

An ice-cold experiment: The samples researchers at the Max Planck Institute for Chemical Physics of Solids are investigating are cooled in this dilution fridge to below minus 273 degrees Celsius. This is done by carefully lowering the instrument into a well-insulated cryostat.

Photo: Sven Börring

# Superconductivity Is Pair Work

Electric cables that routinely conduct electricity without loss – physicists have been motivated by this idea ever since superconductivity was discovered 100 years ago. Researchers working with **Bernhard Keimer** at the **Max Planck Institute for Solid State Research** in Stuttgart and **Frank Steglich** at the **Max Planck Institute for Chemical Physics of Solids** in Dresden want to gain a detailed understanding of how unconventional superconductors lose their resistivity.

TEXT **ROLAND WENGENMAYR**

**A**pril 8, 1911. At the University of Leiden in the Netherlands, two men sit in a darkened booth. Only their instruments tell them what is happening in the cryostat next door. A man in his late fifties with a striking walrus mustache fiddles with this enormous thermos flask: Heike Kamerlingh Onnes has been famous ever since he became the first person to succeed in liquefying helium in 1908. This enabled him to reach the extremely low temperature of 4.2 Kelvin, which is around 4 degrees above absolute zero, at minus 273.2 degrees Celsius. For this achievement, Kamerlingh Onnes would be awarded the Nobel Prize for Physics in 1913.

The cryostat now contains a small glass tube filled with mercury. The Leiden-based physicists want to use it to observe, for the first time, how the electrical resistivity of metals behaves when the temperature approaches absolute zero. At 4.2 Kelvin, minus 269 degrees Celsius, something unexpected happens: the display indicating the

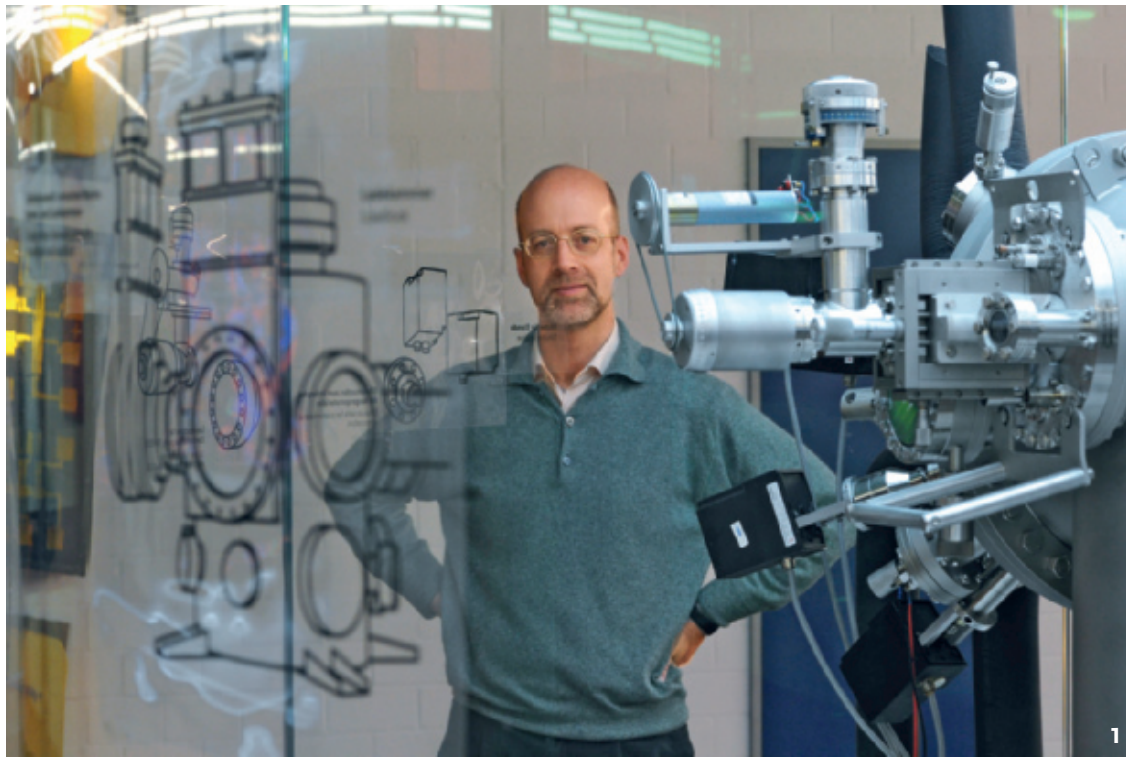
electrical resistivity of the mercury drops abruptly to zero. And there it remains. The researchers' first reaction is that it must be an error. However, subsequent experiments show that they have discovered a new phenomenon. In 1913, Kamerlingh Onnes called this effect superconductivity.

