



Superconductivity in compressed hydrogen-rich materials: Pressing on hydrogen



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ABSTRACT

Periodic table of elements starts with hydrogen, a simplest element of all. The simplicity is lost when the element is compressed to high densities or participates in a chemical bonding in compounds, being subjected to “chemical pressure” of surrounding atoms or molecules. The chemical nature of hydrogen is dictated by its simplest electronic shell, which has only one electron. Hydrogen can donate this electron and behave like alkali metal, or accept an extra electron and form a hydride ion with closed shell resembling a group VII element. The complexity of hydrogen goes beyond these simplest configurations, when hydrogen is involved in a multicenter bonding or in hydrogen bonds. This complex behavior is tightly related to the ability of hydrogen to participate in the process of electronic transport in solids and potentially be able to contribute to the superconductivity in a material. Hydrogen by itself when compressed to immense pressures of 400–500 GPa may form a simple atomic phase with very high critical superconducting temperatures (T_c) well above room temperature. While this theoretical insight awaits confirmation at pressures at the limit of current experimental capabilities, a variety of other hydrogen-rich materials have been suggested recently to have record high T_c values. The very existence of many of these materials still lacks experimental confirmation. In this review article, we will present an extensive list of such predicted materials. We will also review superconductivity in classical hydrides (mostly metal hydrides) and current theoretical understanding of relatively low T_c 's in metal hydrides of transition and noble metals.

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1. Introduction

As we may expect, chemical nature of hydrogen dictates its participation in transport phenomena in solids. “Dual” nature of hydrogen as an electron donor or acceptor, and its tendency to

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form multicenter bonds of various degree of complexity [1], provides for a variety of chemical environments for hydrogen [2]. While “ionic” character of a hydride ion or a proton in most of these environments [3] is leading to insulating properties, a multicenter or metallic bonding [1] promotes materials with metallic conductivity. Within a BCS (Bardeen, Cooper and Schrieffer) scenario of superconductivity [4] high vibrational frequencies of hydrogen atoms raised hopes [5] for a high critical temperature in conducting hydrogen and hydrogen-rich materials [6]. However, multiple attempts to find a material with high critical superconducting temperature in hydrides of transition and rare-earth metals did not produce a high- T_c material. The highest T_c 's observed in hydrides of Pd and Pd–Au, Pd–Cu alloys did not exceed temperatures of the order of 15–17 K [7,8]. Moreover, substantial inverse isotope effect was observed in PdH and PdD, at first raising doubts in the validity of the electron–phonon coupling mechanism for superconductivity in these materials, and later leading to the understanding of the role played by anharmonicity of hydrogen vibrations in such “simple” hydrides [9]. It should be noted that there are published claims of nearly room-temperature superconductivity in PdH_x materials [10], which have not been confirmed by other experimentalists and have no theoretical backing at the moment.

The ability to create hydrogen-based materials with desired properties has received tremendous boost recently from a variety of government funded programs aimed at a viable hydrogen storage material for automotive and energy-storage related applications [11,12]. Chemical compounds [11], weakly interacting molecular materials [12,13], surface interactions [14] have been attempted with limited success to conveniently store and retrieve hydrogen. However, no practical material for hydrogen storage did emerge from this massive effort so far. Despite the deceptive simplicity hydrogen turned out extremely complex chemical entity as a component of useful materials. The properties of hydrogen in high-pressure environment become even more complex. High energy density [15], high-temperature superconductivity and superfluidity [16] are expected in dense hydrogen and hydrides. Ambient pressure metastable metallic phase of hydrogen, consisting of weakly interacting chains of hydrogen atoms with interatomic distances about 1.06 Å was predicted in 1970'ies by Brovman et al. [17]. Ashcroft [6] proposed a metallic state in hydrogen-rich alloys, where the electronic bands of hydrogen and the host element(s) overlap. In the work that followed, the superconductivity was found with T_c approaching 20 K in transport measurements performed by Eremets et al. [18]. This claim was subjected to experimental (and theoretical) scrutiny as discussed in Section 2 of this review. As a development of this idea, very unusual metallic polyhydrides of lithium have been proposed [19,20] to exist at pressures about 100 GPa, well below the expected metallization pressure of pure hydrogen [21]. Stable polyhydrides of alkali metals have been predicted recently by theoretical analysis of MHn (M = Li, Na, K, Rb, Cs) compounds with variable hydrogen composition [19,20,22–25]. These alkali and alkali earth polyhydrides will be reviewed in Section 3.

