Room Temperature Superconductivity Revolution: Foreshadowed by Victorians, Enabled by Millenials

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Room temperature superconductivity has been the most prominent, highly ambitious, but still imaginable, acme of materials physics for half a century. The struggle toward this revolution was foreshadowed by a Victorian novelist and championed, unsuccessfully, by dogged physicists in the 1960s to 1980s who had a workable theory but uncompliant materials. Discovery of superconductivity of H$_3$S at 200 K in the 160-200 GPa pressure range has renewed anticipation of yet higher values of the critical temperature $T_c$. With the several reports of metalization of hydrogen, and theoretical extensions enabled by modern algorithms and unprecedented computational hardware and spurred forward by the Materials Genome Initiative, it is possible that the room temperature precipice has thereby already been breached in a silent revolution. This concise note draws analogies of this development with an earlier revolution.

Chapter 1. Drawing the lines of battle

*It was the best of times; it was the worst of times*. The quest for a high temperature superconductivity (HTS) revolution roiled in the 1960s, instigated by Bernd Matthias who was also its most zealous experimental practitioner. The maximum critical temperature $T_{c,max}$ increased modestly from 17K to 23K from 1955 to 1973. In that year Bruce Friday, in a letter to Physics Today, recognized a trend in $T_{c,max}$ from the discovery of superconductivity to that time, and endeavored to soothe the hopeful platoons of materials researchers with analysis that indicated the linear-in-time increase, reproduced in Fig. 1, extrapolated to room temperature superconductivity around year 2840. No revolutions would be necessary, nor were any envisioned, by Friday or by the disillusioned proletariat. Friday’s observation served also as an example of quantum observation: that moment in 1973 signaled the collapse from a state of steady increase in $T_{c,max}$ to a state of no increase in conventional $T_c$ for three decades.

During the 1960s Matthias formalized his royal decree for higher $T_c$: (1) use transition metal (TM) based materials, (2) specific electron/atom ratios are best, and (3) cubic symmetry is preferred. These rules were formulated from elemental TMs, TM carbides and nitrides, and a few other TM-dominant compounds, viz. Nb$_3$Sn, whose simple A15 structure is pictured in Fig. 2. The gauntlet was laid down to theorists for successful predictions, with notoriety and careers as the prize, or more likely the cost. Theorists responded with the premier advancements of that age. Scalapino and coworkers formulated the implementation of Migdal-Eliashberg pairing theory of electron-phonon coupling in a material-specific manner. Phil Allen and Bob Dynes demonstrated that M-E theory was correct and robust and that the theoretical foundation imposed no limit on $T_c$. Material systems that seemed poised to confront the frontier of strong coupling and much higher $T_c$ led only to structural instabilities, or to competing order such as magnetic or charge- and spin-density waves, that lay beyond the quantitative theory of the day. *It was the age of wisdom, it was the age of foolishness.*

Chapter 2. Theoretical uprising

A rigorous formalism and computational basis for electronic structure emerged – density functional theory [DFT] – whereby the microscopic understanding and quantitative prediction of electronic structures ballooned in the 70s and 80s. By 1980 the Matthias rules had been
there is prodigious strength
reduce unstable materials. But
atoms; moreover, promising predictions tended to pro-
iment, matrix elements from potentials of rigidly moving
worlds. Phonon frequencies had to be taken from exper-
formal theory had not produced the best of all possible
It was
phonons, calculations of \( T_c \) electrons but including strongly coupled electrons and
superconductors.
Gross’s formulation of and implementation of DFT for
decided by the first decade of the 21st century, with Hardy
the problem except for the relatively small but curious
elements calculated from rigorous linear response, solving
the problem except for the relatively small but curious
Coulomb repulsion. The theoretical struggle was de-
cided by the first decade of the 21st century, with Hardy
Gross’s formulation of and implementation of DFT for
superconductors.\(^\text{[3]}\) For materials with weakly interacting
electrons but including strongly coupled electrons and
phonons, calculations of \( T_c \) became accurate to perhaps
5\% (sometimes claimed to be better than that). It was the epoch of belief, it was the epoch of credulity.

