March towards Room Temperature Superconductivity

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Abstract: The paper reviews the two most important discoveries made this year, one on hydrogen becoming a metal and the other on the most exciting discovery of finding the first room temperature superconductor, both taking place at extremely high pressures which were long standing puzzles for the past several decades.

1 Introduction

This year happens to be an important year for the material science community and to humanity at large as it leads to several important applications in all fields and it is because of the two important path breaking discoveries mentioned below:

- Discovery of Metallic Hydrogen
- Discovery of the First Room Temperature Superconductor

The second one follows the first as superconductivity is found under pressure when certain atoms in the periodic table are added to hydrogen.

It is very important to note at the first instance that both the above mentioned discoveries are found only when extremely high pressures are applied which are of

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the order of the pressure felt at the center of the earth and the production of such pressures in the laboratory has been a challenging task.

It is human ingenuity which led Wigner and Huntington to predict Metallic hydrogen as early as 1935 [1] using pen and paper since computers did not exist those days. Again, Ashcroft had the powerful intuition and predicted room temperature superconductivity in metallic hydrogen in 1968 [2]. It took several decades to realize the above until the 14th of Oct 2020. [3]

2 What is superconductivity?

Superconductivity is a phenomenon in which the electrical resistance vanishes completely in a metal when it is cooled down to very low temperatures. It was accidentally discovered in the year 1911 in mercury at a temperature 4.17^o K by Holst who was an assistant to Kammerlingh Onness. (Fig 1) [4]. This temperature is called its critical temperature (T_c). The natural question to ask is: is it shown by all solids? The answer is NO [5]. Only a few elements in the periodic table and also several thousand compounds show this phenomenon.

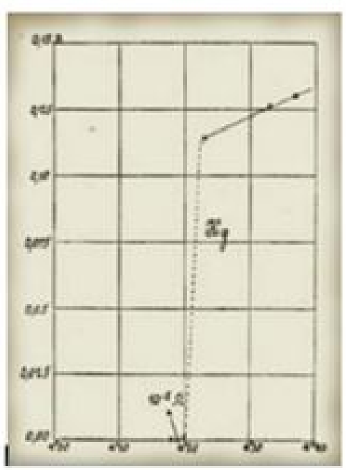


Fig 1 Variation of Electrical resistance as a function of temperature for Hg. Source: Original Picture taken from the notebook of Omnes

Apart from vanishing of electrical resistance, there are abrupt changes in thermal, magnetic and optical properties when the solid passes through its critical temperature. Hence any theory which is proposed to explain this phenomenon should explain all these observations at one stroke which took more than four decades to have an acceptable theory which was proposed by Bardeen, Cooper and Schrieffer (BCS) [6] after its discovery. According to them, superconductivity is due to Cooper pairs, where each Copper pair is made up of two electrons which have equal and opposite momenta with oppositely directed spins. The origin of the Cooper pair formation comes from the attractive interaction arising from the phonons whereas the same phonons scatter the electrons in normal metals giving rise to electrical resistivity.

3 What are the applications of superconductors?

It has a large number of applications in a variety of fields. All MRI (Magnetic Resonance Imaging) machines which are operated in hospitals make use of superconducting magnets capable of generating a magnetic field of 1.5 or 2 tesla. Maglev trains, touching a speed of 400 hundred kilometers, are in operation. Strong electromagnetic pulses produced by very high voltages using superconductors, which can destroy enemy's electronic communications were used by U.S in Iraq war and such E Bombs are also being made in India. The world's costliest experiment done on earth so far is the Large Hadron Collider (LHC) experiment which was able to detect Higgs boson using high power magnets, which was India's contribution to CERN. India's first SQUID (Superconducting Quantum Interference Device) was made by IGCAR, Kalpakkam. It is capable of detecting voltages of the order of 10^{-14} of a Volt or a magnetic field of the order 10^{-10} Gauss and they are used for brain scanning and disorders in the heart. In principle the tiny field variations felt by earth before the occurrence of earthquake can also be detected by SQUID magnetometer.

One of the urgent defense applications is in telecommunication and giants like Google, Microsoft, INTEL and other companies are pouring money to realize quantum computing which makes use of Josephson junctions. Google reports that the Sycamore processor consisting of 53 superconducting qubits (quantum bits) takes only 200 seconds to solve a particular problem to be run whereas it will take approximately 10,000 (ten thousand years) by today's classical supercomputers [7]. Indian Government has pumped in 8000 (Eight thousand crores) of rupees for this year. Of all the countries, China is leading and U.S is concerned because of the potential defense applications as fast information exchange can be executed through quantum computing.

