Superconductivity in sodalite-like yttrium hydride clathrates

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We report ab-initio calculations of the superconducting properties of two high-$T_c$ sodalite-like clathrate yttrium hydrides, YH₆ and YH₁₀, within the fully anisotropic ME theory, including Coulomb corrections. For both compounds we find almost isotropic superconducting gaps, resulting from a uniform distribution of the electron-phonon coupling over phonon modes and electronic states of mixed Y and H character. The Coulomb screening is rather weak, resulting in a Morel-Anderson pseudopotential $\mu^*$ = 0.11, at odds with claims of unusually large $\mu^*$ in lanthanum hydrides. The corresponding critical temperatures at 300 GPa exceed room temperature ($T_c = 290$ K and 310 K for YH₆ and YH₁₀), in agreement with a previous isotropic-gap calculation. The different response of these two compounds to external pressure, along with a comparison to low-$T_c$ superconducting YH₃, may inspire strategies to improve the superconducting properties of this class of hydrides.

The report of a superconducting critical temperature ($T_c$) of 265 K in the lanthanum superhydride LaH₁₀ at 190 GPa [1,2] set a new record for superconductivity only three years after another superhydride, SH₁₀, opened up the high-pressure route to conventional high-$T_c$ superconductivity [3,4]. These breakthroughs stem from two seminal papers of Neil Ashcroft, who first conjectured that high-$T_c$ conventional superconductivity would arise in high-pressure elemental metallic hydrogen [5], and later proposed that the huge threshold pressure for hydrogen metalization might be significantly reduced in binary hydrogen compounds XHₓ, by exploiting the additional internal pressure due to the X atoms [6].

Three years of research resulted in the determination of the high-pressure phase diagrams of most binary hydrides [8,9], clarifying that those hydrides exhibiting high-$T_c$ superconductivity mainly fall into two classes: (i) covalent hydrides, like SH₃ and PH₃, in which H and the other element X form a network of covalent bonds, driven metallic by the high pressure, and (ii) metallic hydrides of alkaline and rare earths, like LaH₁₀, which form hydrogen-rich sodalite-like clathrates (SLC) with highly symmetric structures [10,11,12], whose $T_c$’s are close to, or even higher than room temperature. In class (i), the chance of high-$T_c$ superconductivity is governed by the degree of covalency of the H-X bonds, and X=S seems to approach a sweet spot [5,13,21], in class (ii), the specific electron-phonon leading to high-$T_c$ has not yet been identified as clearly [22,24].

Since in the compounds with highest $T_c$ the H-H distance is close to that of solid hydrogen [25,26], many authors emphasize the role of the H sublattice and regard LaH₁₀ as the first experimental evidence of high-$T_c$ superconductivity in precompressed atomic hydrogen. According to this picture, once the X atoms provide charge to the hydrogen sublattice and sintuitizable a crystal structure with sufficiently small H-H distances, high-$T_c$ superconductivity follows. Recently, however, such an oversimplification lead to wrong expectations [27,28]. In fact, the pre-requisite for high-$T_c$ in high-pressure hydrides is a substantial role of H states in superconductivity, which cannot be guessed based on H-H distances alone. Our aim is to identify the electronic structure features behind high-$T_c$ superconductivity in high-pressure SLC hydrides.

We will re-examine two representative high-$T_c$, high-pressure hydrides of this class, YH₆ and YH₁₀, using the fully anisotropic ab-initio Migdal-Eliashberg theory as implemented in the EPW code [29,31,32], with the aim of identifying a rationale on the physicochemical ingredients needed to reduce their stabilization pressure without reducing their high $T_c$. In this light, we do not address the thermodynamics of the Y-H system, already analyzed by previous works, and concentrate on the high-symmetry SLC structures of YH₆ and YH₁₀ which, according to ab-initio calculations, are stable with record $T_c$’s of 260 K for YH₆ at 120 GPa, and of 303 K for YH₁₀ at 400 GPa [12,13,33]. Since in the Periodic Table yttrium belongs to the same group as lanthanum (one row above), the crystal structures and superconducting properties of its high-pressure hydrides closely track the parallel lanthanum compounds [11,13]. The practical advantage of yttrium is that its $f$ states, way above the Fermi level, play no role in the bonds and bands of its hydrogen compounds. In lanthanum compounds, instead, the $f$ states (troublesome both for density-functional and pseudopotential theory) are near the Fermi level and must be included, although in the end their contribution to stability and superconductivity turns out to be negligible [23].

