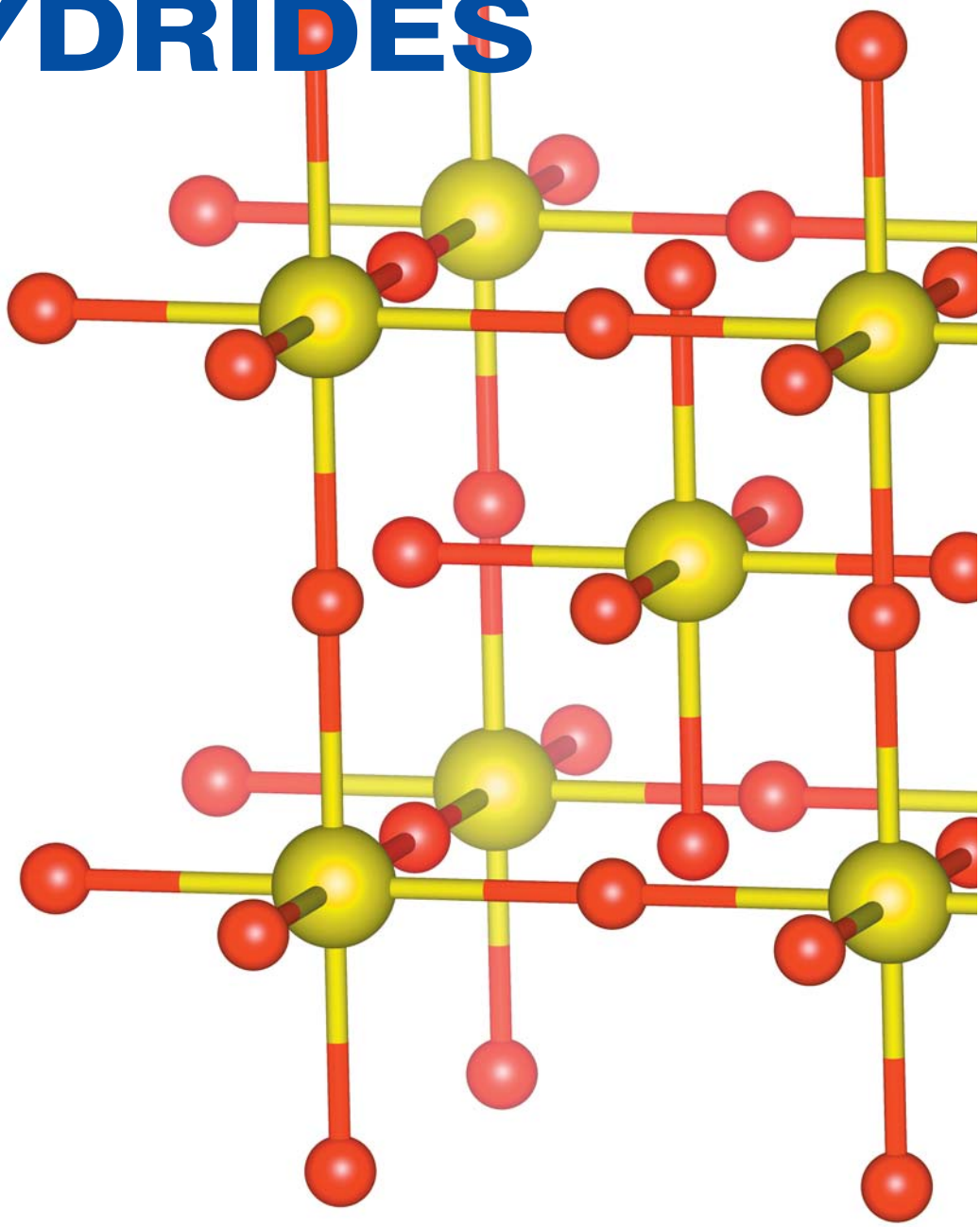
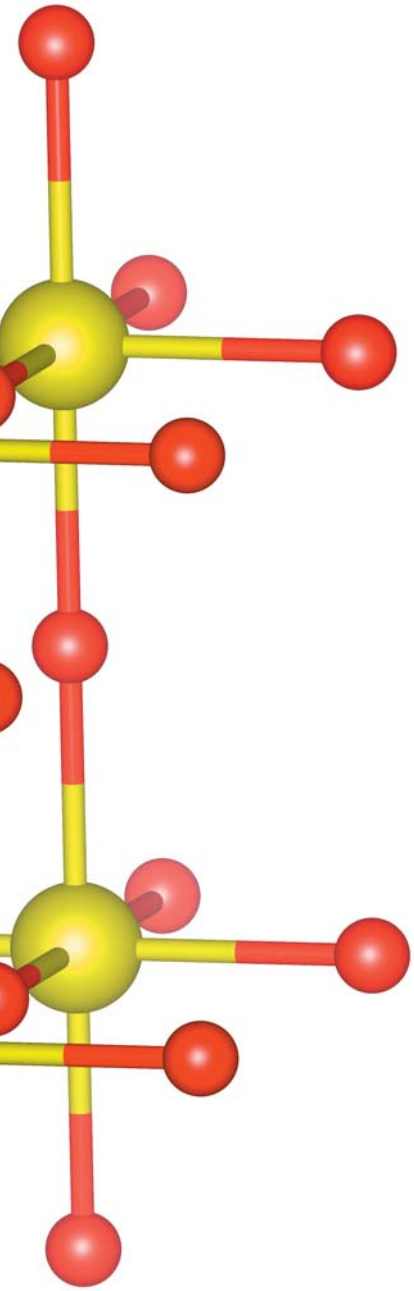
THE QUEST FOR ROOM-TEMPERATURE SUPERCONDUCTIVITY IN HYDRIDES

Warren Pickett and Mikhail Eremets

Whereas previous discoveries of superconductors were largely serendipitous, the latest advances have emerged from the close coupling of theoretical predictions and high-pressure experiments.