Leaving aside all the above mentioned applications, yet another factor is the massive saving which will come if we could find room temperature superconductor and use it in power transmission. In today's world, current is carried by metallic conductors which leads to Joule heating which involves the term I^2RT. In a superconductor, since R is zero and hence line losses will be completely eliminated and today the loss is about 20% leading to a loss of several millions of rupees per year. This needs a conductor which will show superconductivity at room temperature instead of copper or aluminum conductors used today for power transmission. It is also expected to be used as a fuel for future rockets. Some counties have hydrogen bombs and Tokamaks are used in nuclear fusion technology to generate power.

4 Why do we need high temperature superconductors?

Among the elements in the periodic table the highest T_c is possessed by Nb which is 9^o K. Continuous unabated search was made from the existing compounds or by preparing new compounds which will have higher T_c values. Many were involved in this search and mention should be made of Mathias [8] who was responsible for finding the highest T_c till 1986 in a compound NB_3Ge with a T_c of 23.2^o K and this was called in earlier years as a High T_c system. Mention should be made of the fact that T_c values can be increased in certain systems by subjecting them to external pressure. It should be noted that in majority of the applications at present, Nb-Ti wires are used.

5 Birth of High T_c systems

A path breaking discovery was made by Bednorz and Mueller in 1986 who found T_c of 35^oK in a quaternary system $La_{1.85}Sr_{0.15}CuO_4$ [9]. This raised questions on the validity of the BCS theory as T_c almost exceeded the BCS limit. Paul Chu of Houston made an intelligent trick by introducing a smaller atom Y in the place of La. The trick is that he introduced chemical pressure instead of external pressure, thereby raising T_c to 90^oK. The chemical formula of this compound is $YBa_2Cu_3O_7$ [10]. This discovery is of great significance as T_c has crossed the boiling point of liquid nitrogen which is 77^oK. Now, this compound no longer requires costly liquid He to be used as a superconductor and one can use liquid N_2 hereafter to keep it in the superconducting state. This was followed by a series of Cu-O containing systems and the highest T_c went up to 134^oK in Hg based Cuprate and on application of pressure goes to 164^oK [11]. The mechanism operating or the formation of Cooper pairs in these compounds are not due to phonons and these are NON-BCS superconductors and the exact mechanism or the ONE responsible for pairing remains unknown. The milestones which one crosses in reaching the above mentioned T_c can be seen from Fig (2). [5] However, we have come a long way from 4.17^oK to 164^0K in the case of ternary super hydrides. It is hoped that these cuprate classes will reach room temperature. The main advantage will be that they are irreversible. The first superconductor with magnetism and superconductivity co-existing together was $CeCu_2Si_2$. This heavy fermion superconductor along with the cuprates have not been understood from theoretical point of view.

The above gives one of the routes to attain high temperatures. Three important aspects should be mentioned with regard to the cuprates discussed so far: (1) The parent compounds of the cuprates are antiferromagnetic insulators. (2) These com-

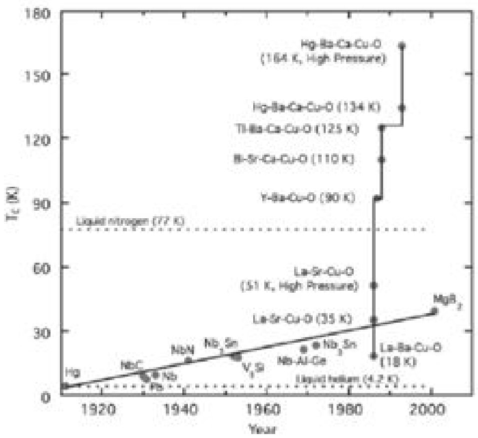


Fig 2. Timeline of Conventional metals and Cuprates

pounds are stable compounds and are not reversible. In the case of Hg based system its Tc is 134 K and no pressure is involved. Under the application of pressure, it goes to 164 K. Up on releasing the pressure Tc goes back to 134 K and the system remains stable thereafter.

6 Role of pressure

Bridgman, who is rightly called as the father of high pressure physics studied the physical properties of a large number of systems mostly in the solid state by subjecting them to high pressure. Before going further, the units which are used to express pressure in the modern day high pressure field is as follows:

Units of Pressure
One Pascal = Kg/M^2 =Newton/Meter^2
One GPa =10,000 bar = 9869 atmospheric pressure
One hundred GPa = One Mega bar (roughly one millions times the atmospheric pressure)
One thousand GPa = One Tera Pascal
Pressure at the center of the earth = 360 GPa (about)

As on date, the highest pressure achievable is around 500 GPa and hence we will stick to the unit GPa in this article. A detailed account of the experiments done on several solids is narrated by Kaveh Edalati and Zengi Horita (12). Bridgman used a hydraulic press of 75 tons to compress solids kept between steel anvils to reach 5 GPa and to raise the pressure still higher up to 10 GPa tungsten carbide anvils were used.

