

Unmasking the record-setting sulfur hydride superconductor

The material's conventional nature puts the spotlight back on superconductivity mediated by phonons.

Hydrogen sulfide (H_2S) is the noxious byproduct of anaerobic digestion that gives swamps their characteristic smell. In 2014 Mikhail Eremets of the Max Planck Institute for Chemistry and his colleagues set out to test a prediction of pressure-induced metallization and superconductivity in the malodorous compound.¹

At a pressure of 100 GPa, the Max Planck group observed the hoped-for disappearance of resistance on cooling their sample below 60 K. But when they further raised the pressure to 150 GPa, the superconducting transition temperature T_c , instead of dropping as theory predicted, shot up to 190 K. Not only had the researchers shattered the previous record for T_c , held by a cuprate superconductor, by 30 K, but they had done so with a conventional phonon-mediated superconductor.

News of the group's discovery set off a flurry of theoretical work to explain the finding.² In the meantime, Eremets and his colleagues extended their work³ to

include magnetic measurements that demonstrated a Meissner effect—the expulsion of external magnetic fields that is taken as a definitive sign of superconductivity. They also raised T_c to 203 K, 8 K greater than the sublimation point of dry ice.

Despite the discovery, the identity of the superconductor was in doubt. The surprising rise in T_c at pressures greater than 100 GPa made Eremets and his colleagues suspect their superconductor was not H_2S but a different sulfur hydride left from the pressure-induced dissociation of H_2S .

As it turned out, Tian Cui and his team at Jilin University in China had independently predicted—before the Max Planck group's announcement—that H_3S should harbor superconductivity around 200 K at 200 GPa.⁴ Other theorists quickly came to the same conclusion.

To experimentally identify the superconductor, Eremets's group teamed up with Katsuya Shimizu and colleagues at Osaka University to perform simultaneous

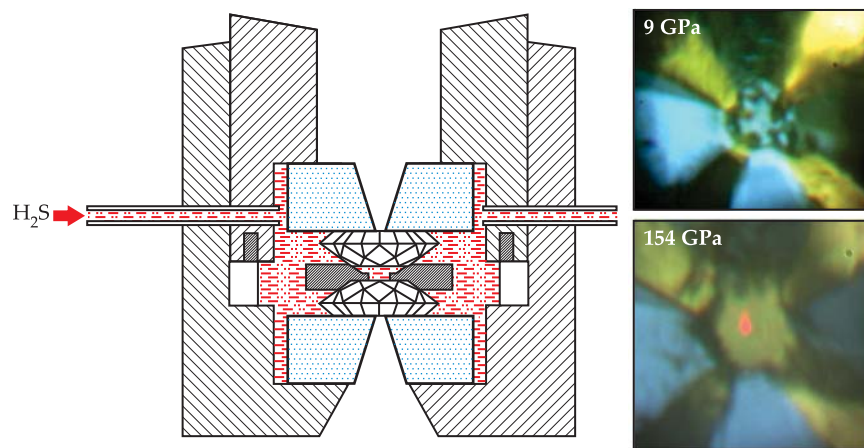


FIGURE 1. SQUEEZING SULFUR HYDRIDE in a diamond anvil cell. The cell is first cooled to 200 K, then hydrogen sulfide (H_2S) gas is sent into the cell through a capillary (left). Inside the cell, H_2S liquefies; only then does pressurization take place. The right panels show a view of the sample through the top anvil at 220 K at different pressures. The sample, in the center of each image, is about 25 μm wide. It is transparent at 9 GPa, so that the blue gasket below it is visible, but the sample becomes metallic by 154 GPa and reflects the red beam from a helium–neon laser. (Adapted from ref. 3.)