Warren Pickett is a distinguished professor in the department of physics at the University of California, Davis.
Mikhail Eremets is a research physicist at the Max Planck Institute for Chemistry in Mainz, Germany.



When a material becomes superconducting below some critical temperature T_c, its electrical resistivity drops abruptly to zero. That complete loss of resistance may seem impossible because current-carrying electrons scatter from atomic vibrations, impurities, and crystal imperfections of the lattice. Electrons also ordinarily repel each other because they have the same negative charge. But two electrons in a metallic lattice can experience an attractive interaction through polarization of the positive ionic lattice, as explained in box 1. Because of that interaction, pairs of electrons with opposite momenta and spin angular momenta can bind together. Those Cooper pairs coalesce into a coherent wavefunction known as the superconducting condensate.

First observed soon after helium was liquefied in 1908 (see the article by Dirk van Delft and Peter Kes, PHYSICS TODAY, September 2010, page 38) and today open to simple tabletop demonstrations, the superconducting condensate holds a unique standing in physics. Rather than being a normal metal in which even small electric voltages drive conducting charge carriers, a superconductor exhibits an energy gap—the energy 2Δ required to split a pair out of the condensate—that is explained in box 2. In BCS theory, developed by John Bardeen, Leon Cooper, and J. Robert Schrieffer in 1957, the gap directly relates to the critical temperature T_c at which electrons no longer scatter from vibrations or impurities: $2\Delta = 3.52\ k_B T_c$, where k_B is Boltzmann's constant.

An energy bandgap, which provides zero conductivity, is the *sine qua non* that distinguishes insulators such as silicon, diamond, and sodium chloride from normal metals. The superconducting gap is far different. It provides, via the underlying condensate, an infinite conductivity. That characteristic reflects the counterintuitive property that superconductors conduct electricity in the absence of any applied electric voltage.

The tabletop demonstrations of a supercurrent include zero resistance and the exclusion of an applied or existing magnetic field. The conduction of electric current without resistance—and thus without heat dissipation or power loss—forms the basis of most applications developed for superconductors. Magnetically levitated trains, for instance, now operate in a few parts of the world, and superconducting magnets are common in hospitals worldwide for MRI machines.

A larger goal is long-range power transmission without energy loss. If industrially applicable materials could be designed, discovered, or engineered, the savings in electrical power would be tremendous. (See PHYSICS TODAY, March 1996, page 48, and January 2008, page 30.) The full story is more complicated, but superconducting power transmission, if it were produced at room temperature, would constitute a transformative technology. The achievement would not be free of complications—even the best material candidates would suffer some dissipation under large current loads. The challenge would be to design an optimal system.

For physicists, chemists, and materials scientists, the challenge is to achieve the superconducting state at increasingly higher temperatures. The primary task in reaching that goal is to understand the theoretical and practical limitations of the superconducting critical temperature. That kind of materials challenge, broadened to applications in clean energy,

national security, and human welfare, was behind the 2011 introduction of the Obama administration's Materials Genome Initiative (www.mgi.gov). The motivating idea was to integrate the rapidly expanding capability of computational simulations of materials with experimental synthesis to speed products' time to market and to stimulate the design and discovery of new materials—for instance, ones that will superconduct at higher temperatures. Therein lies a parable.

In June 1973 PHYSICS TODAY published a letter to the editor (page 11) that included the maximum known values of T_c versus time. The data from 1911 to 1973, presented in graphical form (figure 1), fit well into a straight line of slope three degrees per decade. Its author, Bruce Friday, joked that room-temperature superconductivity was within sight, as long as one's sight extended to the year 2840.

The letter's implied conclusion could hardly have been more discouraging. In 1973 the maximum T_c was a mere 23 K. Fortunately, the outlook improved. Little more than a decade later came the announcement and rapid confirmation that layered copper oxide compounds provided superconductivity near 100 K. With applied pressure, that critical value rose to 160 K. The achievement vitalized the field. The 1987 March Meeting of the American Physical Society featured a marathon session—now known as "the Woodstock of physics"—of about 50 presentations on the superconducting cuprates.

Although some impressive and serendipitous developments have emerged, the 160 K maximum stood for 25 years. A recent article celebrating the history of *Reviews of Modern Physics* observed that "progress in discovering new superconductors has always been linked to the clever performance of making the correct material" (Art Hebard and Greg Stewart, PHYSICS TODAY, February 2019, page 44).