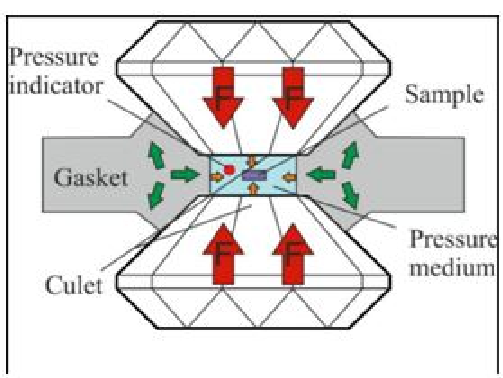
Diamond is the hardest material known to mankind and it is also transparent to both X rays and visible light. Diamond Anvil Cells came into existence from 1959 and several improvements and modifications were made to increase the pressure and the pressure calibration was performed by measuring the shift in the ruby laser line (Fig3). The details of which are described in the review article by Jayaraman [13] as well as the book due to Eremets who is actively engaged now in the field of superhydrides [14]. Present day DACs are capable of generating pressures of more than 500 GPa.

Earliest studies made with high pressure was to study the mechanical property of solids such as to determine bulk modulus and behavior of electrical resistance and phase/structural transitions. Later, X ray, Raman and Brillouin scattering studies were included. Magnetic and superconductivity studies and in particular the phenomenon of pressure induced superconductivity were also made. In most solids, T_c was depressed with applied pressure in most of the solids.

At the time of big bang, we had the IV state of matter, plasma and we had electrons, protons and other fundamental particles. The first atom to be born was the hydrogen atom and later we had the hydrogen as the first molecule. About 75% of the matter in the universe is hydrogen. Hydrogen gas gets liquefied and solidified at low temperatures and the respective temperatures are: -252.87^o C and -259.14^o C.

7 Metallization of hydrogen

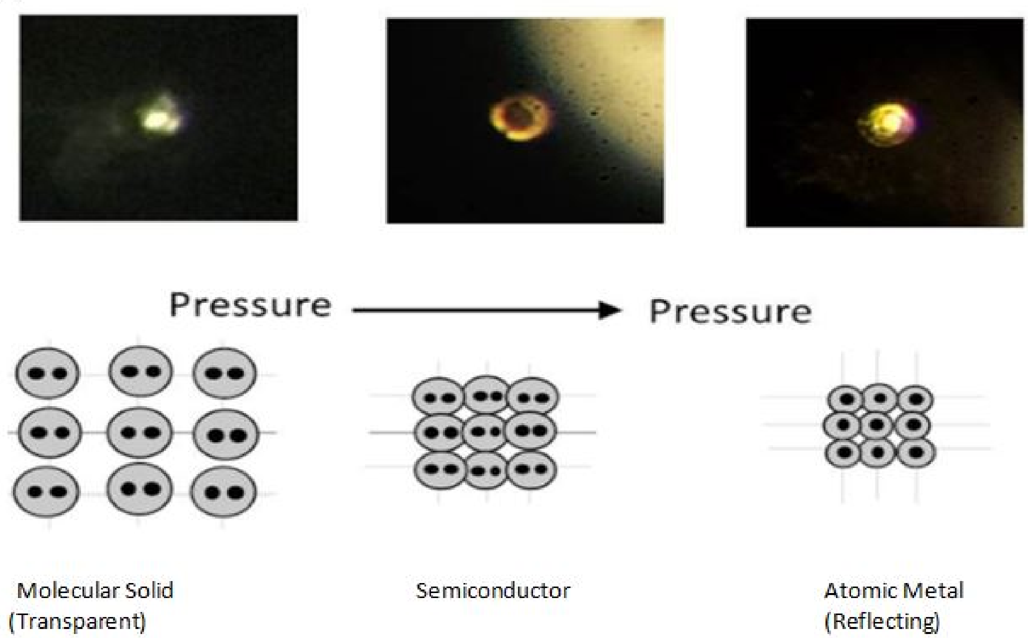
Raga Dias and Silvera, in their attempt to achieve metallic hydrogen, kept solid hydrogen in a high pressure cell and compressed it to a very high pressure exceeding 400 GPa.