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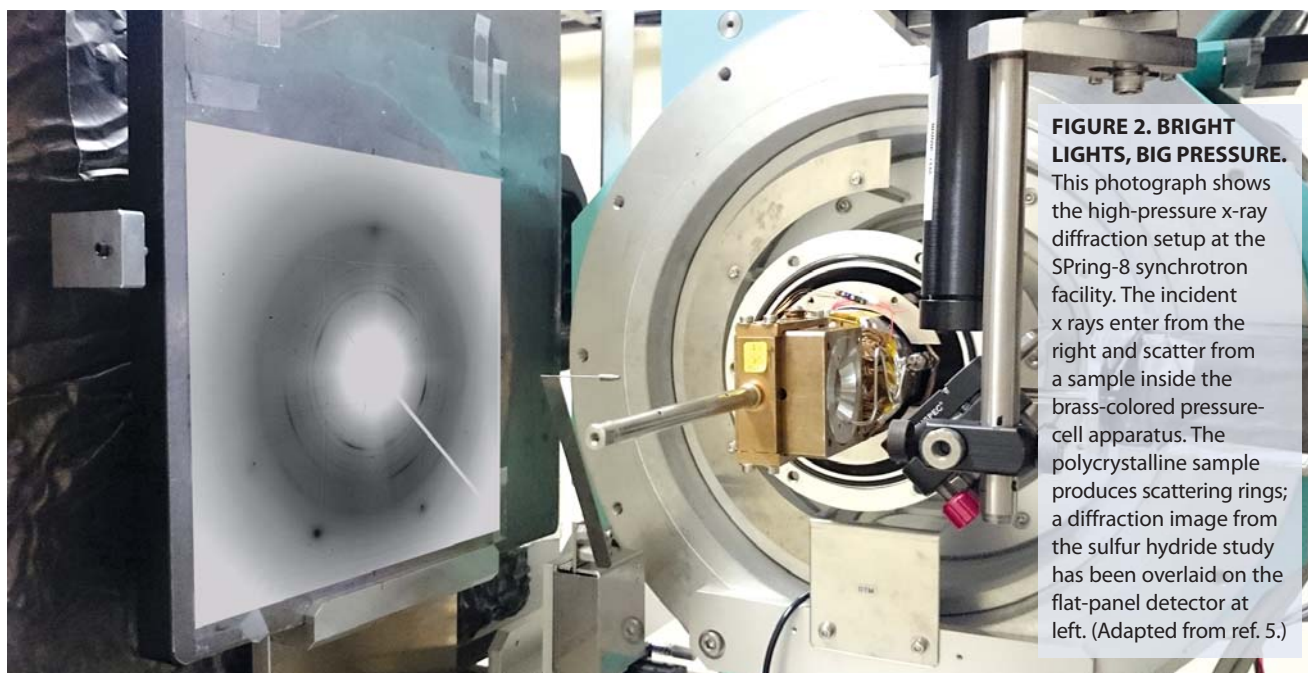


FIGURE 2. BRIGHT LIGHTS, BIG PRESSURE.

This photograph shows the high-pressure x-ray diffraction setup at the SPring-8 synchrotron facility. The incident x rays enter from the right and scatter from a sample inside the brass-colored pressure-cell apparatus. The polycrystalline sample produces scattering rings; a diffraction image from the sulfur hydride study has been overlaid on the flat-panel detector at left. (Adapted from ref. 5.)

resistance and x-ray diffraction measurements.⁵ Their results confirm the theorists' prediction that the superconductor is indeed H_3S .

Unconventionally conventional

Intriguingly, superconductivity in H_3S is of the conventional variety. That is, it's described by the venerable Bardeen-Cooper-Schrieffer (BCS) theory, which explains how pairs of electrons are nudged together by lattice vibrations (phonons) to become Cooper pairs. When the Max Planck researchers replaced hydrogen with deuterium, they observed a telltale sign of BCS superconductivity, an isotope effect: The greater mass of the deuterium atom lowers the phonon frequency and, with it, T_c .

The BCS theory has a deceptively simple recipe for achieving high T_c : Create a high density of conduction-electron

states and couple the conduction electrons to high-frequency phonons. But before H_3S , the highest-temperature BCS superconductor was magnesium diboride, with a T_c of 40 K. (See the article by Paul Canfield and George Crabtree, *PHYSICS TODAY*, March 2003, page 34.)

High-frequency phonons come from light elements, and hydrogen is the lightest of all elements. The search for metallic hydrogen has been ongoing since 1935, when Eugene Wigner and Hillard Huntington predicted that hydrogen would become metallic under pressure. Neil Ashcroft added extra motivation in 1968 when he used BCS theory to argue that metallic hydrogen would be a high-temperature superconductor. Signs of a metallic fluid phase of hydrogen have been spotted (see *PHYSICS TODAY*, September 2015, page 12) but metallicity in solid hydrogen remains an elusive goal.

