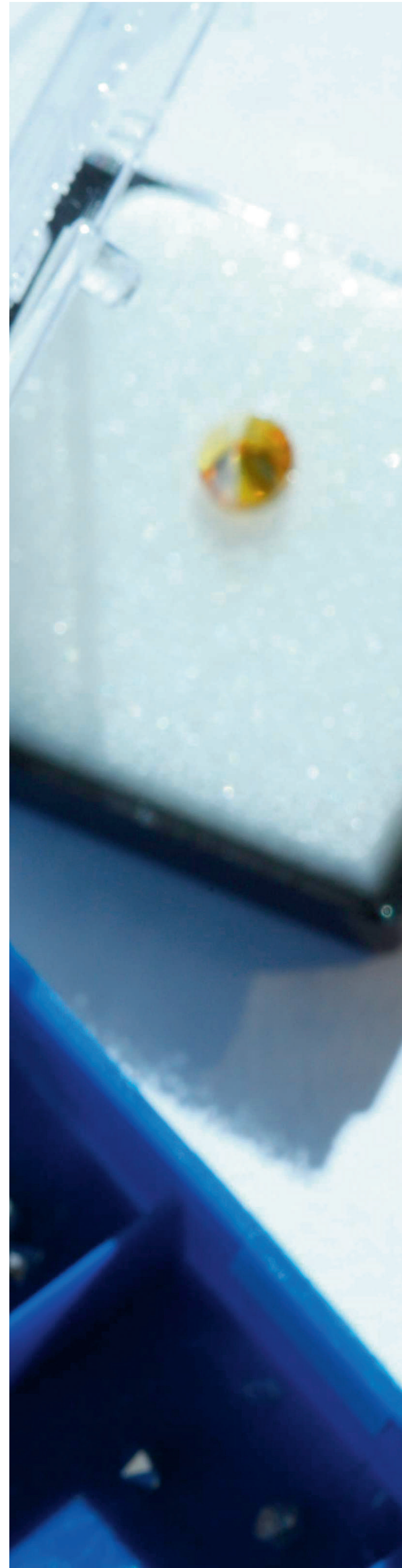
Elemental **Metamorphosis**

The inside of planets, stellar shells and numerous other uncomfortable spots in space have one thing in common: matter there is under extreme pressure of several million atmospheres. **Mikhail Eremets** and his colleagues produce such cosmic pressures in their lab at the **Max Planck Institute for Chemistry** in Mainz – and they do so in surprisingly simple experiments. They are researching which unique transformations gases, but also metals, undergo under these conditions.

TEXT **ROLAND WENGENMAYR**

The cosmos is full of places where the extreme is normal. "In the core of Jupiter, for example, the pressure is more than 30 million atmospheres," explains Mikhail Eremets at the Max Planck Institute for Chemistry in Mainz: "And planetary researchers have long suspected that hydrogen, which is the primary component of these gas planets, is metallic there." American physicists Eugene Wigner and Hillard Bell Huntington predicted this strange, solid state of hydrogen as far back as 1935. Until recently, though, it remained just speculation. It wasn't until 2011 that the small Max Planck team led by Mikhail Eremets, a Russian, provided certainty with its experiments. In fact, the Mainz-based scientists were the first to observe how hydrogen becomes a metal – at an enormous pressure of more than 2.7 million bar, or 2.7 million atmospheres.

