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Superconductivity above the lowest Earth temperature in pressurized sulfur hydride

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Abstract – A recent experiment has shown a macroscopic quantum coherent condensate at 203 K, about 19 degrees above the coldest temperature recorded on the Earth surface, 184 K (\(-89.2^\circ\text{C}, -128.6^\circ\text{F}\)) in pressurized sulfur hydride. This discovery is relevant not only in material science and condensed matter but also in other fields ranging from quantum computing to quantum physics of living matter. It has given the start to a gold rush looking for other macroscopic quantum coherent condensates in hydrides at the temperature range of living matter \(200 < T_c < 400\) K. We present here a review of the experimental results and the theoretical works and we discuss the Fermiology of H\textsubscript{3}S focusing on Lifshitz transitions as a function of pressure. We discuss the possible role of the \textit{shape resonance} near a \textit{neck disrupting} Lifshitz transition, in the Bianconi-Perali-Valletta (BPV) theory, for rising the critical temperature in a multigap superconductor, as the Feshbach resonance rises the critical temperature in Fermionic ultracold gases.

In March 2014 Eremets and his collaborators recorded in their logbook the first evidence of high-temperature superconductivity in the high-pressure metallic phase of H\textsubscript{2}S \cite{1,2}, as he reported at the Superstripes 2015 Conference \cite{3}. Independently, at the same time, Li \textit{et al.} \cite{4} published the theoretical prediction that the metallic phase of H\textsubscript{2}S at high pressure should be a stable superconductor with high \(T_c\). In the fall 2014 the work of Duan \textit{et al.} \cite{5} predicted high-temperature superconductivity in metallic H\textsubscript{3}S, formed by pressure-induced disproportion of \(2(\text{H}_2\text{S}) + \text{H}_2\) at around 100 GPa.

The record of superconductivity at 190 K in pressurized H\textsubscript{2}S was reported in December 2014 by evidence of zero resistivity \cite{1} followed by the Meissner effect in June 2015 \cite{3} with a maximum \(T_c\) onset of 203 K \cite{2} establishing a record for the superconductor with the highest critical temperature. The previous \(T_c = 164\) K record was held by doped HgBa\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{8}, at a pressure of 15 GPa \cite{6} as shown in fig. 1. The theoretical works on the structure prediction have been performed using the USPEX
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Fig. 2: (Color online) The left panel shows the high-pressure $Im\bar{3}m$ phase of H$_3$S. Yellow large spheres indicate sulfur atoms and the red small spheres indicate hydrogen atoms. The $Im\bar{3}m$ is formed by two intertwined set of chains made of S-H-S covalent bonds. The right panel shows a picture of the complex 3D space filling made of bitruncated cubic tiling on the borderline between crystals and quasicrystals.

(Universal Structure Predictor Evolutionary Xtallography) algorithm [7], already applied to predict superconductivity in LiH$_n$ [8].

High-temperature superconductivity in pressurized H$_3$S has been confirmed and the predicted $Im\bar{3}m$ crystal structure [5] has been found [9,10]. This structure (see fig. 2) is on the borderline between crystals and quasicrystals [11,12]. H$_3$S is expected to show a short hydrogen S-H bond [5] giving large-amplitude anharmonic hydrogen vibrations in a double-well potential, see fig. 3, related with a large electron-electron coupling [13,14].

The separation $\Delta$ between the minima of the double well decreases with pressure, so the amplitude of H zero-point motion decreases with increasing pressure. The experimental structure [9] shows a minor divergence from theory predictions [5] (see fig. 3). The system is quite inhomogeneous with broad line-shapes of diffraction profiles becoming sharper at high pressure. Moreover, the system shows a large increase of the critical temperature by annealing the sample temperature at 300 K, see fig. 4, like in oxygen-doped cuprates [15]. Therefore an intrinsic optimum inhomogeneity favors superconductivity, like in A15 compounds [16], cuprates [17,18], diborides [19] and iron chalcogenides [20].

In the past decades the search for new high-temperature superconductors has provided evidence for a large variety of different materials with high $T_c$. A binary intermetallic Nb$_3$Ge, with A15 crystalline structure, has hold the record of $T_c = 23$ K for many years [16]. This record was exceeded in 1986 by Bednorz and Muller with the discovery [21] of 35 K superconductivity in doped La$_2$CuO$_4$, which was followed by the discovery of many superconducting cuprate perovskites made of CuO$_2$ atomic layers intercalated by a large variety of spacer layers. The record of $T_c = 160$ K critical temperature in cuprates was achieved by optimization of mainly three physical parameters: a) the misfit strain [22–25] between the CuO$_2$ layers and different spacer layers; b) the amount of added dopants

Fig. 3: (Color online) Upper panel: the spatial separation $\Delta$ between the minima of the expected double-well potential for hydrogen along the S-S direction in H$_3$S typical of the S-H hydrogen bond. Lower panel: the S-H bond distances in H$_3$S (filled red dots) and D$_3$S (black squares) as a function of pressure [9] and the prediction of Duan et al. (black solid line) [5]. The error bars show the amplitude of the expected fluctuations of the S-H bond calculated by the difference between the two minima of the double-well potential for the H-atoms.