In this article we illustrate how that paradigm is shifting. Computational theorists and experimentalists are currently partnering to design and discover new superconducting hydrides with the highest critical temperatures ever found. Three years ago, one of us (Eremets) found that pressurized sulfur hydride superconducts at 203 K (see PHYSICS TODAY, July 2016, page 21). And more recently, reports have emerged that lanthanum hydride superconducts at temperatures as high as 280 K (see "Pressurized superconductors approach room-temperature realm," PHYSICS TODAY online, 23 August 2018.)

Progress in context

BCS theory provides an understanding of superconductivity as arising from the pairing of electrons via quantized lattice vibrations, or phonons. A primary result was an expression for the critical temperature in the form $T_c \sim \Omega \exp[-1/(\lambda - \mu^*)]$, where Ω is the characteristic phonon vibration frequency, λ the electron–phonon coupling constant, and μ^* the Coulomb pseudopotential—a measure of the Coulomb repulsion between electrons.

The BCS expression is valid for when the coupling λ is weak. In the late 1960s William McMillan of Bell Labs extended the BCS analysis to moderately strong coupling. His equation for T_c was extrapolated beyond its regime of validity to fortify claims that 30 K would be the upper limit for electron–phonon coupling. But rigorous analysis of strong-coupling theory in 1975 by Philip Allen of Stony Brook University and Robert Dynes of Bell Labs demonstrated that T_c continues to increase (rather strongly) with increasing coupling strength, everything else being equal.

Although substantial experimental searches persisted, no superconductors with T_c higher than 23 K were found over a 15-year period. In 1986 Georg Bednorz and Alex Müller, of IBM Zürich, discovered an entirely new class of superconductors, the magnetic copper oxides. The initial values of T_c were around 30 K, but shortly thereafter they were extended by other researchers to 160 K under pressure. What's more, the magnetism found in those cuprates rendered conventional BCS theory inapplicable.

Aoyama Gakuin University's Jun Akimitsu's 2001 discovery of BCS superconductivity at 40 K in magnesium diboride (MgB_2)

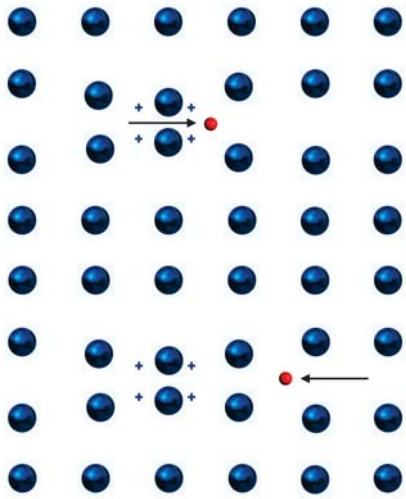
Box 1. Superconducting pairing of electrons

BCS theory—named after its authors John Bardeen, Leon Cooper, and J. Robert Schrieffer—established the two features underlying the superconducting state: the pairing of electrons and subsequent coalescence of those pairs into a coherent superconducting wavefunction. Each pair has an energy within a range of 2Δ of the Fermi energy (the highest energy of occupied electronic states), has equal and oppositely directed momenta **k**, and has oppositely directed spin angular momenta σ, conventionally called up and down.

The pairing is a consequence of the effective interaction strength λ between electrons. Although the direct Coulomb interaction is repulsive, an effective interaction due to lattice vibrations or magnetic fluctuations may become attractive. The electron–phonon coupling term λ is then defined as positive, and larger λ leads to a higher critical temperature T_c, at which a material starts superconducting. (See the article by J. Robert Schrieffer, PHYSICS TODAY, July 1973, page 23.)

Fast-moving electrons become coupled to heavier, slow-moving atomic cores. As shown here, a negatively charged electron (red) with quantum numbers **k** and σ careens through the lattice, distorting positively charged ions in its wake. Traveling in the opposite direction, the pairing electron with $-\mathbf{k}$ and $-\sigma$ feels the attraction of the deformed lattice and becomes bound—in energy if not in real space—to the initial electron. Although the interaction occurs over a long time, the electrons are spatially close for only a short time, and the repulsive Coulomb interactive assumes a minor role.