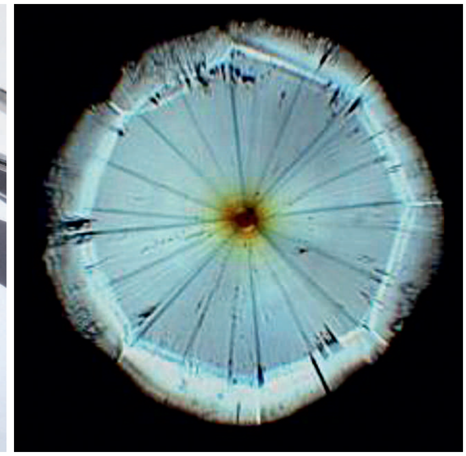
Since this world-record-setting measurement, many chemists, materials scientists and physicists are contemplating new, fascinating questions: Does hydrogen even become superconducting at room temperature at even higher pressure – in other words, does it conduct electricity entirely without electrical resistance? That is precisely what theoreticians predict. Only residents of Jupiter – if there were any – would be able to use superconductive extreme-pressure hydrogen in electrical cables. However, the discovery of room-temperature superconductivity in hydrogen could help in solving the mystery of high-temperature superconductors and in tailoring these materials for technical applications. Ceramics lose their resistance at higher temperatures than conventional superconductors, but still too far below zero to really be technologically useful. >



The researchers in Mainz store their diamonds, not in a pocket-type safe, but in an anvil cell. They produce up to 4.4 million atmospheres of pressure between the flattened tips of the precious stones.

Photo: Thomas Hartmann





Creating pressure through a gentle turn: An Allen wrench and four screws are sufficient to produce pressures of several million atmospheres inside the anvil cell. Only diamonds can withstand this load. However, the stones turn brown where they crash into each other, as can be seen by looking through one of the diamonds in the cell (right).

Regardless of potential new findings for energy technology, the experiments with hydrogen are of interest to physicists and chemists for a very basic reason: hydrogen is the simplest atom and the most common of all chemical elements in the cosmos. This makes it the model organism, the *Drosophila*, of quantum physics. In fact, it was the attempt at a physically precise description of the hydrogen atom that first gave rise to modern quantum mechanics. At the provisional end of this quantum revolution stands the semiconductor electronics that catapulted our culture into the Internet age.

As a matter of fact, at more than 2.2 million atmospheres, hydrogen, too, first becomes a semiconductor before it mutates into a metal. This is another thing the group in Mainz observed for the first time – even imaginative theoreticians didn't expect this behavior. It is precisely this transformability under increasing pressure that makes hydrogen so fascinating for science, which aims to use such experiments to draw basic conclusions about the matter in our cosmos. But how do the Max Planck scientists in Mainz manage to study their samples under such extreme conditions?

In any case, they don't need, for example, expensive space probes that crash into the bottomless abyss of the gas planet Jupiter. So, at the institute in Mainz, there aren't millions and millions of kilometers of cosmic travel separating us from the answer to our question. The solution is located right in Eremets' cramped study, where an old clock placidly ticks away the time. It's lying on a workbench with a stereomicroscope, and at first glance, it looks almost disappointingly unspectacular.

EXPERIMENTS AT A PRESSURE LIKE THAT INSIDE THE EARTH

Smiling, Eremets hands his visitor a compact metal tube. The brass-colored object has the diameter of a large coin and vaguely resembles a specialty part of a water fitting, but the massive caps that seal the two ends of the metal tube dispel this impression. Through small, thick windows, they permit a glimpse of the inside. And precisely there, in a volume of about five micrometers in diameter – one micrometer is one-thousandth of a millimeter – pressure conditions like those inside the earth prevail. At least when the device is in operation.

Of course this raises the question of which materials can withstand such enormous pressure. In answer, one might borrow Marilyn Monroe's immortal song "... but diamonds are a researcher's best friend." Diamonds are, in fact, the high-pressure researcher's best friends. The diamond anvil cell, as the small tube is called, contains two diamonds. However, they are quite small, explains Eremets, "the largest one is just 0.1 carat." He picks up a little box with small, glittering stones, all of which shattered in experiments. Even the hardest material can't withstand every pressure, and that's what makes this field of research so difficult.

Eremets and his colleague Ivan Troyan, who is also Russian, even had to become experts in precision grinding of diamonds. The shape they require has nothing in common with the grinding that gives diamonds their fire. The Max Planck scientists first give the small diamonds a basic conical shape. Then they grind a tiny piece of the tip off. This creates a flat surface there measuring just around 20 micrometers in diameter. Then the researchers put their diamonds – flattened tips pointed toward each other – into a tiny, ring-shaped mount that is likewise highly stable.