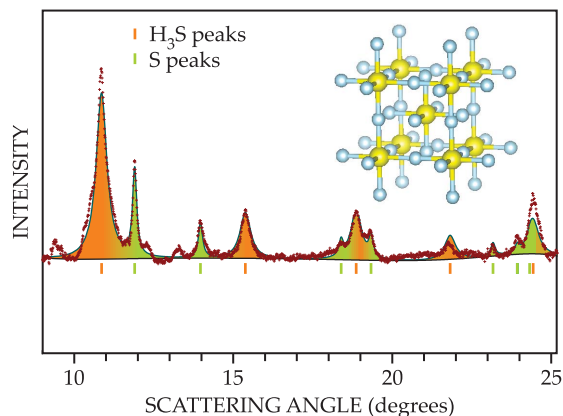


FIGURE 3. INTEGRATION OF THE RINGS from figure 2 produces this diffraction pattern. The orange peaks are from sulfur hydride (H_3S), and green peaks from elemental sulfur. The inset shows the cubic crystal structure of H_3S (yellow S and blue H), determined from analyzing the positions of the compound's diffraction peaks. (Adapted from ref. 5.)

In 2004 Ashcroft chimed in again with the idea of looking at crystals of hydrogen-rich molecules. He reasoned that the hydrogen atoms in compounds such as silicon hydride are chemically precompressed, so the pressure required to metallize the hydrogen would be substantially less. Following Ashcroft's prescription, researchers have studied various hydrides in search of metallized hydrogen and possibly high-temperature superconductivity. For the moment, H_3S with $T_c = 203$ K at 150 GPa is the hottest find from that search.

The big squeeze

High-pressure experiments are notoriously difficult. Eremets and company discovered that H_2S , a gas at room temperature, couldn't simply be loaded into a diamond anvil cell and pressurized. The sample would decompose before reaching the required high pressures, and all the researchers would detect was elemental sulfur.

To make a stable sample, the diamond anvil cell had to first be cooled to 200 K. Then, as shown in figure 1, H_2S gas was passed through a capillary into the cell, where it liquefied. The top anvil was then pushed down to clamp some of the liquid inside a gasket. The cell was heated to 220 K to evaporate away the H_2S outside the gasket. Only then could the researchers increase the pressure.

For the x-ray diffraction experiments, the Max Planck team prepared four sam-

ples in Germany—two for H_2S and two for D_2S . Eremets hand-delivered the loaded diamond anvil cells to Japan.

Figure 2 shows the experimental setup at Japan's SPring-8 synchrotron facility, where the x-ray diffraction measurements were performed. Because the sample is polycrystalline, the measured pattern comprises rings that correspond to particular scattering angles.

Integrating the intensities around the rings and plotting the result as a function of the scattering angle gives the graph shown in figure 3. The diffraction pattern contains the signatures of H_3S and elemental sulfur, the other byproduct of the dissociation of H_2S . By analyzing the scattering angles at which the peaks occur, the researchers could identify the crystal structure of H_3S .

At high pressure, superconducting H_3S has the cubic structure shown in the inset of figure 3. Because hydrogen atoms scatter x rays weakly, their positions in

the crystal lattice couldn't be precisely determined. That information will have to await other measurements, such as NMR, that can probe the hydrogen positions at high pressure.

Theory and experiment

Mari Einaga, the lead author of the new x-ray paper, sees renewed interest in BCS theory, which, she explains, "was largely abandoned because of the discovery of cuprates and other unconventional superconductors." Theorists have developed sophisticated computational tools based on density functional theory to search for stable compounds and predict their crystal structures. And unlike unconventional superconductivity, whose origin remains uncertain, BCS superconductivity is understood well enough that its likelihood and T_c can be predicted.

To appreciate the accuracy with which theorists can calculate the electronic structure of hypothetical materials, one

need only revisit the early predictions for H_3S . "Amazingly, all the calculations predicted T_c around 200 K," says Eremets. "Basically, all our results were quickly and consistently explained."

Einaga notes, "Our work was initiated by theory, and further understanding of the superconductivity is the result of close interplay between theory and experiment." That successful partnership raises hopes that theory can guide future searches for new high-temperature superconductors.