COURTESY OF AMBER CRENNA-ARMSTRONG

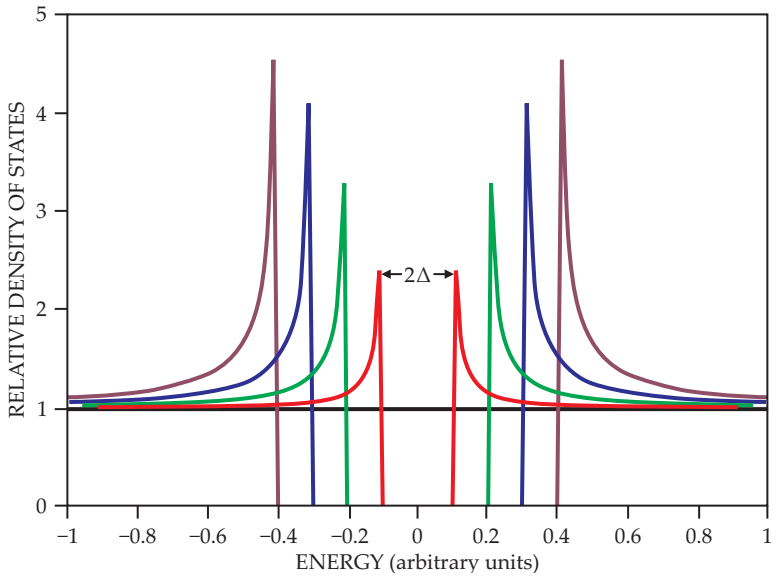


Box 2. Metals versus superconductors

The defining property of a metal is that it conducts electricity in response to an imposed electric field. The microscopic quantum mechanical description invokes the electron's dispersion relation, energy $E_{\mathbf{k}}$ versus wavevector $\mathbf{k}$. Although $E_{\mathbf{k}}$ is quantized at each $\mathbf{k}$, crystalline solids have energy bands in which momenta are continuous and the bands can be measured. Those bands are crucial for extracting charge and heat-transport coefficients, but much electronic behavior can be described by a density of states function $N(E)$, whose value at energy E is obtained from all bands where $E_{\mathbf{k}} = E$. States are occupied by accommodating all the electrons in the crystal up to an energy maximum, the Fermi energy E_F. Electrical and thermodynamic properties at and below room temperature are determined by states near E_F, with a relative concentration of states being the density of electron states at zero energy, $N(0)$.

Superconductors are metals that are cooled below their superconducting transition temperature T_c. (Note that many metals never superconduct, no matter how cold they become.) At and below T_c, electrons bind with each other in pairs and condense into a single coherent superconducting wavefunction Φ. The state described by Φ possesses a finite energy gap 2Δ. The gap, centered at E_F, is an energy range in which no states exist; the states that fall in that energy range above T_c have been repelled into regions just above or just below the gap. The number of such states that are affected is 2Δ $N(0)$. The larger the density of states $N(0)$, the larger the number of pairs, the larger the value of 2Δ, and the higher T_c becomes.

The figure illustrates the density of states of a superconductor. A metal has a constant value, normalized to unity here, drawn as the horizontal black line. The red, green, blue, and brown curves show the superconducting $N(E)$ for progressively larger energy gaps 2Δ of 0.2, 0.4, 0.6, and 0.8, respectively, as temperature is lowered.



brought to light yet another new class of superconductors—those in which strong covalent bonds are driven metallic by chemistry.[1] (See PHYSICS TODAY, April 2001, page 17, and the article by Paul Canfield and George Crabtree, PHYSICS TODAY, March 2003, page 34.) That event also energized the field but did little to alter entrenched opinions about the limit of T_c.

In 2014 Eremets and colleagues at the Max Planck Institute for Chemistry reported[2] yet another major achievement: the discovery of superconductivity in sulfur hydride at a T_c of approximately 200 K at 150 GPa. The H_3S discovery was also the first time that a previously unknown material was predicted to be superconducting and, at roughly the same time, experimentally confirmed to be so.

The history goes back decades. In the late 1960s Neil Ashcroft of Cornell University and Vitaly Ginzburg of the P. N. Lebedev Institute in Moscow proposed, at about the same time, that the critical temperature of metallic hydrogen should be high because its lattice vibrations are high,[3] even while the material retains a high λ. Metallic hydrogen is tremendously difficult to study, though. For one thing, it requires pressures of the order of 500 GPa, or 5 million atmospheres, to make measurements in the superconducting state.

In 2004 Ashcroft proposed focusing on hydrogen-rich materials,[4] namely methane and its silicon-based cousin, silane (SiH_4), under pressure. The materials' solid forms can be considered chemically "precompressed" hydrogen—the important atomic nature of hydrogen is achieved at much lower pressure than it can be in elemental form. The metallic yet covalent hydrides have the potential to superconduct at high T_c for the same reasons that hydrogen does at extreme pressures.

Although precompressed, the hydrides still require 100–200 GPa to be driven into the metallic state. Such pressures are generated by confining a sample (typically tens of square microns in size) within a gasket compressed by two opposing diamond anvils, as illustrated in figure 2. Such tiny samples can be probed with various experimental techniques, including resistivity measurements, optical absorption, reflection spectroscopy from the IR to the UV, Raman scattering, and x-ray diffraction. Magnetic-susceptibility measurements are also possible on tiny samples at high pressure.

Ashcroft's focus on hydrides opened a broad and abundant class of materials to study. However, initial experimental searches were largely unsuccessful. Some materials, such as methane, ammonia, and water, resist transforming into metals even at the highest available pressure. Fortunately, theory was coming to the rescue: Computational developments based on density functional theory were making realistic first-principles predictions of stable new materials and calculations of their critical temperatures.