Our results confirm that, in addition to a reasonably small H-H distance, both the superconducting behavior and the dynamical stability under pressure of these YHₙ hydrides are determined by the peculiar geometry of such a densely connected H lattice (similar to a sponge of H filaments whose cavities are occupied by Y atoms), and not by the chemical details of the enclosed atom.
Figure 1. The crystal structures of fcc YH$_3$ (left), bcc YH$_6$ (center), and fcc YH$_{10}$ (right) appear as space-filling polyhedral hydrogen cages (H = small pink balls) with an yttrium atom (Y = large green balls) in their middle, whose radius, for visual clarity, was chosen equal to 1.62 Å (midway between core and covalent radius). In this picture the H-H distances correspond to an external pressure of 300 GPa: $d_{HH} = 1.74$ Å for YH$_3$, $d_{HH} = 1.19$ Å for YH$_6$, and two slightly different lengths $d_{HH} = 1.03, 1.11$ Å for YH$_{10}$ (see text).

Fig. 1 shows the two high-$T_c$ yttrium hydrides considered in this work [34], YH$_6$ and YH$_{10}$, together with the low-$T_c$ YH$_3$ crystal, experimentally observed above 10 GPa, whose predicted maximum $T_c$ is 40 K at 18 GPa [35, 36]. In YH$_3$ and YH$_6$ a hydrogen atom sits on each of the 14 (24) vertices of the fcc (bcc) Wigner-Seitz primitive cell; in YH$_{10}$ it sits on each of the 32 vertices of a chamfered cube. For each such polyhedron well-known relations connect the edge length (the H-H distance $d_{HH}$), the volume $V$ (the unit cell volume of the corresponding crystal), the average radius, etc. For example $d_{HH} = 0.69 V^{1/3}$ in YH$_3$, $0.45 V^{1/3}$ in YH$_6$, and $0.38 V^{1/3}$ in YH$_{10}$. Geometrical constraints not only control (i) the H-H distance, important for high-$T_c$, but also (ii) the Y-H distance, important for the involvement of Y in the e-ph interaction, and (iii) how tight or loose is the host clathrate cavity where the (fixed-size) guest atom sits; which, in turn, triggers the onset of their dynamical instability at “low” pressure, discussed later [34].

We now focus on the two high-$T_c$ superconductors [37], whose bands (left) and densities of states (DOS, right) are shown in Fig. 2 for YH$_6$ (top) and YH$_{10}$ (bottom).

Unless otherwise stated, all subsequent results refer to a pressure of 300 GPa, where both YH$_6$ and YH$_{10}$ are dynamically stable, and their $T_c$ is close to its maximum. The color gradient indicates the projection onto H (blue) and Y (orange) states. In both compounds the hydrogen-derived bands have a total bandwidth of $\sim 40$ eV. Remarkably, by taking into account the materials’ lattice geometries, their dispersion over this energy range is well described by quasi-free-electron bands [38], with largest deviations where the H- and Y-derived states significantly hybridize, i.e., $\sim 25$ eV below the Fermi level (4p semicore states) and in a region of $\sim 10$ eV around the Fermi level (4d, 5s states). The Fermi level cuts the band structure where both H and Y contributions to the electronic structure are sizable: In particular, around the Brillouin zone center ($\Gamma$) the bands have mostly Y character, while at its boundaries they are mostly H [39].