## WAITING FOR SUPERCONDUCTORS FOR EVERYDAY USE

Superconductors have excited the imagination ever since they were discovered. Even Kamerlingh Onnes dreamed of transporting electricity in power grids with no losses whatsoever. The discovery of so-called high-temperature superconductors in 1986 at the IBM research laboratory near Zurich created a great deal of euphoria. The two men who made the discovery, Karl Alex Müller and Johann Georg Bednorz, were awarded the Nobel Prize for Physics as early as 1987. A more sober atmosphere has now returned, however, as has happened so often in the history of superconductors.

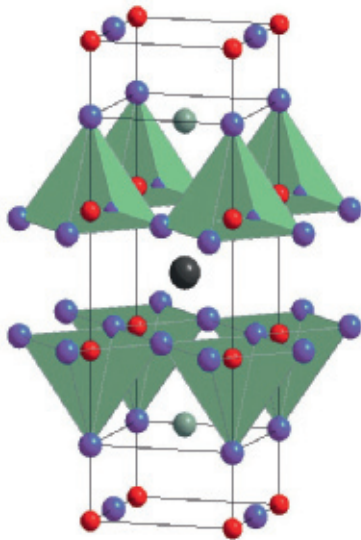
Although superconducting technology has become indispensable in basic research, it is encountered on a routine basis only in magnetic resonance imagers, because the complex cooling is expensive. The solution would be superconductivity at room temperature, but such materials have remained a dream. Since 1993 it has not been possible to raise the temperature record any higher. It currently stands at minus 138 degrees Celsius (135 Kelvin) and is held by a high-temperature ceramic superconductor with the complicated name of  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$  (Hg: mercury, Ca: calcium, Ba: barium, Cu: copper, O: oxygen).

Bernhard Keimer relates that company representatives recently asked him when superconductivity at room temperature could be expected. "They were disappointed when I told them that no one had an answer yet," he says, smiling. The Director at the Max Planck Institute for Solid State Research in Stuttgart and this year's recipient of the prestigious Leibniz Prize ought to know – after all, he has been researching high-



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temperature superconductors for many years. The scientist wants to obtain a detailed understanding of how these materials lose their resistivity – in order to create the basis on which everyday superconductors can be developed.



Layers with zero resistivity: In the superconductor, which goes by the name of YBCO and consists of yttrium (gray), barium (green), copper (red) and oxygen (blue), the Cooper pairs move along the copper oxide planes (pyramids).

This is also the motivation for the research being undertaken by Frank Steglich, a Director at the Max Planck Institute for Chemical Physics of Solids in Dresden. The honor of having been awarded the most valuable prize in German science is not all that Steglich and Keimer have in common: both researchers work in the field of “unconventional superconductors,” although Steglich’s team in Dresden works on so-called heavy fermion systems, which become superconducting at very low temperatures.

“In order to understand what unconventional superconductivity means, classical, conventional superconductivity first needs to be explained,” Steglich emphasizes. It was 1957 before the three Americans John Bardeen, Leon Cooper and Robert Schrieffer managed to crack this tough nut. In 1972 they received the Nobel Prize for Physics for this work. The BCS theory – the name derives from their initials – can be understood only by immersing oneself in the physics of solids.

