopic sample inside a DAC is difficult. Performing both measurements on the same sample is nearly impossible.

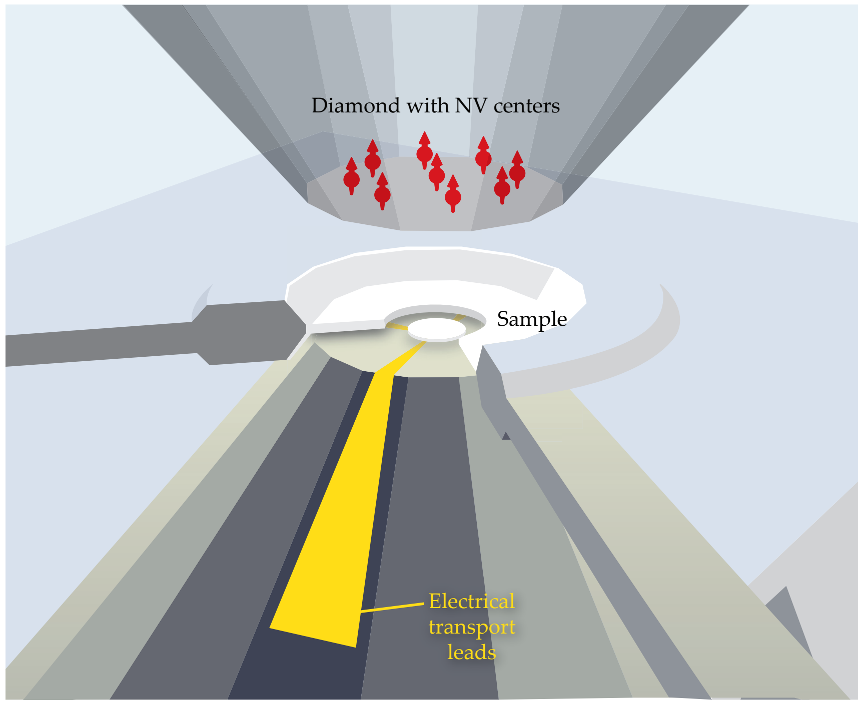

FIGURE 1. A DIAMOND ANVIL CELL, the standard tool for high-pressure measurements, doesn't have much room in it for instruments to probe the compressed sample. But magnetic measurements can now be made with nitrogen–vacancy (NV) centers embedded in the diamond itself. (Adapted from ref. 1.)

Furthermore, there's been no good way to fine-tune the high-pressure synthesis protocols, because there's been no way to tell how finely tuned they are to begin with. Diamond is transparent, so it's possible to view the compressed sample optically. But simply looking doesn't reveal much about whether the whole sample is superconducting or just part of it.

Both those problems may now be solved, thanks to new work by Norman Yao (formerly of the University of California, Berkeley; now at Harvard University), Christopher Laumann (Boston University), and their colleagues. They developed a way to perform spatially resolved magnetometry measurements inside a DAC by using defects called nitrogen–vacancy (NV) centers implanted in the diamond itself.[1]

Combining the NV magnetometry with electrical transport leads, as shown in figure 1, yields a device that can both create and characterize high-pressure superconductors. The technique could establish once and for all whether any given pressurized material is a superconductor or not. And because magnetic fields around different parts of the tiny sample can be measured separately, it provides unprecedented information about how well the superconductor synthesis is working.