In the late 1980s, researchers began making *ab initio* predictions of new high-pressure phases of Si. Those predictions became more relevant following Ashcroft's 2004 proposal.[4] (See references 5 and 6 for reviews of the literature.) Once the most stable structure at a given pressure was found computationally, the electron and phonon spectra, the material's coupling constant λ, and T_c could be calculated. Many such calculations

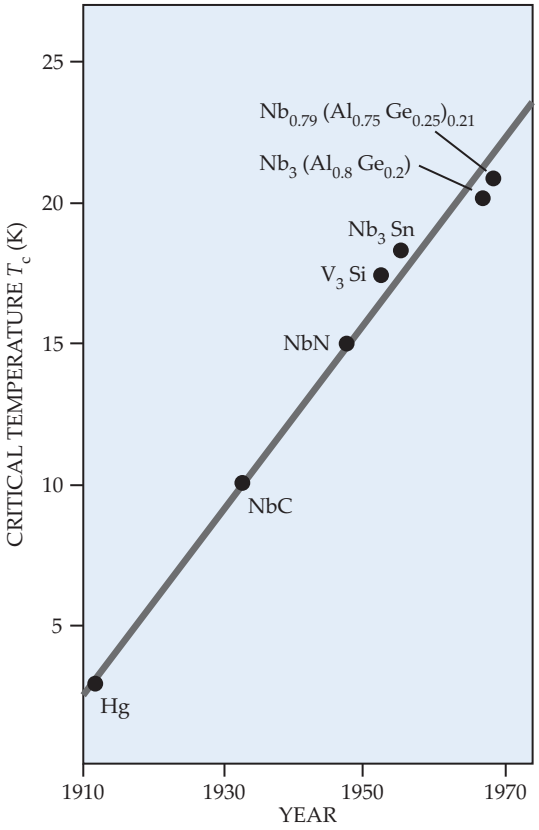


FIGURE 1. BRUCE FRIDAY'S 1973 GRAPH of maximum transition temperature T_c of all known superconductors as a function of time. A linear extrapolation of the plot suggested that not until the year 2840 would experimentalists be likely to discover a room-temperature superconductor. (Adapted from PHYSICS TODAY, June 1973, page 11.)

predicted that several hydrogen-rich compounds superconduct between 100 K and 300 K. But at the time, several of the results struck researchers as implausibly high.

From H_2S to H_3S

Early experimental attempts to verify the calculations were discouraging. Although predicted to have a critical temperature of 166 K at 200 GPa, SiH_4 was found to superconduct at a modest 17 K. Five years ago Yanming Ma of China's Jilin University and his colleagues published a computational study of hydrogen sulfide (H_2S) under high pressure.[7] Their predicted T_c of 80 K at 160 GPa was twice as high as the best BCS superconductor at the time, MgB_2. Previously, H_2S had not seemed particularly promising because of its small atomic fraction of hydrogen.

Experimentally, the material is attractive because the sample can be prepared from commercially available gas by direct condensation in the diamond anvil cell. The outlook improved as signals of T_c at 50–60 K were detected. Those values were at least comparable to predictions and would be record breaking for conventional superconductors.

The sulfur hydride (H_3S) discovery came on the heels of a surprising realization: During the usual pressure and temperature cycling used to prepare the sample for testing, H_2S transforms into H_3S at high pressure, and it stabilizes at 200 K after the material is first heated to room temperature. The H_2S sample used by the researchers decomposed into sulfur particulates and a phase richer in hydrogen. The hydrogen's higher content in the new phase was thought to be responsible for the increase[2] in T_c. Subsequent testing—in particular, x-ray measurements consistent with cubic H_3S as the superconducting phase—bore out that suspicion.[8]

The superconductivity in H_3S was supported by several measurements: zero resistance; a large susceptibility swing at T_c, which signals a superfluid response; a reduction in T_c due to an applied magnetic field that acts to align spin directions of pairing electrons; and a large, downward "isotope shift," shown in figure 3. When deuterium is substituted for hydrogen, its mass (twice that of hydrogen) reduces the phonon frequency and T_c with it. (For an early description of the effect, see the article by Emanuel Maxwell, PHYSICS TODAY, December 1952, page 14.)

One crucial measurement, the Meissner effect—the exclusion of a magnetic field by the onset of the superconducting state—required a new technique in diamond anvil cells. The effect had been measured previously in materials only at more modest pressures, one-tenth the pressure required for H_3S. The expulsion of a magnetic field from a superconductor can be measured with a sensitive magnetometer such as a superconducting quantum interference device. A new pressure cell that could accommodate a SQUID less than 9 mm in size was built within two months and applied successfully. Other experiments determined the superconducting gap from IR spectroscopy.[9] (For a detailed history, see M. I. Eremets, A. P. Drozdov, *Physics Uspekhi* volume 59, page 1154, 2016.)

At roughly the same time the experimental discovery was published,[2] Ma's paper was followed by the stunning prediction[10] from Tian Cui's group, also at Jilin University, of superconductivity in H_3S. Cui and colleagues calculated its T_c to be around 200 K at 200 GPa pressure. The stable structure, pictured on page 52, is cubic, one of the simplest possible structures for a binary compound with a 3:1 composition. Several theoretical groups quickly confirmed the new predictions of the material's structure and T_c.

Superconductivity in H_3S can be understood as atomic hydrogen driven to a superconducting state by the hybridization of hydrogen's 1*s* orbitals with the 3*p* orbitals of sulfur.[11] The effect of sulfur is to preclude the formation of molecular H_2 in favor of atomic hydrogen, for which electron–phonon coupling is maximized. Researchers subsequently established computationally that the dominance of vibrations of hydrogen has important consequences for H_3S. Among other things, the hydrogen's light mass leads to anharmonic vibrations and quantum zero-point motion effects in sulfur hydride.[12,13]

The success of the theory–experiment synergy bodes well for the future of superconductivity, as other hydrides will likely be studied in expectation of yet higher T_c or lower pressures. That synergy also points the way toward the next frontier: metallic atomic hydrogen.