The HTS revolution of copper-based oxides in 1986,
延长至 160K 但在压力下，和铁基材料
rals at 55K in 2008 extending to 75K in single layers,
largely energized the proletariat. The superconducting
but unyielding A15 structure royalty had been magnifi-
cently overthrown; commoners could synthesize high \( T_c \)
samples. After seeming cons (30 years, and 8 years, re-
spectively) theory has produced no quantitative picture
of pairing in these materials.

Chapter 3. Unleashing the computational artillery

The Materials Genome Initiative (MGI) of 2011 for-
malized a new paradigm: introduce large scale, high
throughput computation into the synthesis & charac-
terization cycle to accelerate the design & discovery of
novel materials with improved functionality. To date,
however, applying the MGI approach to superconductors
has been limited to a few intrepid musketeers. Mathias
Klintenberg and Olle Eriksson\(^\text{[5]}\) searched for cuprate-like
electronic structures using modern battlefield technol-
y: high-throughput computing and data-filtering algo-
rithms. With a similar goal, the EFRC Center for Emer-
gent Superconductivity has focused on searches based on
structural motifs. Success is yet to be demonstrated, but
such challenges are meant to be confronted and overcome.
It was the season of light, yet it remained the season of
darkness.

Thus on the topic of superconducting materials, as of
2015 the MGI approach had yet to knit new materials to
higher superconducting \( T_c \): the spring of hope remained
hidden beyond the winter of despair. Still, it may now
not be too soon to reconsider how MGI and the available
computing capabilities can best be applied, and Mike
Norman has provided a broad overview of MGI in relation
to the search for better superconducting materials\(^\text{[9]}\) The more realistic promise for HTS+MGI remains, at this
writing, within the phonon-coupled paradigm, though early efforts\(^\text{[3]}\) had focused on the cuprate paradigm.
Not only was the \( \text{MgB}_2 \) insurgency of 2001, led by
Jun Akimitsu’s group\(^\text{[10]}\) a stunning overthrow of the
established order, so also was the rapid response with
which DFT musketeers devised the underlying mech-
anism - covalent bonds driven metallic by chemistry -
and reproduced the observed \( T_c=40\text{K} \), remarkable for
a phonon mechanism. Though phonon mediated and far from optimal\(^\text{[11]}\) \( \text{MgB}_2 \) violated each of the emperors' (Matthias’s) dictates. Transition metals are not essential
and not even optimal, being overthrown by a broader
dict: covalent bonding in a metal. Large \( N(0) \) is not
the target, high \( T_c \) is the target. Hexagonal and two
dimensional can be better than cubic. Very simple to
understand, very difficult to improve on, as a handful of
attempts has demonstrated. Were we all going directly
to heaven, or were we all going direct the other way?

Chapter 4. A synergistic revolution

The revolutionary announcement in 2015 by Mikhail
Eremets’ group\(^\text{[12]}\) of superconductivity at 200K under
very high pressure (160-200 GPa), in putrid but otherwise unremarkable hydrogen sulfide, provided a primitive application of the MGI paradigm, in that the extraordinary value of $T_c$ resulted from theory spurring experiment and further theory, rather than the standard paradigm of experiment spurs theory.

Figure 3: The simple, beautiful, and cubic bcc crystal structure of the current highest temperature superconductor H$_3$S. Yellow spheres: sulfur; gray spheres: hydrogen. Comparisons with the A15 structure are striking: each is one of the three simplest cubic $A_1B$ structures; each has dominant electron-phonon coupling arising from a single atomic species; each displays a sharp and narrow density of states peak lying precisely at the Fermi level.