Warming up

Superconductors have always been cold. The first known superconductor, mer-

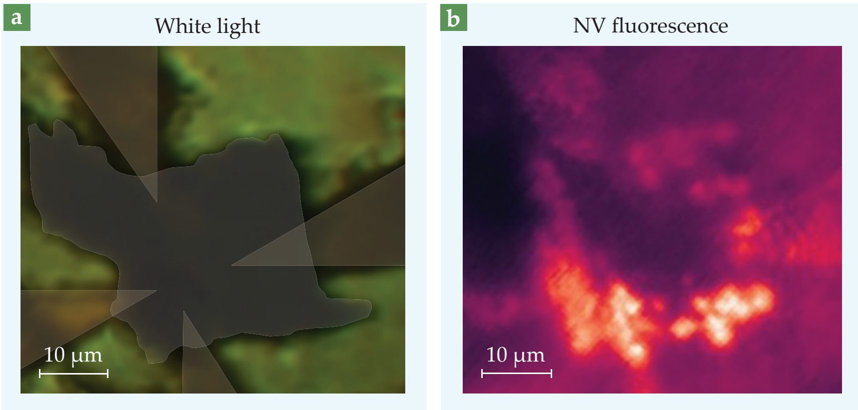

FIGURE 2. SPATIALLY RESOLVED MEASUREMENTS on pressurized samples have always been challenging. **(a)** Optical microscope images, such as this one, can be taken of the inside of a diamond anvil cell, but they don't reveal much about the sample's material properties. **(b)** Through the fluorescence of nitrogen–vacancy (NV) centers, researchers can learn much more about their samples. The bright spots in this image just indicate regions of higher NV center concentrations. But by zooming in on any bright spot and analyzing its fluorescence spectrum in detail, researchers can measure the local magnetic field—a key measurement for understanding whether the sample is a superconductor. (Adapted from ref. 1.)

cury, was discovered in 1911 to superconduct at a chilly 4.2 K, the temperature of liquid helium. Other ordinary metals superconduct at roughly similar temperatures, and the phenomenon is well explained by the Bardeen-Cooper-Schrieffer (BCS) theory of the 1950s: Vibrations in the atomic lattice nudge the fermionic electrons to team up into boson-like Cooper pairs, which condense into a superfluid and flow without resistance.

Even so-called high-temperature superconductivity, whose discovery in a family of cuprate ceramics rocked the physics world in the late 1980s, typically requires cooling to liquid-nitrogen temperature. The unconventional superconductors are not covered by BCS theory, and despite decades of work, the mechanism of their superconductivity is still unknown.

With the latest push for a room-temperature superconductor, researchers are turning back to the field's BCS roots, following two proposals from theorist Neil Ashcroft more than 35 years apart.[2] In the first, Ashcroft predicted that if hydrogen were compressed into a metal, vibrations of the lightweight atoms could be enough to form Cooper pairs even at high temperatures. The requisite pressure, however, was about 500 GPa, which is tough to reach, even with a DAC. So his second proposal—which predicted that hydrogen-rich compounds of heavier elements could manifest the same hydrogen-superconductivity effect at more modest pressures of 100–200 GPa—offered a more practical map for superconductor hunters to follow.

Ashcroft focused on compounds, such as methane, that are stable at ambient pressure. But most experimental implementations of his idea use hydrides that exist only at high pressure. The exotic materials must be synthesized inside an already pressurized DAC, usually by packing the cell with reactants and zapping it with a laser. And that's what makes studying the materials so challenging.

In principle, it's straightforward to measure the electrical conductivity of a sample inside a DAC: Just fit the cell with tiny electrical transport leads, like the ones depicted in figure 1, and measure the resistance when a current is passed between them. But the hallmark of superconductivity—zero electrical resistance—appears only if the superconductor spans the entire gap between the leads. "On the other hand, the leads can short-circuit due to thermal deformation," says Laumann. "So if cooling and heating the cell brings the leads in and out of contact, it can look like you're seeing a superconducting transition when you're not."

To conclusively show that they've found a new hydride superconductor, therefore, researchers must corroborate their electrical measurements with magnetic ones. But the latter measurements are even trickier than the former. There's no good way to put a standard laboratory magnetometer—a wire loop or coil—inside a DAC. So researchers have resorted to putting the DAC inside the magnetometer. "But then you're measuring the magnetism of the whole cell: the screws, leads, wires, and everything," says Laumann. "So it's hard to figure out what the contribution is of just the sample."

Furthermore, the two signatures of superconductivity are almost incompatible measurements to make on a pressurized sample. A DAC that's big enough to contain transport leads is too big to fit in a magnetometer. The usual approach is to use two DACs, one large and one small, for the two measurements. But the two cells may not contain the same material. In fact, given the unreliability of the high-pressure synthesis methods, they probably don't. "Even in the best groups in the world, only a third to a half of their samples show the signals of superconductivity," says Yao.

Much-needed clarity could come from a DAC that's capable of performing electrical and magnetic measurements on the same sample. But how?

Green with NV

An expedient solution is promised by NV centers. As the name suggests, an NV center consists of two adjacent sites in the diamond crystal lattice replaced by a nitrogen atom and a vacancy. The resulting point defect is an atom-like system whose state is readily controlled and probed with visible-wavelength light. Because of their easy manipulability and long coherence times, the centers are often used as qubits (see the article by Christopher Anderson and David Awschalom, Physics Today, August 2023, page 26). And because their spectra are sensitive to magnetic fields, they're also used as miniature magnetometers (see, for example, Physics Today, August 2018, page 16).