The origin of high T_c

In BCS superconductors, as described above, T_c is set by a few materials parameters: the electron–phonon coupling strength λ, a representative phonon energy scale Ω, and a dimensionless Coulomb repulsion strength μ^*, which varies little from the range 0.10–0.15. For H_3S—and likely for most other potential

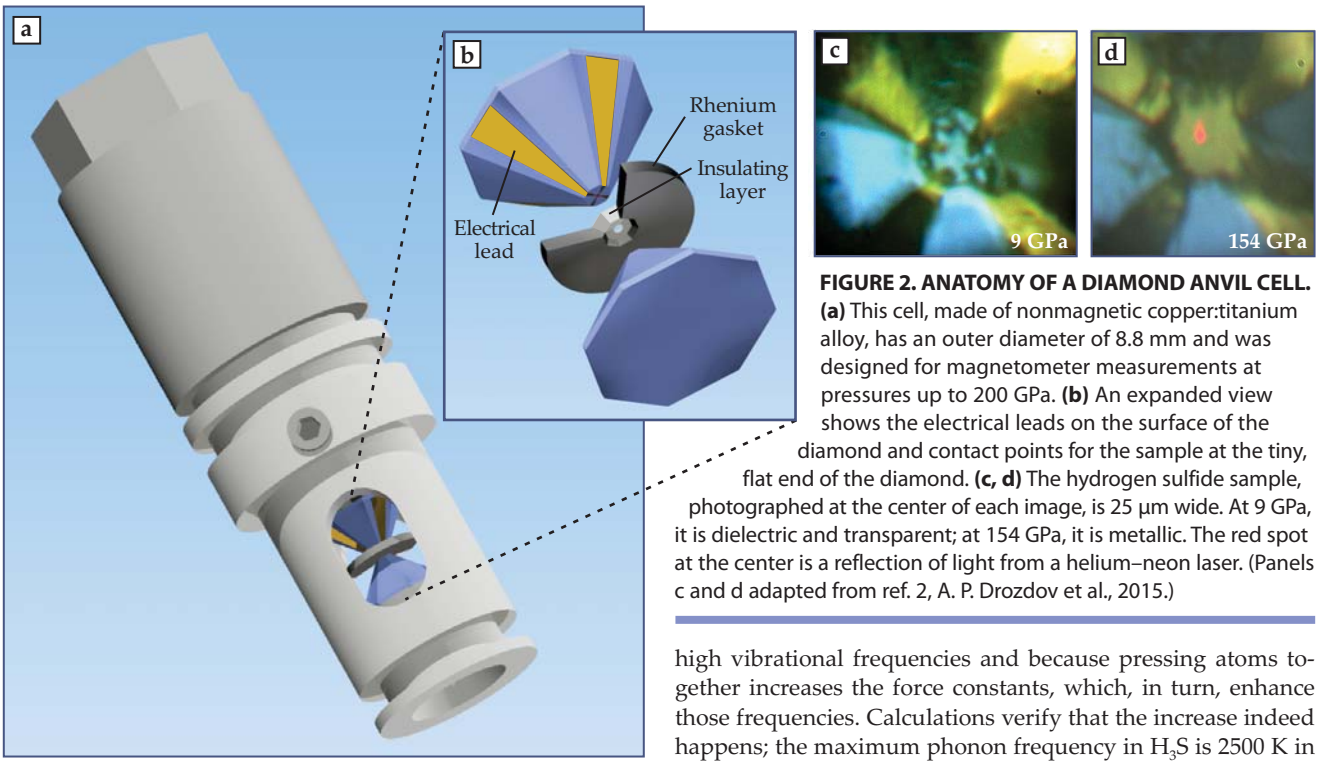


FIGURE 2. ANATOMY OF A DIAMOND ANVIL CELL. **(a)** This cell, made of nonmagnetic copper:titanium alloy, has an outer diameter of 8.8 mm and was designed for magnetometer measurements at pressures up to 200 GPa. **(b)** An expanded view shows the electrical leads on the surface of the diamond and contact points for the sample at the tiny, flat end of the diamond. **(c, d)** The hydrogen sulfide sample, photographed at the center of each image, is 25 μm wide. At 9 GPa, it is dielectric and transparent; at 154 GPa, it is metallic. The red spot at the center is a reflection of light from a helium–neon laser. (Panels c and d adapted from ref. 2, A. P. Drozdov et al., 2015.)

high-T_c hydrides—the contribution to T_c is dominated by hydrogen, as noted earlier. For an elemental superconductor (which H_3S approximates), one can express the coupling strength in terms of Ω and the atomic mass M as

$$\lambda = N(0)I^2/M\Omega^2.$$

The electronic density of states at zero energy, where electron pairs form, is $N(0)$, and I^2 is the square of the matrix element that describes the scattering of electrons by displacements of hydrogen.