Before an experiment, the Mainz-based researchers fill the tiny volume between the diamond tips in a closed box with ultra-pure hydrogen – or with another material: sodium and nitrogen have also been used in the cells in Mainz. Now the enormous pressure is needed. Mikhail Eremets demonstrates how amazingly easily this is done. He doesn't need a gigantic press, as a layperson might expect. All the scientist needs is a screwdriver and the ring of precision screws that enclose each of the two windows in the metal caps.

Photos: Thomas Hartmann (left, 2); MPI for Chemistry (right)

» At a pressure above 2.2 million atmospheres, hydrogen initially becomes a semiconductor, before mutating into a metal. The researchers in Mainz were the first to observe this phenomenon.

The rest is pure and simple mechanics. By slowly tightening the screws around the coin-sized surface of the cap, the researcher applies growing pressure to the inside of the cell. This pressure, which can reach up to one ton, focuses the conical internal workings on the tiny diamond tip. Its surface is just a few square micrometers in size, while the cap surface, on the other hand, measuring a few square centimeters, is huge in comparison. This extreme area ratio acts like an enormous transmission gear, allowing a couple of delicate turns of the screws to ultimately result in one, two, three or more million atmospheres of pressure in the core of the cell. The absolute record for the group in Mainz is currently 4.4 million atmospheres.

THE PRINCIPLE IS SIMPLE – THE DEVIL IS IN THE DETAIL

So the principle is surprisingly simple, especially considering how much technical effort other disciplines, such as particle physics, expend to reach – admittedly yet more extreme – states of matter. And still there are only a few research groups worldwide that can play in the top extreme-pressure league with the Max Planck scientists in Mainz. This is by no means due to a lack of interest in such experiments. The reason is the many difficulties in the details, which cause even experienced researchers to fail. The story of this years-long battle is also told in precisely those shattered diamonds in Eremets' little box. Persistence is what helped his group succeed with its ex-

At the trigger: Ivan Troyan (left) and Mikhail Eremets prepare an experiment in which they compress hydrogen to an extreme extent. In doing so, they discovered the previously unknown semiconducting state of the gas, and turned the lightest of all the elements into a metal for the first time.

