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Theory-orientated discovery of high-temperature superconductors in superhydrides stabilized under high pressure

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A dream long held by physicists has been to raise the critical temperature (T_c)—the temperature below which the material exhibits no electrical resistance—of a superconductor to room temperature. The most recent excitement in that regard has centered on rare-earth superhydrides, of which LaH_{10} at 190 GPa has a remarkably high T_c of 260 K, approaching room temperature (Fig. 1)[1–4] and originating from the appearance of a peculiar so-called "clathrate" structure in the crystal lattice that was reported for the first time in CaH_6.[5]

The first hydride superconductor (Th_4H_{15}, T_c = 8 K) was discovered at ambient pressure in 1970.[6] Importantly, that work initiated the search for superconductors among hydrogen-rich compounds as inspired by the proposal of high superconductivity in a metallic form of hydrogen, which is the lightest element, possibly giving rise to a high Debye temperature and a strong electron–phonon coupling necessary for a good phonon-mediated superconductor. Subsequent studies of Pd–H and Pd–Cu–H systems found T_c below 10 K. The low superconductivity is intimately related to the negligible contribution from hydrogen to the electronic density of states (EDOS) at the Fermi level (FL). After more than 30 years of silence, the search for superconductors among hydrogen-rich compounds was renewed by Ashcroft in 2004[7] via a "chemical pre-compression" effect that was proposed earlier by a pioneering theory in 1971.[8]

Superconductivity in hydrides is influenced by two key criteria, namely (i) a large hydrogen-derived EDOS at the FL and (ii) large modifications of the electronic structure in response to the vibration of hydrogen atoms,[9] but the hydrogen-poor metal hydrides known at the time fit neither criteria. Ashcroft proposed the possibility of finding good superconductors among hydrides including those containing a rich amount of H_2 molecules.[7] However, once there is a stabilization of H_2 molecules in the lattice, hydrides naturally fail to satisfy criterion (i) because hydrogen electrons in a major portion will occupy low-lying energy states far below the FL, arising from the formation of intramolecular H–H sigma bonds. There is a great wish to find hydrides containing as much atomic

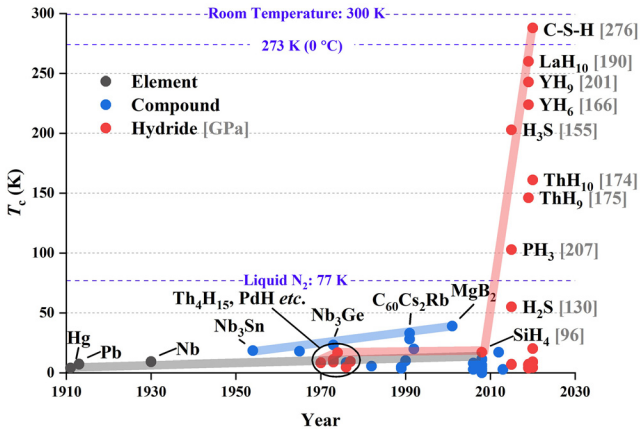

FIG. 1. Chronological evolution of superconducting critical temperature (T_c) for various conventional superconductors.

hydrogen as possible to satisfy both criteria and realize high-T_c superconductivity. Here, theory should play a leading role in aiding such a discovery.

It has long been believed that SH_2 will dissociate into elemental hydrogen and sulfur under pressure. In 2014, this was revived by the appearance of theoretical work on the prediction of a superconductive structure (T_c = 80 K) at megabar pressures that is energetically stable with respect to elemental hydrogen and sulfur.[10] Stimulated by this prediction, two distinct S–H superconductors were synthesized in experiments:[11] (i) the one prepared at low temperature has T_c = 30 K–150 K, in accordance with the predicted SH_2 superconductor;[11] (ii) the one annealed at room temperature has an unexpectedly high T_c of 180 K–203 K, which is ascribed to a stoichiometric change from SH_2 to SH_3.[9] Notably, SH_3 is a known stoichiometry of $(SH_2)_2H_2$ that has been synthesized at 7 GPa and is predicted to be a 200-K superconductor at megabar pressures.[12] The finding of SH_3 is a typical material-by-design success, with theory guiding the experimental discovery.

In 2012, a hitherto unknown superhydride of CaH_6 with a remarkably high T_c of 235 K was predicted at megabar pressures in a Ca–H system via a structure-searching simulation.[5] The high superconductivity arises from the peculiar clathrate structure comprising H_{24}-cage units with encaged Ca.[5] This CaH_6 can be viewed as Ca-doped metallic hydrogen in which the hydrogen takes atomic form and contributes majorly to the EDOS at the FL. The clathrate structure is likely the first structural model for superhydrides in which hydrogen makes the dominant contribution to the EDOS at the FL. Subsequent structure-searching simulations revealed that clathrate structures in superhydrides are formed commonly in rare-earth superhydrides under pressure.[1,2] Motivated by these theories, considerable experimental progress has been made, and the three best-known superconductors of LaH_{10}, YH_9, and YH_6 were synthesized with T_c values of 260 K, 243 K, and 227 K, respectively.[3,4,13] The finding of record-breaking superconductors among clathrate-structured rare-earth superhydrides highlights again the leading role of theory in the discovery.

A literature survey shows that nearly all binary hydrides have been investigated by structure-searching simulations. To date, the clathrate structure for metal superhydrides and the SH_3 structure for covalent superhydrides are the two best structural models for hydride superconductors. To search further for a room-temperature superconductor, one must target ternary or quaternary superhydrides. So that the hydrides contain no H_2 molecules, a useful strategy for achieving optimal superhydrides is to introduce extra electrons via metal doping into the lattice, thereby allowing the occupancy of H_2 antibonding states for their dissociation; this is exemplified by a designed ternary Li_2MgH_{16},[14] mimicking the doping of Li into MgH_{16} whose lattice is rich in H_2 molecules. This superhydride has the highest T_c of 473 K at 250 GPa and can be regarded as a hot superconductor. Indeed, recent experimental progress has shown high T_c values of 288 K[15] and 550 K[16] for C–S–H and La–B–N–H systems, respectively, but the information about compositions and structures is missing.

Although the present perspective gives several examples of theory-orientated discoveries of high-temperature superconductors in superhydrides, the main drawback of these materials is the destabilization at ambient pressure. There is a strong desire to discover high-T_c superhydrides that are quenchable at ambient pressure for practical use. However, direct synthesis at ambient pressure seems infeasible because there is a high energy gain for forming H_2 molecules in the lattice. An alternative route is to seek synthesis at low pressures. In previous studies, we predicted that certain rare-earth superhydrides can be synthesized at moderate pressures, such as YbH_6 at 40 GPa.[1] With improved algorithms and computer power, structure-search computational schemes become extremely important aids for discovering new materials, and we expect theory-orientated discoveries of superconductors at room temperature or higher in superhydrides stabilized under pressure.

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