The equation for T_c mentioned earlier involves the prefactor Ω and an expression involving λ and μ^*. Ashcroft reasoned that Ω would be large in hydrides under pressure.[3,4] That's because hydrogen is the lightest possible nucleus and thus promotes high vibrational frequencies and because pressing atoms together increases the force constants, which, in turn, enhance those frequencies. Calculations verify that the increase indeed happens; the maximum phonon frequency in H_3S is 2500 K in temperature units. That's an impressive prefactor for T_c, and it's produced by the high pressure and the small proton mass.

Modern electronic structure methods estimate λ at around 2.5 in H_3S. That's comparable to the electron–phonon coupling strength of strongly coupled conventional superconductors such as lead, for which $\lambda = 1.55$ and $T_c = 7$ K. Some lead alloys have λ that exceed 2. But the atoms in those alloys have large masses, roughly 180 times the proton mass. The alloys themselves are also soft, which means they have weak force constants and exceedingly low vibration frequencies, hence low T_c.

Why is H_3S so different from previously found conventional superconductors? The straightforward answer is that H_3S manages to retain a large λ in spite of a large increase in Ω, whose square occurs in the denominator of λ and thus tends to decrease it. The small mass of the proton certainly helps, but another key aspect is that the numerator in the expression for λ is relatively large (and increases under pressure). The density of states $N(0)$ is not exceptionally large; rather, the magnitude of the hydrogen scattering (I^2) is what's crucial. Obtaining an understanding, and thereby control, of I^2 is one of the most important remaining questions in researchers' quest to further increase T_c or to reduce the necessary pressure.

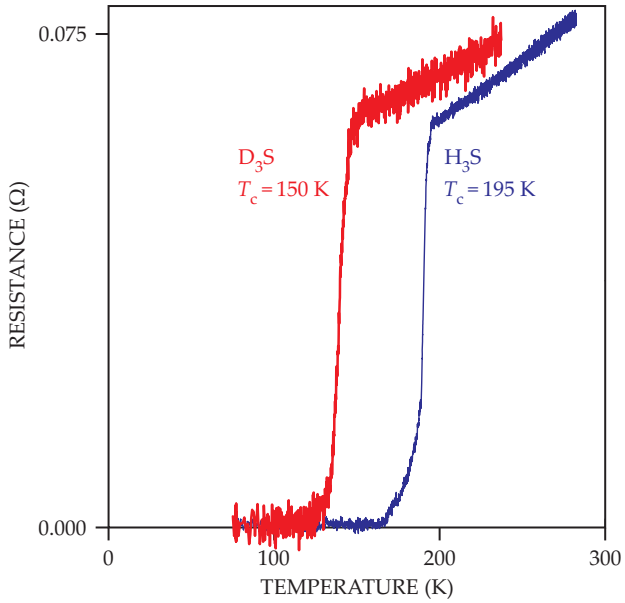


FIGURE 3. THE ISOTOPE EFFECT IN SULFUR HYDRIDE. A plot of resistance versus temperature in sulfur hydride (H_3S), the decomposed phase from a compressed sample of hydrogen sulfide (H_2S), shows the superconducting transition to zero resistance at 195 K. The onset of superconductivity shifts to 150 K in the deuterated D_3S compound. That downward isotope shift arises from the heavier isotope's lower vibrational frequencies and is a signature of electron pairing. (Adapted from ref. 2, A. P. Drozdov et al., 2015.)

The next challenge

Since the H_3S breakthrough, attention has returned to Ashcroft's original idea of superconductivity in metallic atomic hydrogen.[3] In that solid, T_c should be high for the same reasons

discussed for hydrides: The mean vibrational frequency Ω sets the scale for T_c, and yet hydrogen scattering remains strong. However, due to the large binding energy of the H_2 molecule, metallization has remained elusive. In 1935 Eugene Wigner and Hillard Bell Huntington estimated the pressure of metallization at 25 GPa. But it's actually at least 20 times as high, around 500 GPa according to calculations[14] and experiments.

Extreme pressure isn't the only requirement. Unless care is taken to mitigate the damage, the small hydrogen atom gets driven into the diamond anvils themselves. The defects introduced into the diamonds become cracks that eventually break the diamond lattice. What's more, the experimental signatures of superconductivity, listed above, become ever more challenging to measure as pressure rises.

In high-pressure experiments, H_2 becomes semimetallic, with a low density of electron and hole carriers. Further increasing the pressure increases the overlap of valence and conduction bands, and hydrogen becomes a good metal. With a sufficiently large density of states $N(0)$, it becomes a superconductor. Theoretical studies of superconductivity in molecular hydrogen predict that T_c might approach the temperature scale found in H_3S, whereas in atomic hydrogen, T_c should exist well above room temperature.

Researchers have been taking steps toward hydrogen metallization. But they are plagued by the material's dependence on the details of pressure–temperature cycling and other experimental complications. After some earlier reports, Eremets and coauthors obtained evidence of semiconducting dense hydrogen[15] at 360 GPa. In 2017 Ranga Dias and Isaac Silvera of Harvard University reported evidence of metallic atomic hydrogen at 495 GPa and 5 K from reflectivity data.[16] Several groups expressed reservations though. Hua Geng of the Institute of Fluid Physics in China offered an informal account of the issues at the time:[17] As pressures rise, determining those pressures accurately becomes increasingly difficult and measurements themselves become more challenging and less definitive.