Sung Chang

References

1. Y. Li et al., *J. Chem. Phys.* **140**, 174712 (2014).
2. See, for example, N. Bernstein et al., *Phys. Rev. B* **91**, 060511 (2015); I. Errea et al., *Phys. Rev. Lett.* **114**, 157004 (2015); D. Duan et al., *Phys. Rev. B* **91**, 180502 (2015).
3. A. P. Drozdov et al., *Nature* **525**, 73 (2015).
4. D. Duan et al., *Sci. Rep.* **4**, 6968 (2014).
5. M. Einaga et al., *Nat. Phys.* (in press), doi:10.1038/nphys3760.

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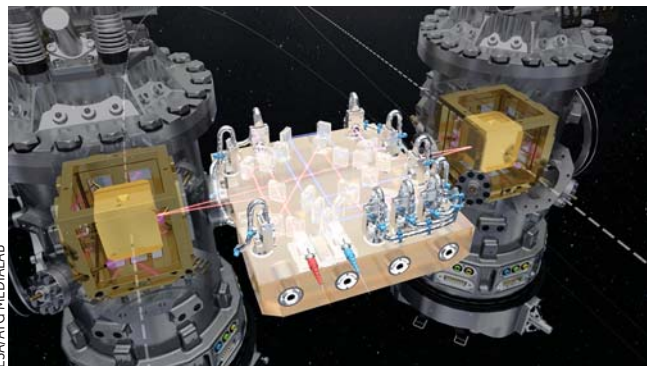
These items, with supplementary material, first appeared at www.physicstoday.org.

THE FREEST OF FREE FALLS

The European Space Agency plans to launch a gravitational-wave observatory in 2034, likely based on the Laser Interferometer Space Antenna (LISA) model. Once it is operational, mission scientists will look for tiny, oscillating changes in the million-kilometer lengths separating a triangular arrangement of test masses—the signal that a gravitational wave has passed by. The

LISA concept requires that the test masses at each vertex be maintained in nearly perfect free fall. Any other accelerations—due to stray charges or radiation pressure, for example—could

spacecraft could be shielded to the exacting demands of LISA. Today the mission team announced its first result: To within 25%, it has already achieved LISA's shielding goal. *LISA Pathfinder* has two cube-shaped test masses that are separated by roughly 40 cm; each is made of a gold-platinum alloy with a mass of about 2 kg. (The figure shows the cubes and, between them, a position control system.) Lasers measure the separation between the two masses; electrostatic nudges keep it as constant as possible. Meanwhile, thrusters apply micronewton forces to the spacecraft, maneuvering it to keep the test masses centered in their housings. From several days' measurements of the mass separation and from the size of the electrostatic nudges, the *LISA Pathfinder* team deduced the amount by which test-mass motion deviated from free fall. The single biggest cause of deviation is likely damping by residual gas in the cubes' housings. (M. Armano et al., *LISA Pathfinder* collaboration, *Phys. Rev. Lett.* **116**, 231101, 2016.) —SKB



mimic the effects of a gravitational wave; the test masses must therefore be exquisitely shielded from all forces other than gravity. Enter *LISA Pathfinder*, launched on 3 December 2015 and designed to establish that a pair of test masses floating inside the

TRACKING GREENLAND'S MELTING ICE WITH SEISMIC WAVES

Greenland's ice cap contributes nearly 20% to Earth's mean rate of sea-level rise of 3 mm/y. To monitor the thinning ice sheet, scientists typically rely on periodic surveys taken by airborne and satellite radar, laser altimetry, and NASA's Gravity Recovery and Climate Experiment (GRACE) mission, whose twin spacecraft orbit Earth and measure perturbations in its gravity field. MIT's Germán Prieto, his postdoc Aurélien Mordret, and their colleagues have now adapted a seismic-wave method to do the same job. Originally developed to monitor active volcanoes and fault zones, the method exploits ambient noise signals, such as the crashing of ocean waves on the shoreline, recorded at an array of seismometers inland. (See the article by Roel Snieder and Kees Wapenaar, *PHYSICS TODAY*, September 2010, page 44.) Seismic waves propagate at speeds that depend on the porosity of the crust and upper mantle: The more porous the rock, the slower the waves