In a superconductor, when two or more orbitals/bands...
at the Fermi surface couple to phonons with different intraband strengths, an anisotropic superconducting gap $\Delta_{\mathbf{k}l}$ results. Its behavior can be obtained entirely from first principles within the anisotropic Migdal-Eliashberg (ME) theory. The anisotropic $\epsilon$-ph Eliashberg functions are calculated within the linear-response theory, using the Wannier interpolation technique implemented in the Erw code \cite{31, 32} and the $GW$ approximation for the fully screened Coulomb interaction \cite{41, 42}. We do this for the first time for YH$_6$ and YH$_{10}$, showing our result in the right panels of Fig. 3.

Before we comment this figure, let us discuss the main features of the phonon spectra and Coulomb interaction \cite{43, 45}. In both YH$_6$ and YH$_{10}$ the Eliashberg spectral function (Fig. S3-S4 in the Supplemental Material \cite{40}) shows a rather uniform distribution of the $\epsilon$-ph coupling over all phonons, including the low-energy modes which are essentially of Y character. Compared to YH$_6$, the shorter, stiffer H-H bonds of YH$_{10}$ translate into 20\% larger frequencies for the high-energy, bond-stretching modes. The average $\epsilon$-ph matrix elements are also higher, leading to a larger $\epsilon$-ph coupling in YH$_{10}$ ($\lambda = 2.41$) than in YH$_6$ ($\lambda = 1.73$). According to our calculations, the Coulomb pseudopotential is the same in both compounds: $\mu^* = 0.11$, resulting from a $GW$-screened Coulomb interaction $\mu_c = 0.11$ and a negligible Morel-Anderson renormalization. This is, to our knowledge, the first $ab\text{-initio}$ estimate of Coulomb screening in H clathrates; the value $\mu^* = 0.11$ places these compounds in the same ballpark as most conventional metals. It is reasonable to assume that similar values of $\mu^*$ occur in SLC hydrides formed by other metals as well. On this basis the anomalously large $\mu^* \approx 0.22$ invoked in Ref. \cite{22} to theoretically reproduce the experimental $T_c$ appears unlikely.

Back to Fig. 3, we observe that while in YH$_6$ and YH$_{10}$ the distribution of Y and H character on the Fermi surface is uneven (left panels), this only yields minor (±10\%) fluctuations of the superconducting gap around its average value (right). This quasi-isotropic gap is restored by the strong Y-H interorbital interactions due to the compact, quasi-spherical geometry of the system: All lattice vibrations, including bending and breathing modes of the cages, modulate the Y-H distance and thus the overlap between Y and H orbitals, which, in turn, washes out most anisotropic effects on superconductivity \cite{20}.

We studied the temperature dependence of the superconducting gap by solving the anisotropic ME equations at different temperatures; Fig. 4 displays the temperature evolution of its energy distribution function over the Fermi surface. Well below $T_c$, i.e. for $T < 80$ K in Fig. 4, this distribution is nearly independent of temperature, and shows a broad maximum around 65 meV (55 meV) for YH$_{10}$ (YH$_6$), originating from the two zone-boundary Fermi surfaces and the two large zone-center Fermi surfaces, plus a smaller tail at lower energies (52 meV for YH$_{10}$ and 36 meV for YH$_6$), due to the two smallest zone-center Fermi surfaces (see Fig. 3 and Supplemental Material \cite{40}). The gap closes at a critical temperature of 290 K in YH$_6$ and 310 K in YH$_{10}$ \cite{17}. Since in both compounds the dependence of $T_c$ on pressure is very weak, as shown in panel (a) of Fig. 5, our predictions for $T_c$ amount to a remarkable agreement with Ref. \cite{13}, which, using the isotropic Migdal-Eliashberg theory and $\mu^* = 0.10$, estimated 264 K for YH$_6$ at 120 GPa and 303 K for YH$_{10}$ at 400 GPa.