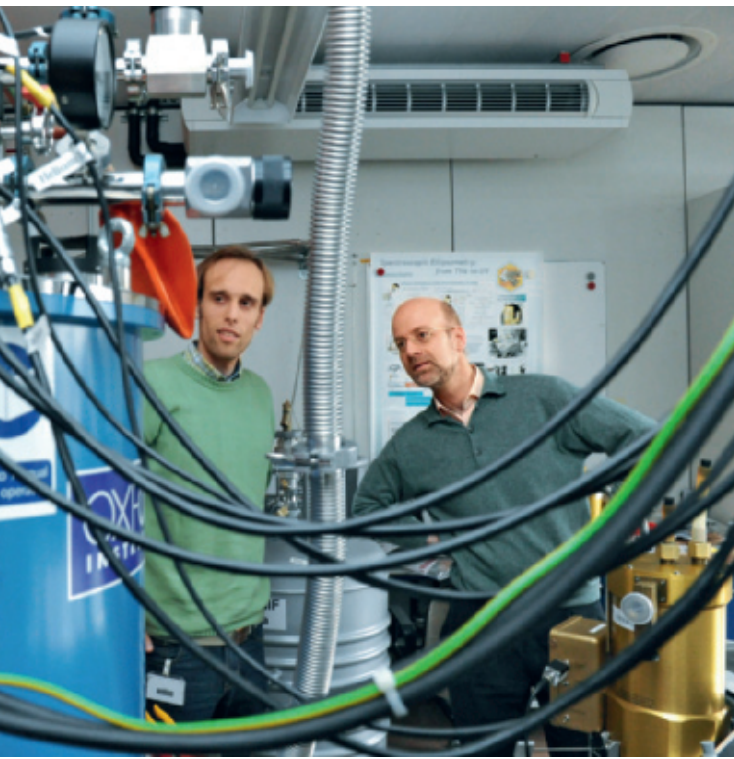
Like most solids, superconducting materials consist of crystals in which the atoms organize themselves into a regular spatial lattice. Nature loves or-

der if it helps to save energy. And the atoms in crystals succeed in doing just that, as they can share certain electrons among each other. These electrons provide the glue, the chemical bond, between the atoms. This works only with the aid of quantum physics: since electrons, as quantum particles, are also spatially extended waves, they can bind neighboring atoms to each other.

In metals and semiconductors, however, not all electrons act only as glue for the crystal. Some of them escape from the atoms and move with almost complete freedom through the lattice, but they require a certain energy to do this in semiconductors. These free conduction electrons carry the electric current. This loss leaves the “atomic cores” with a positive electric charge.

### GENTLE VIBRATIONS BIND TWO ELECTRONS

“The conduction electrons can even move through a perfect crystal without meeting any resistance,” explains Frank Steglich. This is due to the uniform arrangement of the atoms: if the distances between the peaks and troughs of the



- 1 To gain a better understanding of high-temperature superconductivity, Bernhard Keimer and his colleagues use the apparatus in the far right of the picture to produce thin crystalline layers with customized superconducting properties.
- 2 Daniel Pröpper and Bernhard Keimer observe how the cryostat in the foreground cools the sample of a high-temperature superconductor that loses its resistivity only at temperatures far below freezing point.

electron wave match the distances between the atoms, the electron can leap unhindered through the crystal.

But perfect crystals do not exist. Every crystal lattice has its flaws. They do not match the rhythm of the electron waves, which is why they literally ricochet off them. And even if crystals with perfectly ordered atoms did exist, the temperature would prevent the current from flowing with zero resistivity, because the higher it becomes, the stronger and faster is the vibration of the crystal's atomic lattice – like a mattress being jumped on with wild abandon. This also interferes with the crystalline perfection and hinders the wave of conduction electrons.

In conventional superconductors, the vibrations of the atomic mattress become slow and gentle at low temperatures – as happens in essentially all materials. When a conduction electron races through the lattice on its path, it electrically attracts the positively charged atomic cores. With a soft lattice, the atomic cores totter along sluggishly behind the electron and only return to their original position much later.

“In conventional superconductors, this lattice vibration is extremely slow compared to the motion of the electrons,” emphasizes Frank Steglich. “This is very important!” If a second electron now passes, it is attracted by this more concentrated positive charge. As a consequence, the lattice

binds it with the first electron, although the two particles violently repel each other because they have the same, negative charge. Only the large temporal and thus also spatial separation of up to one micrometer – a thousandth of a millimeter – between the two allows the marriage in the soft lattice bed. For comparison: the distance between the atoms in the crystal lattice is around one thousand times smaller, around one tenth of a nanometer – one nanometer is a millionth of a millimeter.