Because NV centers are housed in diamond, the very material that's the basis for a DAC, Yao and Laumann's approach of inserting NV centers into the diamond surfaces may seem obvious in hindsight. But NV centers, like many people, don't perform well under pressure. As was first noted in 2014, the more an NV center is squeezed, the noisier its spectrum gets, until at 50 GPa its spectral features all but vanish.[3]

So in 2019, when three groups (including Yao's) published their first explorations of integrating NV centers into DACs as a tool for high-pressure magnetometry, they all focused on pressures of a few tens of gigapascals—too low to access the superconducting hydrides that were starting to emerge.[4] "And even at those pressures, we lost so much in the signal-to-noise ratio," says Prabudhya Bhattacharyya, Yao's former student and the first author on the new paper. "For each measurement, we'd have to wait half a day to a day to see if we were even getting a signal at all."

University of Chicago theorist Giulia Galli helped Yao, Laumann, and colleagues pinpoint the problem. A DAC diamond is usually cut so that the diamond's [100] surface presses against the sample, because that's the crystal surface that's easiest to polish. But in that configuration, an NV center's axis—the line between the nitrogen atom and the vacant site—is oblique to the surface. The pressure at that angle distorts the defect's symmetry, and it's the loss of symmetry that destroys the spectroscopic signal.

By switching to diamonds cut so that the [111] surface faces the sample instead, the researchers positioned the NV centers perpendicular to the sample surface, which preserves their utility up to much higher pressures. "And the signal-to-noise ratio is so much better," says Bhattacharyya. "Now we can get a measurement in 10 or 20 minutes."

Full circle

The NV-endowed diamonds appear to be somewhat weaker than pristine ones, so it remains to be seen how high a pressure the new DACs can actually reach. But once they'd achieved 100 GPa, the researchers realized that they were ready to start testing superconducting hydrides. To begin, they chose cerium hydride, whose superconducting temperature of 91 K is modest by hydride standards—but, importantly, its requisite pressure of around 90 GPa is too.

For the sample synthesis, they turned to Xiaoli Huang and her student Wuhao Chen at Jilin University in China, who'd done the initial electrical-resistance measurements on the material and were some of the only researchers in the world with the knowhow to synthesize it.[5] "I've never met Wuhao in person," says Bhattacharyya, "but we've sent our samples back and forth so many times. One of our samples must have been around the world three or four times." Usually—but not always—the DAC is robust enough to survive the trip through the mail, even under pressure.

Images of the sample are shown in figure 2. On the left, figure 2a shows a white-light microscope image; until now, images like that, along with x-ray diffraction structures, were all the spatially resolved information about their samples that researchers got.

On the right, figure 2b shows an image of NV-center fluorescence. The bright patches in the image don't have anything directly to do with the cerium hydride sample—they're just regions in the diamond with more NV centers. But the researchers can zoom in on any spot with appreciable fluorescence, measure the NV-center spectrum, and deduce from that the local magnetic field.

At a spot that's not directly above the sample, the NV-measured magnetic field was always equal to whatever magnetic field the researchers applied—as expected. At a spot above the sample, however, the local magnetic field was suppressed. Again, that's what's expected for a superconducting material that expels magnetic fields.

But not every spot above every sample showed the same results. "These samples are actually very inhomogeneous at the 5- to 10-micron scale," says Laumann. "There was never a way to characterize them on that scale before—to say, 'Is this grain superconducting and that grain not?'" Cerium hydride indeed appears to be a superconductor, but there's a lot left to learn about how to reliably make it.

Solid footing

With technical improvements to their setup at Yao's new lab at Harvard, the researchers have expanded the range of pressures that they can achieve, and most of the putative superconducting hydrides are now within their reach. "We were starting to study lanthanum hydride," says Laumann, "and we just had our first sample synthesized. But it was one of the unlucky ones that didn't survive shipping back to the US."

A method for reliably testing hydride superconductors could help calm the controversy in the field, but the question remains of whether the materials themselves will ever have practical applications. Certainly, in their present form—existing only in microscopic amounts and under immense pressures—they do not. But as the field advances and the materials are better understood, they could yet reveal clues that lead to a material that really does superconduct under near-ambient conditions.

And importantly, superconducting hydrides aren't the only materials that can benefit from the new high-pressure NV-center measurements. NV-center spectra are sensitive not only to magnetic fields, but also to temperature, stress and strain, and other properties. "We're also working on serpentine, which is a mineral that's relevant to deep earthquakes," says Laumann. "It's kind of an open question what causes those and whether it's a serpentine phase transition."

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References

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