Fig. 4: (Color online) The critical temperature of H$_3$S samples pressurized at low temperature (red squares) and annealed at room temperature (black dots) [2,9]. The experiment shows a metastability in the pressure range between 140 and 205 GPa, where the critical temperature depends on different thermal and pressure treatments. Calculated critical temperature by Duan et al. [5] (green diamond), Jarlborg et al. [61] (blue triangles), and Flores-Livas et al. [72] (pink triangles).
and the interpolated \( T_c \) calculated from the critical temperature \( T_c \) of \( \text{H}_2\text{S} \) at the same pressure. The isotope coefficient, (red triangles) calculated from the critical temperature \( T_c \) of \( \text{D}_2\text{S} \) at the same pressure and the interpolated \( T_c \) of \( \text{H}_2\text{S} \) at the same pressure from the data reported by Drozdov et al. [2] and Einaga et al. [9].

in the spacer layers (oxygen interstitials) [15,17,18]; c) the application of an external pressure, 15 GPa, in \( \text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8} \) (Hg1223) [6].

In 2001 the record for intermetallics was obtained by Akimitsu and his colleagues measuring transport properties in an intermetallic compound made of light elements \( \text{MgB}_2 \), known since 1953 and already in the market, finding the superconducting transition at \( T_c = 40 \text{ K} \) [26]. The unexpected superconductivity in iron oxide layered compounds [27,28] has triggered the iron age of iron-based superconductors with the record of \( T_c = 100 \text{ K} \) in the FeSe monolayer deposited on doped \( \text{SrTiO}_3 \) [29].

Eremets et al. followed for many years the research direction for high-temperature superconductivity at high pressure [30–33]. They discovered that metallic silane becomes superconductor with \( T_c = 17 \text{ K} \) at 96 GPa [34] and recently they have found that \( \text{PH}_6 \) shows a \( T_c = 100 \text{ K} \) at high pressures [35]. The computational materials discovery is now addressed to hydrides considered to be pre-compressed phases of solid hydrogen such as \( \text{YH}_3 \) and \( \text{YH}_6 \) [36], tellurium hydrides [37], \( \text{VH}_2 \) [38], \( \text{AlH}_3 \) [39], \( \text{SbH}_4 \) [40] and polonium hydrides [41]. Superconductivity was predicted in \( \text{LiH}_6 \) with \( T_c = 82 \text{ K} \) at 300 GPa [42], in \( \text{KH}_6 \) with \( T_c = 70 \text{ K} \) at 166 GPa [43], with the computed record of \( T_c = 235 \text{ K} \) in \( \text{CaH}_6 \) at 150 GPa [44].

Many years before high-temperature superconductivity in pressurized hydrides and hydrogen was proposed by Aschroft [45–50], Ginzburg [51,52] and Maksimov [53,54]. The theoretical predictions of high \( T_c \) in solid hydrogen and hydrides at high pressure were based on the search of a system i) with a high-energy phonon mediating the pairing, because of the small mass of the hydrogen ion, ii) with a negative dielectric constant [52–54] and iii) at the verge of the superfluid-superconductor transition [49], where the transition temperature principally increases through the reduction in the associated Coulomb pseudopotential.

The isotope effect in \( \text{H}_2\text{S} \) [1] provided a direct evidence for the conventional phonon-mediated pairing. Therefore theories of unconventional pairing based on the exchange of magnetic interactions have been ruled out. From the results in ref. [2], the isotope coefficient as a function of pressure was reported by [55]. Figure 5 shows the pressure-dependent isotope coefficient from the data in ref. [9]. The isotope coefficient shows a minimum of \( \alpha = 0.2 \) at 200 GPa, a maximum, \( \alpha = 1 \) at 140 GPa and a second maximum \( \alpha = 0.3 \) around 240 GPa. A similar pressure-dependent isotope coefficient has been found in cuprates superconductors as a function of doping [56,57] with anomalies at Lifshitz transitions [58,59] of the L1 type, appearing of a new Fermi arc, or of the L2 type, neck disrupting [60] (see fig. 6). Therefore the data in fig. 5 have been interpreted [55] as indication of the presence of Lifshitz transitions in the pressure range showing high-temperature superconductivity. The Lifshitz transitions, i.e., the electronic transitions in the Fermi surface topology of \( \text{H}_2\text{S} \) as a function of pressure in the range from 80 GPa to 250 GPa have been identified by band structure calculations in refs. [55,61], which have been confirmed [62]. The giant effect of sample annealing in the range 140–200 GPa in \( \text{H}_2\text{S} \) is due to the predicted arrested phase separation near Lifshitz transitions [63,64] as for cuprates, where intrinsic phase separation and inhomogeneity are key features of high-temperature superconductivity [17,18,65].