### POWERFUL VIBRATIONS DESTROY THE COOPER PAIRS

This is how two free electrons form one Cooper pair, which is named after Leon Cooper, one of the three fathers of BCS theory. His idea provided the breakthrough for the explanation of conventional superconductivity in 1957. In order to understand the properties of Cooper pairs, their “spins” are also required. To put it somewhat nonchalantly, spins describe a sort of quantum pirouette by the particles, turning them into tiny quantum magnets. According to the strict rules of quantum physics, however, spins are not allowed to align themselves with each another arbitrarily. In the Cooper pairs, they can be oriented only parallel or antiparallel to one another, like rotary switches snapping into place.

The properties of the Cooper pairs are radically different from those of the electrons. Pursuant to the rules of quantum mechanics, electrons possess a half-integer spin. They thus belong to the group of particles known as fermions. These are quite acquisitive, each requiring a quantum state for it alone. In the Cooper pair, the two half-integer spins of the two electrons either subtract to a total spin of zero or, more rarely, they also add up to one.

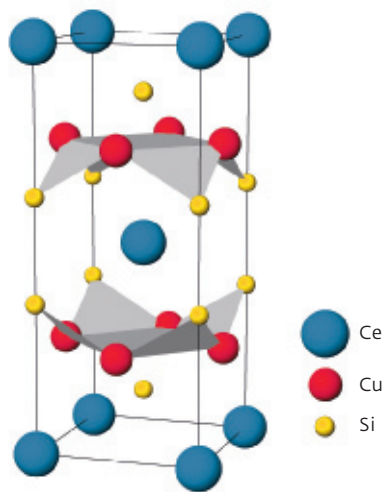
Quantum particles with integer spin, however, belong to the group of particles known as bosons. Bosons are so sociable that they all like to condense together into one quantum state if the heat energy in the system becomes low enough for this to happen. For Cooper pairs, this is the superconducting state in which many Cooper pairs permeate each other to form one “macroscopic” quantum state. This large quantum object can simply “slip through” the many small flaws in the crystal without noticing them. This is how the electrical resistivity disappears. “In superconducting cables, this macroscopic quantum state can extend over kilometers,” says Bernhard Keimer. “That’s quite remarkable!”

In conventional superconductors, the Cooper pairs, which have a wide spatial extent, always have a total spin of zero. Decisive for the properties of conventional superconductors are the lattice vibrations, which are slow, com-

» There is still no conclusive theory, but one thing is clear: superconductivity and magnetism work in close collaboration in unconventional superconductivity. This is surprising, because magnetism is pure poison for conventional superconductors.

pared to the speed of the electrons, and which bind the two conduction electrons to a Cooper pair. Since crystal lattices vibrate with ever-increasing speed and amplitude as the temperature increases, this destroys the Cooper pairs. Conventional superconductivity can therefore be observed only at relatively low temperatures.

High-temperature superconductors become superconducting at much higher temperatures. They must therefore contain a much stronger Cooper-pair glue in order for the lattice vibrations not to rip the pairs apart. Many indications point to the fact that these quantum superglues function in a completely different way than lattice vibrations. This is thus taken to be the characteristic of unconventional superconductivity. There is still no conclusive theory, but one thing is clear: superconductivity and magnetism act in close collaboration in unconventional superconductivity.



An unconventional superconductor: The material made from cerium (blue), copper (turquoise) and silicon (yellow) owes its special properties to specific electrons in the rare earth metal cerium.

This is surprising, as magnetism is pure poison for conventional superconductors. "A magnetic atom contamination of less than one percent in the crystal already destroys its superconductivity," explains Frank Steglich. Magnetic atoms introduce an electron into the crystal lattice, whose unshielded spin acts as a small magnet at the site of the atoms. If, in a conventional superconductor, an electron of an extended Cooper pair now passes by, the local spin forces it to reverse its spin appropriately. But this love affair destroys the weak bosonic marriage with the distant "Cooper partner." If this happens too often, the superconductivity breaks down.

### COOPER PAIRS WITH PARTICULARLY STRONG GLUE

With unconventional superconductors, in contrast, certain forms of magnetism seem to be really helpful. This also applies to heavy fermion superconductors, which have fascinated Frank Steglich for more than three decades: "We currently know almost 40 of them!" Most heavy fermion superconductors lose their resistivity only at very low temperatures. "If we have around 2 Kelvin, or minus 271 degrees Celsius, we are very happy," says Steglich's colleague Steffen Wirth, explaining the challenge. Nevertheless, the Dresden-based researchers hope that such superconductors can also help them contribute to solving the mystery of the gluing mechanism in high-temperature superconductors. But what exactly is a heavy fermion?