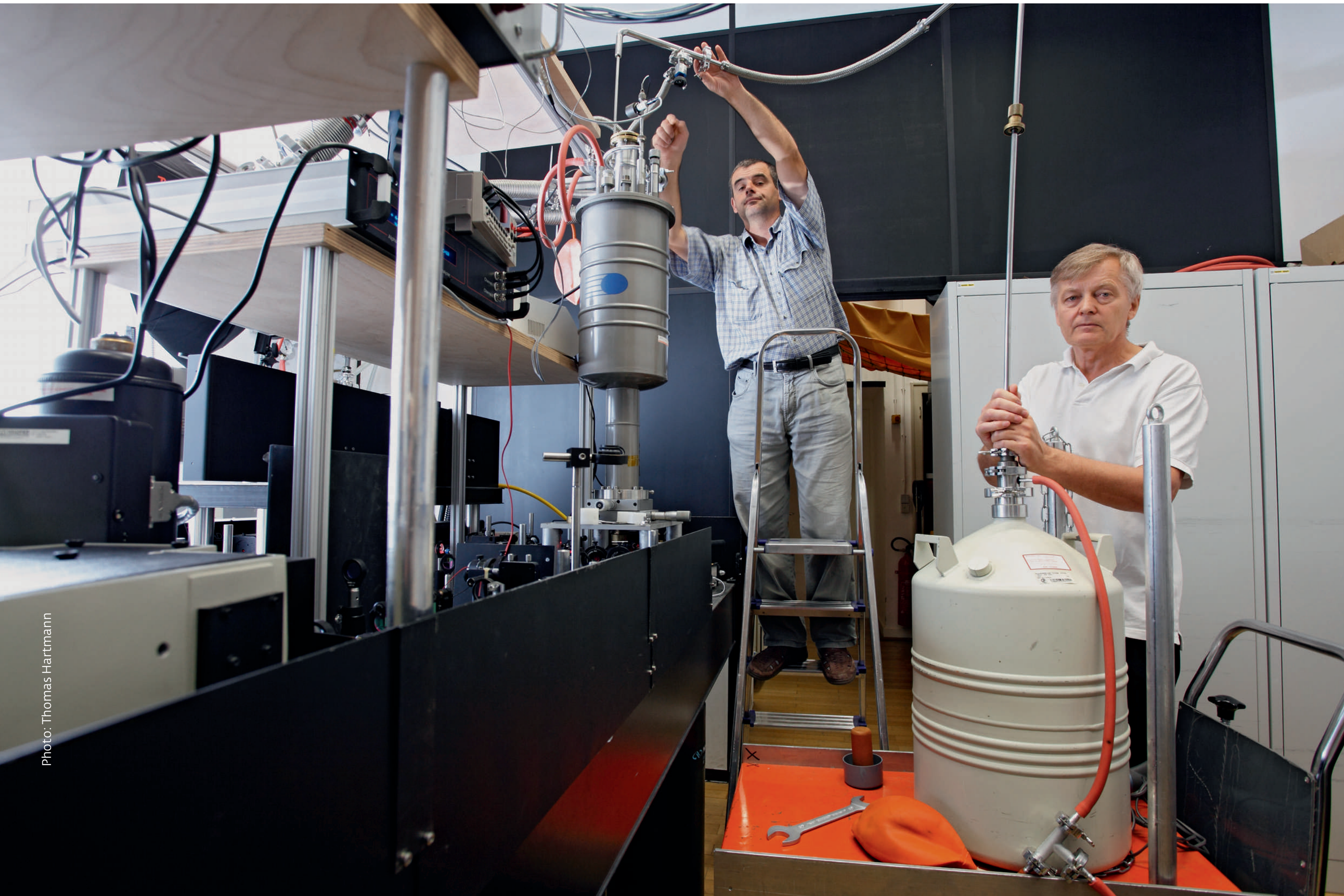


Photo: Thomas Hartmann

> » The European Research Council has been supporting the group since 2011, to the tune of 1.9 million euros – a great acknowledgement of the research field and the team's discoveries.