The superconducting temperature in sulfur hydride was interpreted by a series of theoretical papers using the standard BCS approximations. First, the \textit{dirty}
The limit approximation reducing multiple bands, crossing the chemical potential, to a simplified metal with a single effective band. Second, the Migdal approximation considering the chemical potential very far from band edges so that the electronic and ionic degrees of freedom can be rigorously separated in agreement with the Born-Oppenheimer approximation. The superconducting temperature was predicted by employing the Allen-Dynes modified McMillan formula [5,66], the Migdal Eliashberg formula [67–71], and the more advanced self-consistent density functional theory [72,73]. The superconducting condensate has been described in the frame of isotropic pairing with a single gap $\Delta 0$ in the BCS regime $\Delta 0/\EF \ll 1$ and in the Migdal approximation $\omega_0/\EF \ll 1$, where the Fermi energy $\EF$ is the energy separation between the chemical potential and the bottom of valence bands at is the energy separation between the chemical potential, to a simplified metal with a single effective band. Second, the Migdal approximation considering the chemical potential very far from band edges so that the electronic and ionic degrees of freedom can be rigorously separated in agreement with the Born-Oppenheimer approximation. The superconducting temperature was predicted by employing the Allen-Dynes modified McMillan formula [5,66], the Migdal Eliashberg formula [67–71], and the more advanced self-consistent density functional theory [72,73]. The superconducting condensate has been described in the frame of isotropic pairing with a single gap $\Delta 0$ in the BCS regime $\Delta 0/\EF \ll 1$ and in the Migdal approximation $\omega_0/\EF \ll 1$, where the Fermi energy $\EF$ is the energy separation between the chemical potential and the bottom of valence bands at $-25$ eV. The pre-factor, $\omega_0$, in the BCS formulas is very high of the order of 100–150 meV due to a high-energy phonon branch formed by hydrogen ions dynamics [68,72,73]. However both the electron-phonon coupling and the total density of states (DOS) are not very large. The phonon energy of 100–150 meV giving the energy cut-off of the pairing interaction in $\text{H}_2\text{S}$ should be compared with the phonon energy, 70–80 meV, of i) the half-breathing Cu-O-Cu mode mediating the pairing in cuprates [74], and ii) the $e_{2g}$ mode in magnesium diboride [75] that shows a moderate energy softening due to electron-phonon interaction. This moderate softening is due to the fact that these phonons interact only with a small portion of electrons on the Fermi surface: the Fermi arc around the antinodal $(\pi,0)$ point in cuprates, and the small tubular $\sigma$ Fermi surface in MgB$_2$.

Starting from the evidence of Lifshitz transitions the Bianconi, Perali, Valletta (BPV) theory [60,76] was proposed [55,61] to describe high-temperature superconductivity in $\text{H}_2\text{S}$. The BPV theory considers high-temperature superconductivity made of multiple condensates. The optimum critical temperature is predicted for a first condensate in the BCS regime and the second one in the BCS-BEC crossover near a Lifshitz transition of the neck disrupting type as shown in fig. 6.

The BPV theory is based on the general theory of superconductivity [77–79] with no ad hoc BCS approximations. It was proposed in 1996 for cuprates [56], was verified in 2001 in diborides [80], and in 2009 for iron-based superconductors [81,82], where the highest $T_c$ at a neck disrupting Lifshitz transition was observed by high-resolution ARPES experiments [83–86]. Different condensates are formed in different Fermi surfaces with different symmetry and different Fermi energies $\EF$. The shape resonance provides a key quantum interaction increasing the critical temperature, like the Feshbach resonance in ultracold gases. The shape resonance is a contact interaction not included in the standard Eliashberg theory. It is an exchange interaction between first pairs in a first BCS condensate and second pairs in a second condensate in the BCS-BEC crossover regime. It belongs to the class of Fano-Feshbach resonances widely investigated theoretically and experimentally in ultracold Fermionic gases [87–89], where the Feshbach resonance is the only pairing mechanism giving high-temperature superconductivity with $k_B T_c/\EF = 0.2$. Therefore information on the Fermi surfaces is essential for the BPV superconductors made of multiples condensates in multiple Fermi surfaces. The Fermi surface of $\text{H}_2\text{S}$ at 200 GPa, i.e., for $a = 5.6$ a.u., is shown in fig. 7. It is formed by 5 different Fermi surfaces coexist with 3 small Fermi surface pockets (nos. 3, 4, 5) centered at the $\Gamma$-point (FS calculations made by Li [36]).