Fig(3) Diamond Anvil Cell

As shown in Fig (4), initially, the sample was transparent and then turned into black semiconductor. At a particular pressure, the solid started reflecting the light incident on it. It has now undergone a color change or in other words has gone from black to yellow. The fact that light is reflected shows that it has become metallic.

In what follows, we show the process taking place in the conversion of the molecular hydrogen getting transformed into an atomic metal.



Fig(4) Molecular solid transformed into an atomic metal

A molecular insulator has now been transformed into an atomic metal in which free electrons will be floating in a lattice of protons (Fig 4). The experiment which was performed at a pressure of 490 GPa by Ranga Dias and Silvera was claimed by the authors of the paper [15] could not be reproduced the metallization of hydrogen because of the fact that the sample got lost due to disintegration. Their findings were strongly criticized by high pressure scientists as it was not reproduced. They have not provided conclusive evidence [16]. In all, during their experiment, they broke 32 pairs of diamonds each costing 3000 Dollars. However, Eremets et al report molecular hydrogen at a pressure above 350 GPa will show metallic nature [17]. Quite recent papers of Loubeyra et al [18] and Sergo Desgreniers [19] confirm the exciting milestone achieved towards the hunt for metallic hydrogen. Optical reflectivity studies made on solid hydrogen at different pressures are shown in Fig (5).

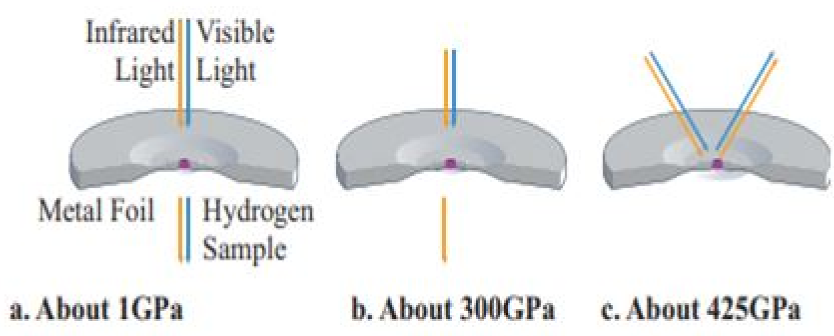


Fig 5. Effects of pressure on cold solid hydrogen. a. Solid hydrogen is transparent to both infrared light and visible light. b. Visibile light is cut. c. Both light are reflected showing that solid hydrogen as become metallic. Adapted from reference [19].

8 First Room Temperature Superconductor

Ashcroft in 1968 raised the question that if hydrogen could be metallised, why can't it become a room temperature superconductor? Hunt for room temperature went on with metallic hydrogen up to a pressure of 400 GPa without achieving any fruitful result.

Human civilization has passed through several ages. We had stone age, bronze age, iron age etc. Nature has shown to us that individual elements were of lesser use. stone consists of silicates and bronze contains mostly copper and other elements such as tin, Phosphorous and aluminium etc. Pure iron is of very little use. All marvellous technological applications came because of doping. Pure iron was doped with carbon and silicon with Al or Ga made them as transistors and gold, of course is to be added with Cu to make jewellery. Hence, additions and alloying become important from the application point of view.

In the same manner protracted failures in detecting room temperature superconductivity with pure hydrogen made Ashcroft to suggest other atoms to be added to hydrogen [20]. This binary hydrogen rich system yielded the desired result. Silane was the first system to show superconductivity under pressure. The table below gives the additions made and the resulting superconducting transition temperatures at high pressures. The Time Evolution towards the room temperature superconductor is explained as follows:

Table1:Historic Milestones in the Discovery of Room Temperature Superconductors

Solid	T_C(K)	Year
SiH_x	17	2008
$BaReH_9$	7	2014
H_3S	200	2015
PH_3	100	2015
LaH_{10}	250	2018
ThH_{10}	160	2019
YH_6	220	2019
YH_9	240	2019
C-S-H	287	2020

The final destination to attain room temperature is shown in Fig (6) with vanishing resistance at a pressure 267 GPa. The long and tiresome journey undertook by many like Cailitet, Amagat and Andrews cannot be forgotten in the process of liquefaction and solidification of gases as shown in the Fig (7).

Periodic Table of Binary Hydride Superconductors

(Adapted from Flores. A Livas, Phys.Rep, 2020[21])

Periodic table of superconducting binary hydrides (0–300 GPa). Theoretical predictions indicated in blue and experimental results in red.