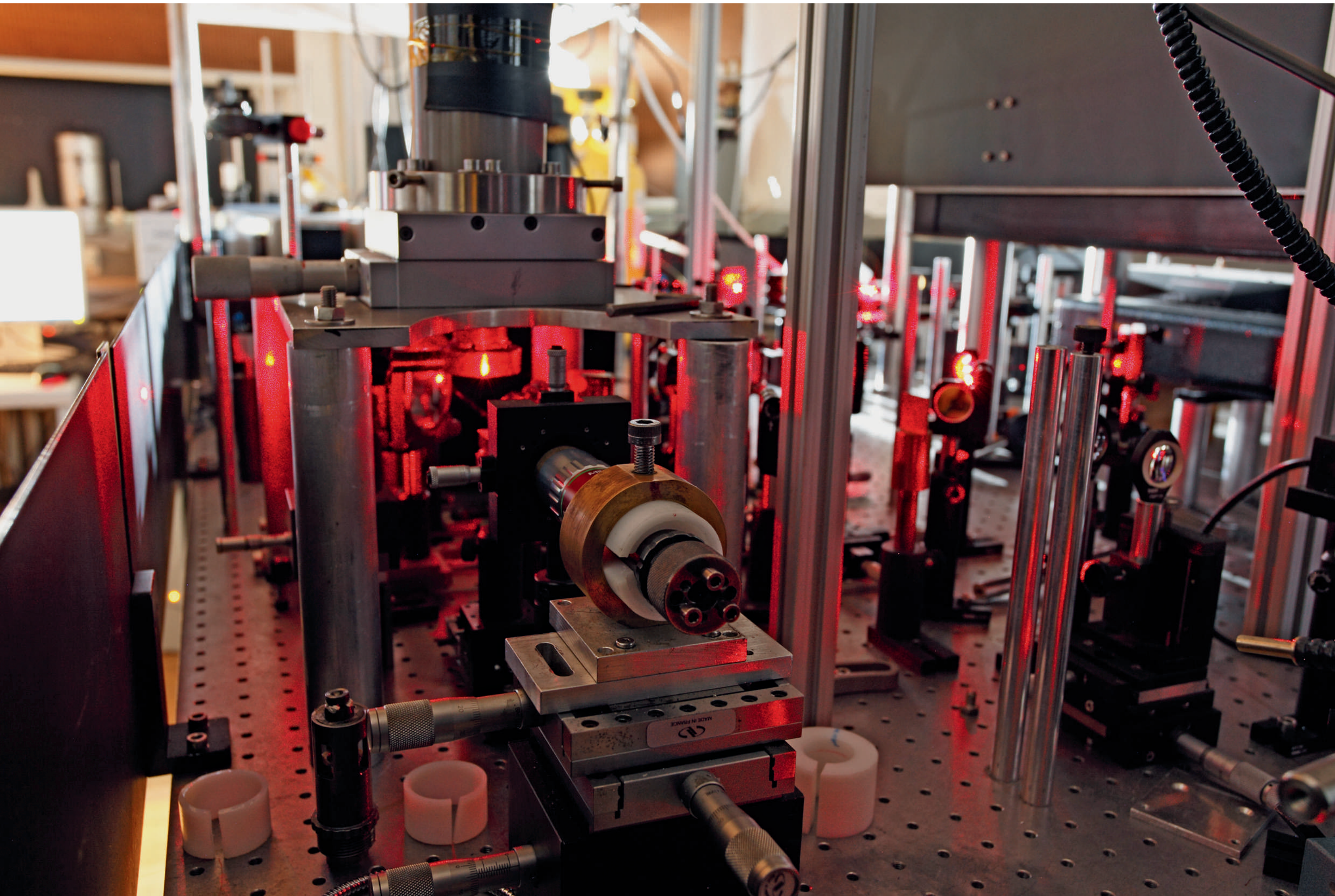
periments. "We also owe it to the good conditions at the Max Planck Society, which allows us to work on long-term projects," stresses Mikhail Eremets.

A METAL FILM PROTECTS THE DIAMONDS AGAINST HYDROGEN

Particularly hydrogen presented challenges that caused the diamonds of all high-pressure researchers to date to shatter. This is due to the fact that no diamond is truly perfect. Even a finely polished cutting surface always exhibits microcracks. Under pressure, the small hydrogen molecules penetrate into these cracks and shatter the stones. For years, this was the cause of failure for every experimenter worldwide. Eremets' group was no exception – until they came up with a crucial idea. They vapor-deposited a metal film, for example of gold, copper or aluminum, on the diamond anvil surfaces. The film is so thin that light can still penetrate it, so it is still possible to look into the chamber. Despite this, it protects the cracked diamonds against the aggressive hydrogen. This trick is what ultimately helped the group in Mainz to become the first to successfully put hydrogen under a pressure of three million atmospheres at room temperature without their diamonds shattering.