![Fig. 7: (Color online) The Fermi surface for $\text{H}_2\text{S}$ with $Im3m$ structure for the lattice parameter $a = 5.6$ a.u. at 200 GPa shown on the top left side of the figure. The Fermi surface is formed by 5 different Fermi surfaces from 1 to 5. The first and second large Fermi surfaces coexist with 3 small Fermi surface pockets (nos. 3, 4, 5) centered at the $\Gamma$-point (FS calculations made by Li [36]).](https://example.com/f7)
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Fig. 8: (Color online) The band structure along the $M$-$\Gamma$ direction of $\text{H}_2\text{S}$ at different lattice parameters. The simple cubic Brillouin zone (sc BZ) is used [61]. The figure shows the shift of the top of a band at about 2/3 in the $M$-$\Gamma$ direction from low pressure ($a = 6.0$ a.u.) to high pressure ($a = 5.4$ a.u.) and at 200 GPa, where it is crossing the chemical potential. The top of this band corresponds to a saddle point on the band dispersion. This crossing point is associated with a neck disrupting Lifshitz transition in the Fermi surface no. 2. Moreover, it is associated with the divergent derivative of the partial density of states (DOS) of band no. 2 on the high-energy side of the sharp DOS peak near the Fermi level. The partial density of states for each band is shown on the left side of the figure.

HNH direction of the bcc BZ, connecting the large petals of the no. 2 Fermi surface. These tubular necks give the flat energy dependence at the peak of the DOS maximum near the chemical potential. The three small Fermi surface pockets (no. 3, no. 4, no. 5) centered at the $\Gamma$-point

Fig. 9: (Color online) The two top (bottom) color pictures show the top (side) view of the Fermi surface of $\text{H}_2\text{S}$ at low ($a = 6.0$ a.u., left panel) and high ($a = 5.4$ a.u., right panel) pressure. The green and pink surfaces are portions of the Fermi surface no. 1. The blue and yellow surfaces are portions of the Fermi surface no. 2. The tubular necks in the Fermi surface connecting the large petals of the Fermi surface no. 2 appear in the high pressure ($a = 5.4$ a.u.) picture. The appearing of the small tubular necks at 5.7 a.u. in the Fermi surface indicates the so-called neck disrupting Lifshitz transition, of $L_2$ type. The red small Fermi surface pockets nos. 3, 4, 5 (see fig. 7), centered at the $\Gamma$-point, appear for $a < 6.0$ a.u. with the change of the Fermi surface topology. This change of the Fermi surface topology is called a Lifshitz transition for a new appearing Fermi surface spot, of $L_1$ type. (FS calculations made by Antonio Sanna [72]).

in fig. 7 correspond with the three tops at the $\Gamma$-point of three rapidly dispersing bands in fig. 8. These bands give a small contribution to the total density of states but are very sensitive to pressure changes. The Lifshitz transitions driven by pressure are shown in fig. 8 and in fig. 9. The tops of the dispersing bands at the $\Gamma$-point in fig. 8 are pushed up by pressure.

The $L_1$ Lifshitz transitions for a new appearing Fermi surface spot occur where the bands at the $\Gamma$-point cross the chemical potential. The side view pictures of all Fermi surfaces in fig. 9 show that the small red closed Fermi surfaces at $\Gamma$ are not present for $a = 6.0$ a.u., while they appear at high pressure as a red sphere, as shown for $a = 5.4$ a.u. The energy shift of the tops of the hole-like bands nos. 3, 4 at the $\Gamma$-point are shown in fig. 10. The $L_1$ Lifshitz transitions for the appearing of the new Fermi surface spots at $\Gamma$ occur around 100 GPa, at the onset of the observed superconducting phase where $T_c$ is close to zero as predicted by the BPV theory.

The $L_2$ Lifshitz transition for neck disrupting (see fig. 6) driven by pressure is due to the top of the band at 2/3 in
The high-frequency phonon mode is a key prefactor but also other factors like an anomalous dielectric constant and heterogeneity should cooperate to drive superconductivity to high temperature. The zero-point motion of the light H-atoms induces strong electronic renormalization [61]. $\text{H}_2\text{S}$ is a multiband superconductor with five different Fermi surfaces with first condensates in the BCS regime and second condensates in the BCS-BEC crossover regime (located on small Fermi surface spots with small Fermi energy). The shape resonance near a 2 Lifshitz transition is neglected in the Eliashberg theory, but it is described by the BPV theory which includes both i) the correction of the chemical potential due to pairing, and ii) the configuration interaction between different condensates which is expected to play a key role in the road map for a theory-driven search of room temperature superconductors.

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REFERENCES