As shown in panels (b) and (c) of Fig. 5, the weak pressure dependence of $T_c$ results from an almost perfect compensation between the average phonon energy $\omega_{\log}$, which increases with pressure \cite{49}, and the $\epsilon$-ph coupling constant $\lambda$, which, instead, decreases. For both compounds this balance approximately holds down to a pressure of ~250 GPa, below which the lowest optical branch ($\Gamma\rightarrow L$ line in YH$_{10}$, $\Gamma\rightarrow H$ line in YH$_6$) gets softer and softer, eventually leading to a dynamical instability at ~226 GPa and ~72 GPa, respectively \cite{49}. The soft branch carries a substantial fraction of the total $\epsilon$-ph coupling, but a glance at the q-dependent electronic susceptibility \cite{19, 50} shows that its softening is not due to nesting and must be related to the $\epsilon$-ph matrix elements.

This, in turn, suggests an intrinsic instability of the Y-H system in the SLC structure, which is robust against minor changes of the electronic structure. The common physical origin of the instability of YH$_{10}$ and YH$_6$ at two very different critical pressures is revealed by their comparison with yet another SLC yttrium hydride: YH$_3$ (green triangles in Fig. 1), which, according to our calculations, remains stable down to the much lower pressure of 11.5 GPa \cite{37}. Panel (e) of Fig. 5 shows the $V$ vs $P$ equation of state for the three compounds, and clearly evince that the three different pressures below which the soft modes become imaginary in YH$_3$ (green), YH$_6$ (blue), YH$_{10}$ (red), correspond to a single volume of ~27 Å$^3$, which, in fact, equals the volume of a sphere.

![Figure 4. Energy distribution of the superconducting gap for YH$_6$ (blue) and YH$_{10}$ (red) as a function of temperature. The rectangles show the extrapolated $T_c$ values.](image-url)
of radius \( \sim 1.9 \) Å, the covalent radius of Y.

This suggests that, for SLC hydrides with chemical formula \( \text{XH}_n \), the minimum stabilization pressure is dictated by the size of the guest atom X: When the size of the primitive cell exceeds it, the hydrogen cage becomes too loose to constrain this atom in its middle, and hence the H lattice breaks down. If this is true, then, for a given atom X, the compounds with larger \( n \) (implying denser hydrogen cages with smaller H-H distances) will require larger stabilization pressures. So, as far as the dynamical stability is concerned, cages with small \( n \) and large H-H distances \( d_{\text{HH}} \) are preferable, because they require lower pressures; on the other hand, besides a substantial contribution of H electronic and vibrational states to superconductivity, the high-\( T_c \) hydrogen superconductivity needs small H-H distances (close to the shortest atomic-solid-hydrogen value \( d_{\text{HH}} = 0.98 \) at 500 GPa)\(^1\)\(^2\)\(^3\), and thus large \( n \).

In other words, the competing requirements for dynamical stability and superconductivity, together with the different geometrical prefactor which affect the dependence of \( d_{\text{HH}} \) on the primitive cell/cage volume \( V \), provide a natural explanation, pictorially summarized by panels (e) and (f) of Fig. 5, why YH\(_6\) (intermediate cage volume, small \( d_{\text{HH}} \)) is better than both YH\(_3\) (smallest cage volume, but too large \( d_{\text{HH}} \), almost twice than in atomic-solid-hydrogen up to 350 GPa) and YH\(_{10}\) (smallest \( d_{\text{HH}} \), but too large a cage volume).

In summary, we have studied the superconducting properties of two high-pressure yttrium hydrides, YH\(_6\) and YH\(_{10}\), using first-principles anisotropic Migdal-Eliashberg theory, including Coulomb corrections. Our calculations confirm the room-temperature superconductivity found by other authors, and show that it results from a strong e-ph interaction which is rather uniformly spread over electronic and vibrational states of both hydrogen and yttrium sublattices. The Coulomb pseudopotential parameter, which for these compounds we computed for the first time \textit{ab-initio} within the GW approximation, is in line with the values found in most conventional superconductors (\( \mu^* = 0.11 \)), in contrast to recent studies, which propose a much larger value for related lanthanum SLC hydrides\(^2\)\(^2\). Due to the peculiar geometry by which the yttrium SLC hydrides implement a dense hydrogen lattice, optimizing their superconducting behavior under pressure requires a careful compromise between H packing and structural stability. Our findings may inspire optimization strategies for other superconducting hydrides of the same class.

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