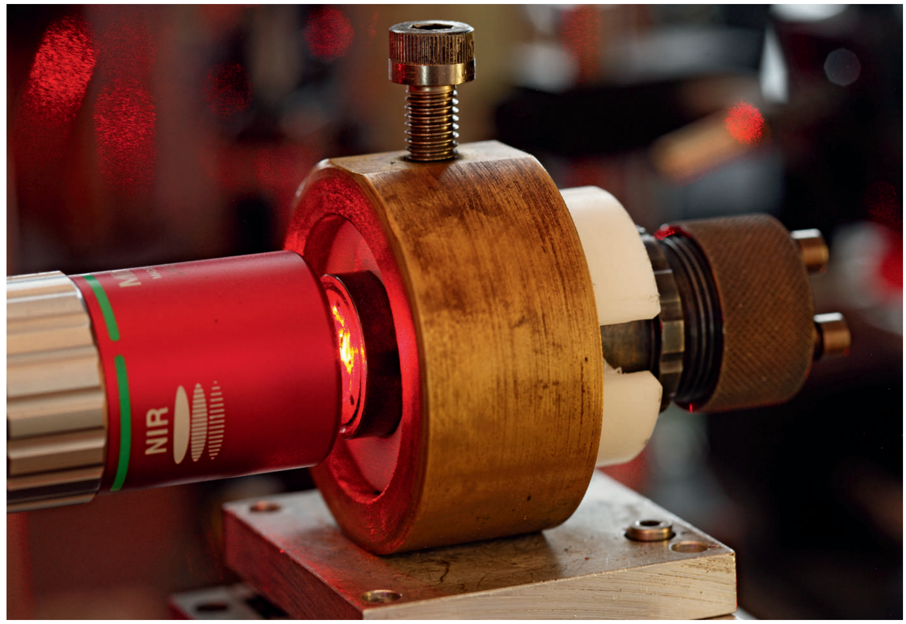
The question of whether the wear on the diamonds is costly brings a smile to Eremets' lips. "We end up with breakage of maybe 20 small diamonds a year," he calculates, "which costs about

The researchers working with Mikhail Eremets used different spectroscopic methods to track what happens in their high-pressure experiments. Here, they shine laser light into the cell. At the same time, this setup allows them to study the electrical properties of their samples at different temperatures.



10,000 dollars, making it cheap compared with many other experiments." The fact that the Mainz-based researchers can replace their losses again and again owes to the 1.9 million euros in funding that Eremets' group receives from the European Research Council. This support, which began in 2011 and is set to continue for several years, is a great acknowledgement of the research field and the team's discoveries. It allows the small group of a half dozen scientists to exert a good deal of pressure, as it were. And to travel with their experiments to the world's great research facilities – another advantage of the exceptionally handy cell. "I can simply put it in my pocket and take it with me," says Eremets enthusiastically.

The transparent diamonds allow different kinds of radiation into the samples, and each one provides different information about the behavior of the molecules, atoms and electrons under pressure. In their lab in Mainz, the researchers shoot a strong laser light in the visible spectrum into the samples. From the light that the sample then reflects back, they obtain detailed information about the behavior of the molecules. Additional information is provided by a particularly perfect kind of infrared radiation from synchrotrons, large accelerator rings for which Eremets and his colleagues travel, for instance, to Grenoble, France, the Swiss town of Villigen, or Chicago or Hamburg.



The Mainz-based researchers use light in the near – that is, relatively short-wave – infrared range (NIR) to conduct Raman spectroscopy, which tells them something about the structural changes under high pressure.

THE MOLECULES BECOME WARM HYDROGEN ICE

X-ray radiation provides important data as well. This electromagnetic radiation is so short-waved that it can sharply image the positions of individual atoms in crystals. This also helps in examining metals, which, like many solids, have a crystalline structure. For all of these highly specialized radiation sources, the researchers need only bring their little cells – there is no elaborate equipment to set up.

Incidentally, it comes as no surprise to chemists or physicists that hydrogen could possess metal-like properties. In the periodic system, it belongs to the same group as the alkali metals lithium, sodium and potassium. At slightly above two million atmospheres of pressure, its diatomic molecules are pressed together into a kind of warm hydrogen ice. "This substance can then be further compressed to a great degree," says Eremets, "to a twentieth of its volume." The hydrogen molecules squeeze ever more tightly together under the increasing pressure.