9 Final onslaught

Tables (1) and (2) depict the roadmap towards achieving room temperature superconductor with binary additions to hydrogen. However the final step follows, but with a ternary system : Ranga Dias et al loaded DAC with solid particles of carbon and suphur and milled together and piped in three gases hydrogen , hydrogen suphide and methane .Then they shined green laser through the diamond triggering chemical reactions that turned the mixture into transparent crystals. When the above was put under a pressure of 148 GPa, it becomes a superconductor at 147^o K and finally when the pressure as raised to 267 GPa, Tc became 287K, 14 degrees in excess of zero Deg Centigrade [22]. (Fig 6). Apart from resistance measurement, magnetic property studies showed it to become a superconductor. This is the end of the story of Room Temperature Superconductor, which is an extraordinary discovery of this century as the quest for room temperature superconductivity is ever since the first discovery of superconductivity started from 1911. The crystal structure of the present ternary system Carbon-Sulphur-Hydrogen is yet to be determined. - .

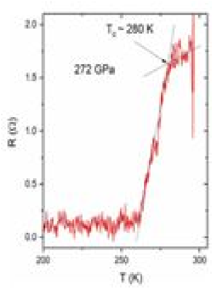


Fig 6. Resistance versus Temperature for the Room Temperature Superconductor

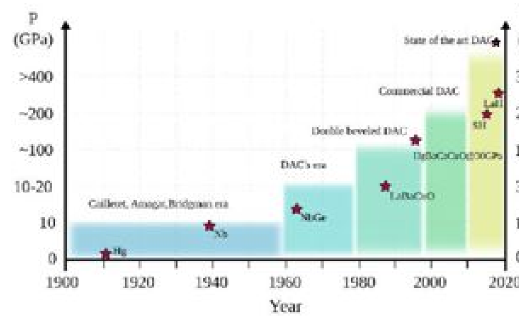


Fig 7: Landmarks of experimentally accessible pressures from early stages (Bridgman era) to the revolutionizing use of diamond as an anvil in the late '50s, to the state-of-the-art DACs (left y-axis). At parallel, the increase in transition temperature of superconductors, from simple metals to cuprates and highpressure hydrides follows the same trend (stars symbol, right y-axis)

10 Theory of a Binary Hydride Superconductors

These binary hydride superconductors gave a new lease of life to the BCS theory, which we have adopted since 1980 for a several systems [23]. It requires electronic structure calculations as has been given for the superconductor LaH_{10}. (Fig 8) [21]. T_c had been calculated using McMillan equation which is given below:

$$T_c = \frac{\theta_D}{1.45} \exp\left\{-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right\}.$$

The details of which are described in the above reference.

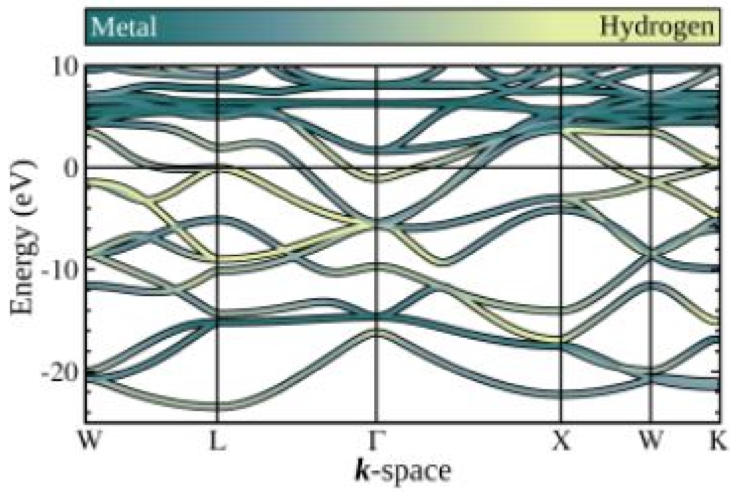


Fig (8) Electronic band structure of LaH_{10}

11 Conclusion

This article has brought to light two astounding physical phenomena whose existence remained unknown for several decades. As of now, there are two different routes to attain room temperature superconductor viz, the cuprate route and hydrogen route. However, from the application point of view, future looks bright as several applications of superconductors can be realized at room temperature.

It is suggested that quaternary and other multi-atom combinations can be tried which will bring down the pressure required or raise the T_c itself [24]. There are several uncertainties in the ingredients in the McMillan equation [25] and basic questions on the BCS theory itself which will be discussed in detail in the next article. The question raised by Ashcroft as to the possibility of hydrogen showing room temperature superconductivity instead of binary or ternary hydrogen rich materials, the moot question still remains! Further, it will be interesting to study Planets such as Jupiter, Saturn and exoplanets that have been found to expel magnetic field lines and are expected to be superconducting.

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