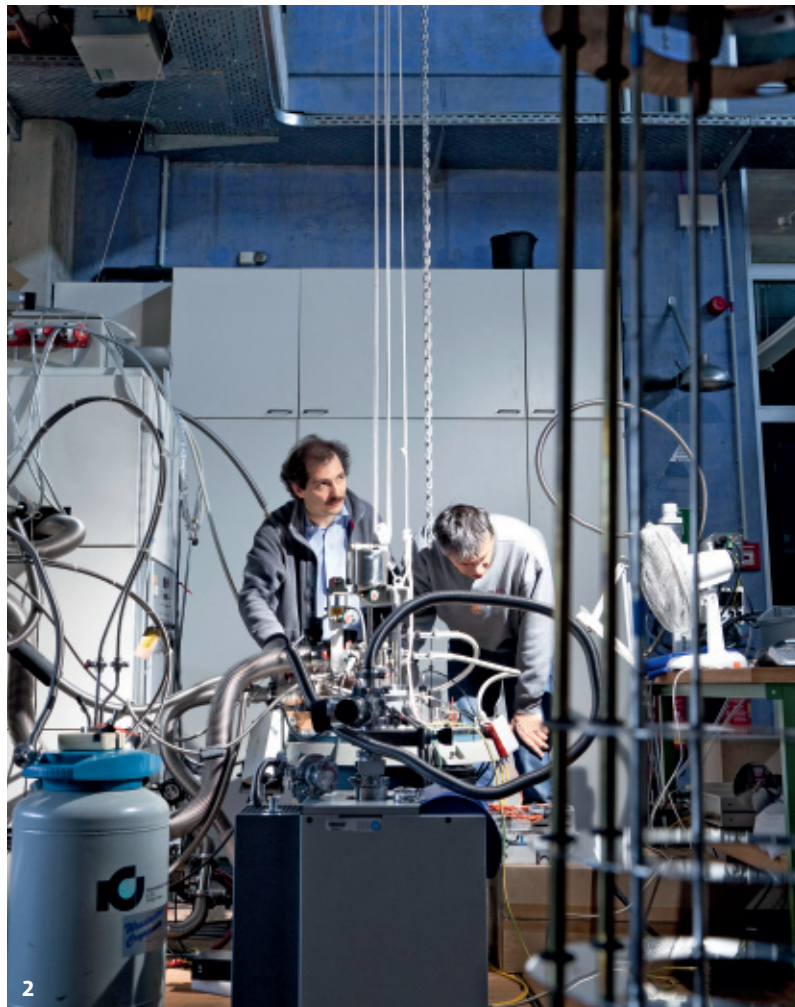
The particles can be found in a crystal lattice whose fundamental building blocks always include a magnetic atom: cerium, for example, takes on this role in the cerium-copper-silicon compound  $\text{CeCu}_2\text{Si}_2$ , in which unconven-

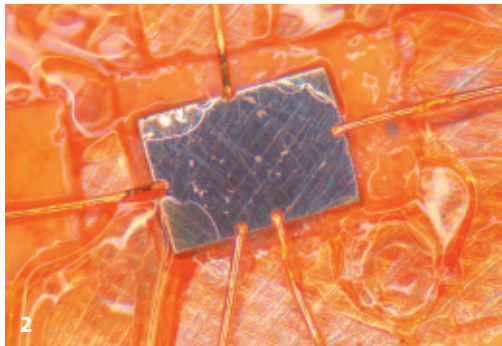
tional superconductivity was first discovered in 1979. The researchers in Dresden know this forefather of the heavy fermion superconductors so well in the meantime that they can adjust its properties when growing crystals: a tiny excess of copper turns it into a superconductor, a small deficit into an antiferromagnet.

In antiferromagnets, the electrons responsible for the magnetism, which in cerium are called 4f electrons after their position in the electronic shell, always orient themselves in the direction opposite to that of the neighboring atom. Their overall magnetic field thus cancels out perfectly on average. This magnetic order is called antiferromagnetism, because it is the counterpart to the ferromagnetism with long-range effect, which takes its name from iron (lat. *ferrum*).

