Hydrogen-modified superconductors: A review

CrossMark

Hasnain M. Syed, C.J. Webb, E. MacA. Gray[*]

Queensland Micro- and Nanotechnology Centre, Griffith University, Nathan, 4111, Brisbane, Australia

ARTICLE INFO

ABSTRACT

We present an overview of hydrogen-containing superconductors, including metallic, cuprate, pnictide and carbon-based materials. Particularly in BCS-like superconductors, hydrogen introduces new phonon modes and these may lead to better or worse superconducting properties, with anharmonicity of the H potential being a decisive factor. The availability of the deuterium isotope, in addition to protium, makes hydrogen an extremely useful extra probe of mechanisms of superconductivity. While hydrogen modification has not so far led to any confirmed remarkable improvement in already existing metallic superconductors, hydrogen plays an important role in the synthesis of novel iron-based superconductors and as a substitutional impurity appears to increase the transition temperature. Most recently, a new record for the superconducting transition temperature of 203 K has been claimed for a metallic hydride under high pressure, H_2S. We survey elemental hydrides and superconductors, discuss techniques for introducing hydrogen into materials, then review and summarise published knowledge about hydrogen-containing superconductors.

© 2016 Elsevier Ltd. All rights reserved.

Contents

* Corresponding author.
    E-mail address: e.gray@griffith.edu.au (E.MacA. Gray).

1. Introduction

Three reasons can be advanced to study the effects of hydrogen absorption by superconductors. First, hydrogen absorption generally causes lattice expansion and so, roughly speaking, the opposite effect to compression by hydrostatic pressure. This provides an additional and valuable way to probe the dependence of superconductivity on lattice structure, electronic structure and the phonon spectrum. Secondly, hydrogen absorption carries the prospect of enhanced critical superconducting properties such as critical temperature (T_c), critical current density (j_c), and critical fields (H_{c1}, H_{c2}), although it must be acknowledged that no technologically worthwhile enhancement has so far been confirmed. Thirdly, compatibility with hydrogen and its isotopes is a potentially significant factor for applications such as superconducting electric power transmission cables and fusion reactors, where exposure of superconducting components to hydrogen may lead to absorption despite protective cladding. There is also the possibility of using hydrogen to switch between the normal and superconducting states.

Superconductivity in hydrogen-containing materials was initially a surprising conjunction of notionally disparate fields: conventional metallic superconductivity and metal hydrides. On the other hand, given that the absorption of a proton, typically into an interstitial site in the metal lattice and an electron, into the band structure, usually significantly affects the crystal structure, band structure, phonon spectrum and therefore all physical properties of many metals, alloys and intermetallics, it is surprising that few metallic superconductors in which hydrogen plays a role are well known. In either case, superconductors created or altered (for better or worse) by uptake of hydrogen have great potential to improve our understanding of superconductivity.

Even at low concentrations, an interstitial solution of H in a metal results in distortion of the surrounding lattice and influences physical properties. Atypical behaviours of the lattice parameters, elastic constants and thermoelectric power of notionally pure metals have been explained as consequences of low concentrations of hydrogen as an impurity [1].

Perhaps the best-known metal hydride (where "hydride" is taken to include non-stoichiometric compositions MH_x for any value $x > 0$) is palladium hydride (PdH_x, where $x \approx 0.6$ at room temperature), reported by Graham in 1866 [2]. Palladium absorbs hydrogen readily from H_2 gas at less than 1 atm pressure at room temperature. Whereas Pd metal is an enhanced Pauli paramagnet owing to the high density of states at the Fermi level, addition of H progressively fills the 0.6-electron hole in the d band, so that for $x > 0.6$ at room temperature the hydride is diamagnetic [3]. Adding electrons into the s band from further H absorption occurs at a higher energy per electron, causing the necessary H_2 gas pressure to rise rapidly. Kilobar H_2 pressures are required to achieve $x = 1$ [4,5]. This system exhibits a strong inverse isotope effect: the thermodynamic critical point of the Pd–H_2 system is reported to be at (273 °C, 24 bar H_2), whereas that of the Pd–D_2 system is reported to be at (283 °C, 39 bar D_2) [6].

Palladium hydride is also the best-known superconducting hydride (although not the first known) and was reported by Skoskiewicz [7] in 1972 to exhibit superconductivity below 2 K at the composition $PdH_{0.87}$ following electrolytic loading, with T_c falling at a rate suggesting $T_c = 0$ at a composition around $PdH_{0.7}$.

The first investigation of superconducting metal hydrides appears to be that of Horn and Ziegler [8], as early as 1947. Hydrides of tantalum and niobium were found to have depressed values of T_c compared to the pure metals.

Superconductivity enhanced by interstitial hydrogen was first reported in 1970 in the thorium–H_2 system, where Satterthwaite and Toepke [9] found Th_4H_{15} to be superconducting below about 8 K, compared to $T_c = 1.37$ K for pure thorium.

In the light of predictions that metallic hydrogen is a superconductor with transition temperature possibly above 100 K [10–13], the ability of Pd to take up hydrogen at high number density (6×10^{28} m^{-3} at 1 H per Pd) led to speculation that metallic hydrogen might be responsible for the superconductivity of PdH_x [14]. This speculation inspired a number of theories and experiments during the 1970s. However, the consistent indication from experiments is that metallic hydrogen is not responsible for superconductivity in PdH_x [14].

Apart from reports from the 1970s concerning superconductivity in the Al–H [15,16] and TaS_2–H [17] systems, hydrides of Nb-based alloys [18–20] and one notable investigation of the high-T_c cuprate superconductor $YB_2Cu_3O_7$ [21], superconducting hydrides attracted relatively little further experimental attention until the discovery of superconductivity in MgB_2 [22,23], with $T_c \approx 38$ K, and the report of increased j_c at high fields owing to implantation of protons [24]. Only a small increase in T_c accompanied the effective uptake of H. Subsequently, Ashcroft [25] argued that the dense group 14 hydrides might exhibit high-temperature superconductivity at pressures considerably lower than required to form metallic hydrogen.

Tripodi et al. [26,27] claim to have repeatedly observed superconductivity in electrolytically loaded PdH_x at much higher temperatures than previously, almost up to room temperature. Lipson et al. [28,29] have reported anomalies in the electrical and magnetic properties of PdH_x at temperatures up to nearly 70 K that were interpreted as indicating filamentary superconductivity.

Very recently Drozdov et al. [30] reported conventional (*i.e.* BCS-like) superconductivity at the extraordinarily high temperature of 203 K in the sulphur-hydrogen system under pressures ~100 GPa. If confirmed, this establishes a new record for the highest T_c claimed in a type II superconductor, given that the claims of Tripodi et al. [26,27] have not been verified. It is believed that sulphur hydride transforms to metal and a superconductor at around 90 GPa, with T_c increasing along with the pressure. This high temperature superconductivity phase is associated with the dissociation of H_2S, and formation of SH_n ($n > 2$) hydrides. The sudden drop of the resistivity to at least 50 times lower than that of copper and the decrease of T_c with applied magnetic field are strong evidence of superconductivity. The strong isotope shift of T_c in D_2S is a confirmation of superconductivity and suggests a crucial role played by phonons in the superconductivity, which appears to be BCS-like.