"In the process, something happens with their electrons," explains the researcher. The hydrogen molecule consists of two hydrogen atoms, and normally its two electrons are bound to this molecule. But now they sense the neighboring molecules closing in on them and essentially expand their radius of action. This interaction between the molecules eventually creates quantum highways on which electrons can fly throughout the entire material unhindered. This is typical for electrically conductive metals.

The group in Mainz observed this transition to nearly freely moving electrons: starting at a pressure of 2.2 million atmospheres, the hydrogen became black and opaque. This is the semiconducting state that the group discovered. In a semiconductor, certain electrons move nearly freely, but not entirely. They need a small energy kick to hop over an energy barrier onto the electron highway. This energy can be provided by light or an electric current.

THE CONDUCTIVITY PROVES THE METALLIC STATE

One can just picture the tension rising right along with the pressure in the lab in Mainz. Finally, at 2.7 million atmospheres, the hydrogen made the desired jump. It switched from the unexpected semiconductor state to the hoped-for metallic state. The freely moving electrons generated the typical shimmering light reflection of a metal. However, this high reflectivity is not yet proof of a metallic state. The electrical conductivity must be measured, and Eremets' group succeeded in doing so.

But an old scientific dream also died in Mainz. There had been a hope that, once the hydrogen had been compressed into a metal, it would remain stable when the pressure subsided. In the lab in Mainz, they saw for the first

Photos: Thomas Hartmann

» It is still not known whether metallic hydrogen is really solid. It could also be liquid like mercury.

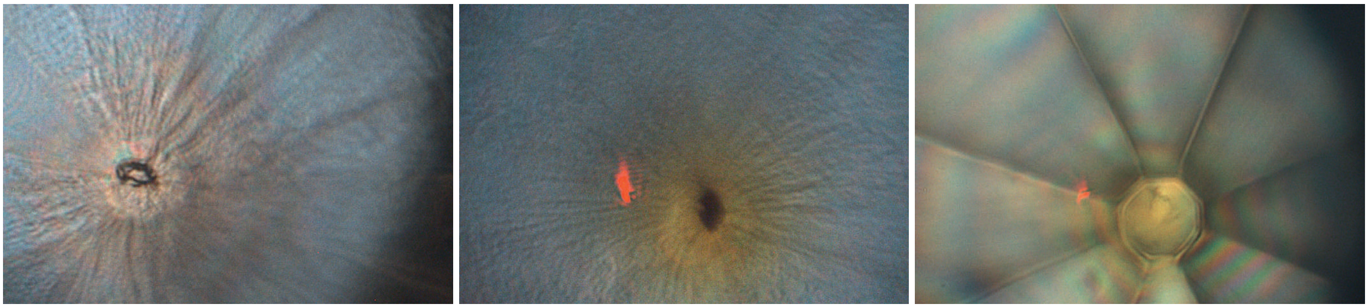
time that it relaxes into a gas again as the pressure is reduced. Too bad, as it might have resulted in the possibility of room-temperature superconductors from a press, as it were. But it is still undetermined whether the metallic hydrogen is really solid. It could also be liquid like mercury, suggests Mikhail Eremets. His team is currently working on clarifying this issue.

The researchers also want to know what happens when they increase the pressure even further. At some point, the hydrogen molecules should be completely crushed. "Theoretically, they should dissolve at about five million atmospheres," the scientist explains. Theoreticians predict that hydrogen could then not only become superconducting, but at the same time, also superfluid. It would then transform into an exotic quantum liquid that combines two extraordinary quantum effects. All known superconductors are solid. Helium, on the other hand, for example, becomes superliquid at very low temperatures.

Like superconductivity, superliquidity is a collective quantum state of many quantum particles that still isn't completely understood. What disappears is not the electrical, but rather the mechanical resistance: such a liquid no longer has any internal friction. As a result, it takes on what, for our everyday understanding,

Ivan Troyan (in the foreground) and Mikhail Eremets follow the images and measurement data on their computers during the experiments. The shiny metallic hydrogen can be seen on the screen in the background.