In  $\text{CeCu}_2\text{Si}_2$ , as a typical example, the local 4f electrons develop a particularly strong influence on the free conduction electrons at very low tempera-

- 1 Frank Steglich (top left), Oliver Stockert and Steffen Wirth (in the window) prepare measurements using a scanning tunneling microscope for very low temperatures. The microscope images atomic structures and stands on its own base that reaches down to the rocky foundation in order to protect the apparatus from vibrations. The soundproof room, whose roof was removed for the work, serves the same purpose.
- 2 Oliver Stockert (left) and Steffen Wirth adjust a dilution fridge, which generates temperatures of below minus 273 degrees Celsius.
- 3 Experiments with a crane: Oliver Stockert instructs a colleague who is lowering a superconducting magnet into a cryostat that sits on its own foundation. The researchers use the superconducting magnet to investigate how the physical properties of their samples depend on the magnetic field.





tures: put simply, they bind them together to form a quantum fluid with the viscosity of honey. The electrons contained therein now sluggishly drag themselves through the lattice – up to a thousand times slower than normal conduction electrons. “These new quasi-particles thus behave like electrons that apparently have a mass up to one thousand times greater,” says Steglich, “which is why we coined the term heavy fermions in the late 1970s.”

The heavy fermions also form the Cooper pairs in such superconductors. Their sluggishness means that the two partners must cuddle up close in order to be able to bond with each other. However, this makes the electrical repulsion between them all the stronger. The glue between them must therefore be much more powerful than in conventional Cooper pairs. This is why it has been clear for more than three decades that the conventional BCS mechanism does not work here.

Although the theoretical physicists proposed alternative glue mechanisms early on, solids are complicated structures comprising enormous numbers of atoms and electrons that exert a reciprocal influence. This makes it very difficult to “take a look inside” them in experiments. Neutrons provide one possibility: these nuclear particles are small and electrically neutral, so they can penetrate matter almost unhindered. Like electrons, however, they have a half-integer spin, which makes them into well-matched little mag-

nets. They thus become probes that react to all electrons with a “free” magnetic moment.

Oliver Stockert, another colleague of Frank Steglich, recently used this method to investigate  $\text{CeCu}_2\text{Si}_2$  at the neutron source of the Institut Laue-Langevin in Grenoble. In the process, his team discovered that the magnetic interactions in the lattice were indeed 20 times as strong as the gluing of the Cooper pairs would require. “This is obviously how they make superconductivity possible,” says Stockert. The measurements with neutrons do not provide proof, but the smoking gun, so to speak. His colleague Steffen Wirth is employing further methods in parallel in order to conclusively complete the picture.

### SHORT-LIVED MAGNETIC FIELDS BIND THE ELECTRONS

This idea is now taking shape. The Cooper pair glue is actually magnetic. Its force originates from spin fluctuations of the heavy fermions. In the general chaos, they form small “bubbles” with short-range magnetic order that form and disappear rapidly. These fluctuations particularly exert their effect close to a state known as the quantum critical point. This point can be reached via low temperatures, the correct chemical mixture in the crystal, magnetic fields or pressure. In  $\text{CeCu}_2\text{Si}_2$ , two very strong effects are competing with each other: the antiferromagnetic order is fighting

against the normal metallic state, which is magnetically unordered. “And if two are busy quarrelling, the third can take advantage of the situation,” says Wirth. Stockert adds: “Very strong spin fluctuations that produce Cooper pairs occur especially at the point where the two cancel each other out.”

With spin fluctuations, the particles involved waggle their spins and influence each other in this way – a disrespectful way of putting it. The short-lived magnetic fields created in this way are sufficient to strongly bond the electrons to form Cooper pairs. Spin fluctuations also play a crucial role in high-temperature ceramic superconductors. Most, if not all, of the physicists conducting research in this field are convinced of this, says Bernhard Keimer – and he includes himself here.

“Although here we have only one electron system, unlike the heavy fermion superconductors,” he explains. This means that there are no local 4f electrons here to create a tendency for latent antiferromagnetism. Instead, it is only the conduction electrons that bring about the interaction between magnetic order and superconductivity.

