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

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(Dated: January 3, 2018)

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 H₃S 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.¹ 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,² recognized a trend in T_c^{max} from the discovery of superconductivity to that time, and endeavored to sooth 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^{max} for three decades.³

During the 1960s Matthias formalized⁴ 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. Nb₃Sn, 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 formulated⁵ 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, 6 and that the theoretical foundation imposed no limit on $\mathbf{T}_c.$ Material systems that seemed poised to confront the frontier of strong coupling and much higher T_c led only to structural instabil-



FIG. 1: Bruce Friday's plot of maximum T_c versus time, from the discovery of superconductivity in 1911 to the time of this plot in 1973. Extrapolation of his linear fit indicated room temperature superconductivity in the year 2840.

ities, or to competing order such as magnetic or chargeand 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



FIG. 2: The simple, cubic, and beautiful crystal structure of the early class of A15 highest temperature superconductors, viz.Nb₃Sn. Dark spheres: Sn; gray spheres: Nb. A dominant feature of the structure is the chain of Nb atoms directed along each of the cubic axes.

understood on a quantitative basis: (i) TMs promote directional bonding – covalent but still metallic – which promotes stiff lattices and hefty electron-phonon scattering matrix elements, (ii) in each of these classes, the density of states at the Fermi level N(0) peaks at specific electron/atom values because each class is rigid band like, (iii) cubic materials have no lattice constant ratio b/a or c/a that can be relaxed to relieve electronic stress [high N(0)], promoting the superconducting onset but competing instabilities as well. The theoretical musketeers were demonstrating strength, portending closer interplay between experiment and theory as driving the next revolution. It was the spring of hope, it was the winter of despair: establishing a detailed theoretical foundation was not leading to discovery of better superconductors.

In 1980 the computational artillery was not in a position to predict T_c from first principles; the advance of formal theory had not produced the best of all possible worlds. Phonon frequencies had to be taken from experiment, matrix elements from potentials of rigidly moving atoms; moreover, promising predictions tended to produce unstable materials. But there is prodigious strength in sorrow and despair. By the 1990s, phonons could be computed accurately from first principles and matrix elements calculated from rigorous linear response, solving the problem except for the relatively small but curious Coulomb repulsion. The theoretical struggle was decided by the first decade of the 21st century, with Hardy Gross's formulation of and implementation of DFT for superconductors.⁷ 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, extending to 160K under pressure, and iron-based mate-

rials at 55K in 2008 extending to 75K in single layers, hugely energized the proletariat. The superconducting but unyielding A15 structure royalty had been magnificently overthrown; commoners could synthesize high T_c samples. After seeming eons (30 years, and 8 years, respectively) theory has produced no quantitative picture of pairing in these materials.

Chapter 3. Unleashing the computational artillery

The Materials Genome Initiative (MGI) of 2011 formalized a new paradigm: introduce large scale, high throughput computation into the synthesis & characterization 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 Eriksson⁸ searched for cuprate-like electronic structures using modern battlefield technology: high-throughput computing and data-filtering algorithms. With a similar goal, the EFRC Center for Emergent 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.⁹ The more realistic promise for HTS+MGI remains, at this writing, within the phonon-coupled paradigm, though early efforts⁸ had focused on the cuprate paradigm.

Not only was the MgB_2 insurgency of 2001, led by Jun Akimitsu's group,¹⁰ a stunning overthrow of the established order, so also was the rapid response with which DFT musketeers devined the underlying mechanism - covalent bonds driven metallic by chemistry and reproduced the observed $\mathrm{T}_{c}{=}40\mathrm{K},$ remarkable for a phonon mechanism. Though phonon mediated and far from optimal,¹¹ MgB₂ violated each of the emperors (Matthias's) dictates. Transition metals are not essential and not even optimal, being overthrown by a broader edict: 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' group¹² 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.



FIG. 3: The simple, beautiful, and cubic bcc crystal structure of the current highest temperature superconductor H₃S. Yellow spheres: sulfur; gray spheres: hydrogen. Comparisons with the A15 structure are striking: each is one of the three simplest cubic A_3B structures; each has dominant electronphonon coupling arising from one atomic species; each displays a sharp and narrow density of states peak lying precisely at the Fermi level.

The earlier computational study of H_2S by Yanming Ma's group¹³ predicting $T_c \sim 80K$ under pressure stimulated the experimental effort of Eremets, which synergistically spurred Tian Cui's group to extend the predictions¹⁴ to H_3S . Their revolutionary effort predicted the outrageous value of $T_c \sim 200$ 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_3S 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 publication¹² 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.¹⁵ 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_3S , 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,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 battlement sheltering 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 brigade¹⁷ but earlier by other groups,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_3S , 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-pressuretemperature phase diagram but might have less affect on the electron-phonon coupling strength λ . Ceperley's group had carried out the necessary calculations¹⁹ 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

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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 far better rest to go to than I have ever known.*

Acknowledgments. The author's involvement in this area of research has over the years been supported in various periods by NSF, DOE, and ONR.

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