The earlier computational study of H$_2$S by Yanming Ma’s group\textsuperscript{[12]} predicting $T_c$~80K under pressure stimulated the experimental effort of Eremets, which synergistically spurred Tian Cui’s group to extend the prediction\textsuperscript{[12]} to H$_3$S. Their revolutionary effort predicted the outrageous value of $T_c$~200 K at extremely high pressure in the 200 GPa (two million atmospheres) regime. Eremets’ confirmation of this prediction demonstrated the remarkable power of theory, first to identify bcc H$_3$S as the stable phase from a variety of competing structures (an MGI-inspired approach), and finally to predict unbelievably high $T_c$ correctly.

Remarkably, the experimental discovery publication\textsuperscript{[12]} references seven theory papers explaining, and agreeing on, the mechanism and the very high $T_c$. This experiment-theory inversion was enabled by the posting of a preprint that had been arXiv’d months earlier\textsuperscript{[12]} The strong theoretical agreement provides the broad view: DFT-based Migdal-Eliashberg theory is robust at least up into the room temperature regime. Deeper analysis is more arresting, with further questions emerging: what is the impact of the two van Hove singularities that conspire to put the Fermi level in the best possible position for large N(0) but in an extremely narrow peak? is anharmonicity good or bad for $T_c$? how much does the quantum nature of the proton affect the properties of H$_3$S, particularly the isotope shift of $T_c$? These unsettling loose ends are succumbing to modern theory and computation.

Chapter 5. Visualizing utopia

As happens after a revolution, new and compelling issues emerge: can room temperature superconductivity be achieved? can related (possibly metastable) materials be tormented into a very high $T_c$ phase at much reduced pressure? We have everything before us, or have we nothing before us.

The search for HTS in hydrogen-based materials owes much to the vision and persistence of Neil Ashcroft\textsuperscript{[16]} yet the success in hydrogen sulfide just mentioned instills pessimism: have we perhaps gone from having too much to work on to having nothing left to accomplish? Stepping into this saga personally, we here boldly propose that the formidable battle shielding the holy grail has been breached: a room temperature superconducting phase has recently been achieved, though yet undetected due to the challenges of making the necessary measurements at ultrahigh pressure. Several reports of metalization of hydrogen in the range of 400-500 GPa have appeared, most vociferously by Ike Silveras\textsuperscript{[17]} but earlier by other groups\textsuperscript{[18]} although the data have not convinced everyone on the battlefield.

Clearly modern electronic structure theory is confronted with a huge challenge in this regime. It seems however that again, as for H$_3$S, this gauntlet has already been challenged and overcome. Several groups have contributed to the determination of the hydrogen phase diagram at ultrahigh pressures including the quantum nature of the proton, which has a tangible influence. This quantum uncertainty affects the structure-pressure-temperature phase diagram but might have less affect on the electron-phonon coupling strength $\lambda$. Ceperley’s group has carried out the necessary calculations\textsuperscript{[19]} in the predicted crystal structure and found $T_c$ to be at or above 350K at pressures attained so far, with substantially higher critical temperatures predicted at increased pressure. There can be no argument that room temperature superconductivity has provided the acme of superconductivity aspirations, and it quite plausibly has been achieved. It remains for experimentalists to confront the challenge: make reproducible measurements to test the predictions.

Chapter 6. The next uprising

With verification of this proposal, viz. that room temperature superconductivity has been achieved, the best of times would seem to be within sight. The next challenge is in place: to produce these elevated critical temperatures at much reduced pressure. The theoretical prowess has been verified, and it can be reasonably expected to accelerate the path, perhaps leading the way, toward meeting future challenges. While the MGI is a far more broadly based initiative than superconductivity, this high visibility field provides an example of much
needed success that should serve as an inspiration to the many researchers who are engrossed in this new crusade. This is no time for the computational musketeers to take the conservative path, which could be stated: *keep where you are because, if (one) should make a mistake, it could never be set right in your lifetime.* Boldness is de regueur.

The MGI concept, and its implementation, is still evolving as it advances. Major discoveries are yet to appear. Still, several groups may be able to say about their effort at design & discovery of high $T_c$: *it is a far, far better thing that I do, than I have ever done; it is a far, far better rest to go to than I have ever known.*

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