Photo: Thomas Hartmann



Inconspicuous spots with spectacular importance: When looking through a diamond into the hydrogen-filled cell, its interior remains transparent as long as the hydrogen is gaseous, at less than two million atmospheres (left). At 2.2 million atmospheres, the element turns a dark color when it changes to the semiconducting state (center). Finally, at 2.7 million atmospheres, the hydrogen takes on the metallic sheen (right).

Photos: MPI for Chemistry (3)

which knows only normal liquids, are strange properties: in the form of an ultrathin film, it can crawl up the sides of a container and run over the edge by itself. It's a good thing our beverages aren't superfluid.

HIGH PRESSURE MAKES SODIUM AS TRANSPARENT AS GLASS

In the high-pressure experiments in Mainz, however, it isn't restricted to gases turning into metals. Conversely, a metal lost its metallic properties. In 2009, the researchers observed that sodium turns black at about one million atmospheres, and at twice that pressure, it becomes as transparent as yellowish glass. In the process, its volume shrank to a fifth of the space it takes up at normal pressure. As it turned out, the sodium transformed into a kind of salt.

Nitrogen, too, behaves strangely under pressure. The nitrogen molecules that constitute 78 percent of our atmosphere are chemically extremely stable: its two atoms cling tightly to each other in a triple chemical bond. It takes a lot of energy to break this bond. In 2004, the team working with Eremets and Troyan approached this tenacious gas with a mix of high pressure and heat. They shot a strong laser into the diamond cell, where there was a tiny black surface that heated up the compressed gas.

At a temperature of more than 1,700 degrees Celsius and a pressure of more than 1.1 million atmospheres, the nitrogen molecule triple bond burst. Each pair was now holding on with just one chemical hand – the triple bond had become a single bond. With their other, now free, hands, they reached for their neighboring molecules, forming a crystal with atoms nicely arranged in a cube shape. "That's something like a nitrogen diamond," says Eremets.

It may even be possible to stably bring this cg nitrogen into normal pressure conditions. This exotic material did, after all, remain stable down to 420,000 atmospheres in the Mainz experiments in 2004. Mikhail Eremets is particularly fascinated by this, because cg nitrogen theoretically contains more chemical energy than any other material. "Then we would have, for example, a fuel that is superior to all fuels in existence today," says the researcher enthusiastically. So, we may one day drive with a tank full of nitrogen cubes. That would then be a further completely unexpected application like those that basic research turns out again and again. ◂

TO THE POINT

- **Extreme pressures of several million bar – one bar is one atmosphere – prevail inside planets and stars. Researchers learn a lot about the basic properties of matter from experiments under such conditions.**
- **Researchers at the Max Planck Institute for Chemistry produce extreme pressures between two small diamonds in a handy metal device; their current record is 4.4 million atmospheres.**
- **Matter takes on exotic characteristics under such conditions: hydrogen becomes a metal, sodium becomes a salt, and nitrogen forms a diamond-like structure.**

GLOSSARY

Superliquid: Substances whose atoms take on a collective quantum state below a certain temperature, losing their internal friction in the process. So far, only the helium isotopes helium-3 and helium-4, and the lithium isotope lithium-6, are known to become superfluid at temperatures near absolute zero, or minus 273.15 degrees Celsius. So far, no substances have been discovered that are simultaneously superconducting and superfluid.

Superconductor: Metals, ceramics and some ferrous compounds that lose their electrical resistance below a certain temperature because their electrons form Cooper pairs and, as such, no longer interact with the crystal lattice.
A distinction is made between conventional metallic superconductors that lose their resistance only at temperatures of less than minus 250 degrees Celsius, and unconventional superconductors, which also include the ceramic high-temperature superconductors. These lose their resistance at the temperature of liquid nitrogen. The current record is minus 135 degrees Celsius.