Finally, we will discuss the prospects for high- T_c hydrogen-rich materials in a high-pressure environment. Both theoretical insights and experimental challenges will be discussed.

2. Phonon-driven superconductivity in hydrides

2.1. Electron–phonon coupling and anharmonic effects

We give below a quick summary of the results for electron–phonon coupling driven superconductivity relevant for the discussion of hydrogen-based superconductors. The critical

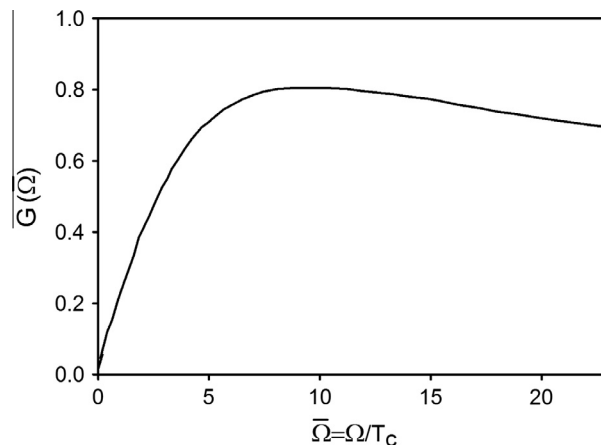


Fig. 1. Function $G(\bar{\Omega})$, $\bar{\Omega} = \Omega/T_c$ is the reduced frequency ($\hbar = 1$, $k_B = 1$). Reproduced from Solid State Commun. from Mitrović and Carbotte [29].

superconducting temperature for a phonon-mediated superconductor can be conveniently represented by modified McMillan formula [26,27]:

$$T_c = \frac{\omega_{\log}}{1.2} \exp \left[-\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right] \quad (1)$$

where ω_{\log} is a logarithmic average of the phonon frequency, λ is electron–phonon coupling constant, and μ^* is the Coulomb pseudopotential of Morel and Anderson [28].

Another useful formula is defining electron phonon coupling parameter λ

$$\lambda \equiv \frac{N(\epsilon_F)\alpha^2}{M\omega_E^2} \quad (2)$$

in terms of the density of the electronic states $N(\epsilon_F)$ at the Fermi level, the phonon frequency ω_E and effective mass M , and the Holstein parameter α , a Fermi surface average of the electronic matrix element of the change in crystal potential as particular phonon mode-related atoms are moved [26]. Partial contribution of phonon modes was analyzed in [29] for weakly coupled phonons; we show a figure with the results of this analysis (Fig. 1).

Fig. 1 shows relative partial derivative of the T_c with respect to small change in the partial coupling strength $\alpha^2(\Omega)F(\Omega)$ at phonon frequency Ω , with broad maximum around $\Omega = 10$. It means that the phonon frequencies contributing mostly to T_c , are about factor of 10 higher in frequency than the T_c (in equivalent units, $\hbar\omega/k_B T_c$). This result along with Eq. (1), strongly favors high vibrational frequencies as a prerequisite of high T_c values. The highest vibrational frequencies are found in hydrogen in hydrides; for this reason hydrogen-rich materials have attracted significant amount of attention in the search for highest T_c values in materials. However, historically the quest for high- T_c hydrogen based materials did not produce any significant results. The early era before high- T_c cuprates, was reviewed in [30]. Despite significant effort, only two families of relatively high T_c materials have been found with Th [31] and Pd [7,32] hydrides. Both systems showed anomalous isotope effect when doped with deuterium; ThH(D)_{3.64} did not show any isotope effect, which initially raised doubts regarding the phonon-mediated mechanism, and PdH(D) showed inverse isotope effect [9]. In the theoretical and experimental papers that followed discovery of PdH superconductor, the anomalous isotope effect was understood as resulting from anomalously large anharmonicity of hydrogen (deuterium) vibrations [33,34,35–37]. While earlier works used empirically scaled experimental phonon spectrum [34], the latest theoretical efforts have explained the observed anharmonicity from the first principles [37]. Since the

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