More than just high T_c

The 2015 revolution in high-temperature superconductivity—the achievement of T_c above 200 K in H_3S at extreme pressure—has not received the acclaim that previous superconductivity advances have enjoyed. Nonetheless, it has reinvigorated the challenge to find ways to further increase T_c or, perhaps more importantly, to maintain the superconductivity at lower pressures.

There also remains the possibility that room-temperature superconductivity will be demonstrated in other metal hydrides rather than in metallic hydrogen itself. Calcium hydride, yttrium hydride, and lanthanum hydride have each been predicted to superconduct at or near room temperature around pressures of 300 GPa or lower,[6] and the precompression that the compounds offer may alleviate some of the experimental difficulties presented by squeezing hydrogen to such pressures.

In fact, those predictions are bearing fruit. Earlier this year two independent groups—one led by George Washington University's Russell Hemley, the other led by Eremets—found superconductivity[18] in LaH_{10} (shown in figure 4) in the reported temperature range of 250–280 K at pressures just below 200 GPa. That range includes the freezing point of water at temperatures common to human experience.

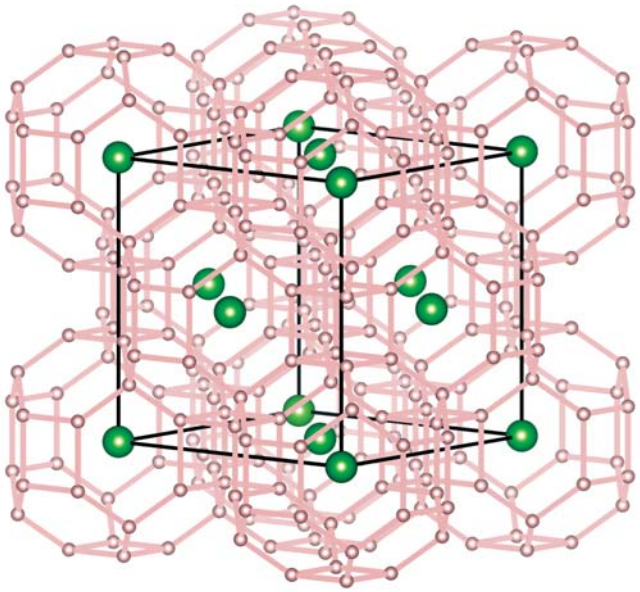


FIGURE 4. SUPERCONDUCTING LANTHANUM HYDRIDE (LaH_{10}) has a clathrate lattice structure. Each La atom (green) resides in the center of a cage of 32 H atoms (pink), each separated by 1.1 Å. (Adapted from Z. M. Geballe et al., *Angew. Chem.* **57**, 688, 2018.)

Computational prediction was combined with experiment to make the advance. Near-room-temperature superconductivity has been achieved eight centuries before the extrapolation of Bruce Friday's 1973 experimental plot. A room-temperature superconductor under such extreme pressure would be a fundamental extension of human understanding, even with no practical application. The hope is that it could offer a path to designing another material that behaves similarly at ambient pressure.

Warren Pickett appreciates support from NSF. Mikhail Eremets thanks the Max Planck community for its support and Ulrich Pöschl and Alex Drozdov.

REFERENCES

1. J. Nagamatsu et al., *Nature* **410**, 63 (2001); J. M. An, W. E. Pickett, *Phys. Rev. Lett.* **86**, 4366 (2001).
2. A. P. Drozdov et al., *Nature* **525**, 73 (2015); A. P. Drozdov, M. I. Eremets, I. A. Troyan, https://arxiv.org/abs/1412.0460.
3. N. W. Ashcroft, *Phys. Rev. Lett.* **21**, 1748 (1968); V. L. Ginzburg, *J. Stat. Phys.* **1**, 3 (1969).
4. N. W. Ashcroft, *Phys. Rev. Lett.* **92**, 187002 (2004).
5. M. L. Cohen, *Supercond. Sci. Technol.* **28**, 043001 (2015).
6. S. Uma, in *Handbook of Solid State Chemistry*, vol. 1, S. Kikkawa, R. Dronskowski, A. Stein, eds., Wiley (2017), chap. 15.
7. Y. Li et al., *J. Chem. Phys.* **140**, 174712 (2014).
8. M. Einaga et al., *Nat. Phys.* **12**, 835 (2016).
9. F. Capitani et al., *Nat. Phys.* **13**, 859 (2017).
10. D. Duan et al., *Sci. Rep.* **4**, 6968 (2014).
11. D. A. Papaconstantopoulos et al., *Phys. Rev. B* **91**, 184511 (2015).
12. W. Sano et al., *Phys. Rev. B* **93**, 094525 (2016).
13. Y. Quan, W. E. Pickett, *Phys. Rev. B* **93**, 104526 (2016).
14. C. J. Pickard, R. J. Needs, *Nat. Phys.* **3**, 473 (2007).
15. M. I. Eremets et al., https://arxiv.org/abs/1708.05217.
16. R. P. Dias, I. F. Silvera, *Science* **355**, 715 (2017).
17. H. Y. Geng, *Matter Radiat. Extremes* **2**, 275 (2017).
18. M. Somayazulu et al., *Phys. Rev. Lett.* **122**, 027001 (2019); A. P. Drozdov et al., https://arxiv.org/abs/1812.01561.

PT