Most copper oxide compounds, including the high-temperature superconductors, are even insulators. Their complex crystal lattice has a sandwich-type structure. Layers of copper and oxygen atoms play a crucial role in this process, which is why these brittle materials are called cuprates. The Cooper pairs move along these copper oxide

- 1 | Sample and carrier: The Dresden researchers use the box to store a sample carrier and the cerium copper silicide crystal after they have investigated its magnetic properties with a neutron beam.
- 2 | In order to study the electric and magnetic properties – or more precisely the Hall effect in ytterbium rhodium silicide – the researchers fixed a platelet of the material with varnish and provided it with electric contacts.
- 3 | A research object that can be handled: Frank Steglich holds a glass model of the cerium copper silicide crystal in his hands.

planes, so their superconductivity is strongly two-dimensional – “flat,” as it were. The conduction electrons required are provided by foreign atoms with which the researchers intentionally contaminate their crystals.

Bernhard Keimer uses diagrams to show how the superconductivity probably operates in cuprates. In the copper oxide planes of the crystals, certain electronic states of the copper atoms overlap each other. These “d-orbitals” form the racetrack for the conduction electrons. The electrons tend to a fluctuating antiferromagnetic order when approaching the superconducting transition temperature: they orient themselves antiparallel as they get closer to it.

If an electric current now flows, individual conduction electrons must migrate through this spin landscape. The rules of quantum physics require them to continuously flip the spin of the electrons they encounter to suit their own spin. “They leave behind a trail of flipped spins, which is very energy intensive,” explains Keimer:

“Their motion through such an antiferromagnetic background is very slow!” The electrons can save the energy they expend here by forming Cooper pairs – which are very small, as they are in the case of the heavy fermion superconductors. With their total spin of zero, they become invisible, as it were, to the antiferromagnetic stubble field of half-integer spins. They slip through without losing any energy whatsoever, and the cuprate becomes a perfect electrical conductor.

### RESEARCH SHOULD SOMEHOW BENEFIT SOCIETY

“It is still just an idea for a model,” says Keimer with a smile. A Stuttgart-based team headed by his colleague Vladimir Hinkov used neutrons at the FRM-II research reactor in Garching and observed that strong spin fluctuations actually do occur. They input the measurement data without “fine-tuning” into a model being developed by the theoreticians in Stuttgart, explains Keimer. This then computed a transition temperature at which the substance would theoretically become superconducting. The first shot at 170 Kelvin was almost twice as high as the substance’s real transition temperature, but Keimer considers this result to be very encouraging: “The closer one looks, the simpler the picture gets.”

The researchers in Stuttgart have also perfected the production of artificial crystals, which they now want to use to imitate the layer structure of the cuprates. They hope this will take them a few more steps along the learning curve. “It is possible to make great

progress in high-temperature superconductivity with simple models,” states Keimer optimistically. These findings may one day contribute to developing a material that conducts current at room temperature with zero resistivity. Bernhard Keimer keeps this long-term objective in mind. “As a basic researcher, I have a vision, of course, that this research will benefit society one day.” ◀

### GLOSSARY

#### Transition temperature

The temperature below which a material becomes superconducting.

#### Fermion

A particle with half-integer spin; fermions such as electrons each require a quantum state of their own.

#### Heavy fermion superconductors

The unpaired electrons they contain, which in some metals stay very close to the atomic nucleus, contribute to superconductivity. They therefore move extremely slowly, which is why they appear heavier than they actually are.

#### Cooper pair

Two electrons that are fermions combine to form a Cooper pair and become a boson. At sufficiently low temperatures, a very large number of Cooper pairs occupy a quantum state in which they no longer experience the flaws and vibrations of the crystal – the resistivity disappears.

#### Bosons

Particles with integer spin; unlike fermions, they all occupy a single quantum state in the ground state.

#### Spin fluctuations

The spin or intrinsic angular momentum gives the electron its magnetic moment. The orientation of the spin thus determines the magnetic order in a material. Even before it assumes a certain magnetic order – ferromagnetic or antiferromagnetic, for example – this order can already form temporarily in some regions because the spins fluctuate – that is, change their orientation.



Sample mosaic: Bernhard Keimer’s team mounts around 100 YBCO single crystals onto a support in order to produce a sample with as large a volume as possible. The researchers use inelastic neutron scattering to investigate the magnetic properties.