Conventional Superconductivity at 190 K at High Pressures

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January 25, 2015 (HP90). The highest critical temperature of superconductivity ($T_c$) has been achieved in cuprates [1]: $T_c = 133$ K [2] at ambient pressure and 164 K at high pressures [3]. As the nature of superconductivity in these materials is still not disclosed, the prospects for a higher $T_c$ are not clear. In contrast the Bardeen-Cooper-Schrieffer (BCS) phonon mediated theory of superconductivity gives a guide for achieving high $T_c$: it should be a favorable combination of high frequency phonons, strong coupling between electrons and phonons, and high density of states. These conditions can be fulfilled for metallic hydrogen and covalent hydrogen dominant compounds [4, 5]. Numerous subsequent calculations supported this idea and predicted $T_c = 100-235$ K for many hydrides [6], but only moderate $T_c = 17$ K has been observed experimentally [7].

In the presented work [8] we studied experimentally sulfur hydride (H$_2$S). We found that it transforms at $P \sim 90$ GPa to a metal and superconductor with $T_c$ increasing with pressure to $\sim 60$ K at $P < \sim 150$ GPa (Figure 1a,b) in general agreement with recent calculations of $T_c = 80$ K for H$_2$S [9]. In contrast to the calculations we found a dramatic increase of $T_c$ at higher pressures (Figure 1b). Moreover we found superconductivity with $T_c \approx 190$ K in a H$_2$S sample pressurized to $P > 150$ GPa at $T > 220$ K (Figure 2). The superconductivity was proved from (a) the drop of the resistivity to a value $\sim 100$ times lower in comparison with copper, (b) the shift of the superconducting transition step with magnetic field, and (c) the strong isotope effect measured with D$_2$S evidencing a major role of phonons in this superconductivity.

The sharp increase of $T_c$ to $\sim 150$ K with pressure (Figure 1b) and the near 190 K superconductivity in sulphur hydride (Figure 2a,b) are both most likely associated with the dissociation of H$_2$S to SH$_n$ ($n \geq 2$) hydrides plus elemental sulfur. Precipitation of sulfur might be of particular interest, because sulfur forms impurities or clusters in a host lattice which can promote an increase of $T_c$ through surface enhanced effects, instabilities, and disproportionation which are common features of high temperature superconductors. Calculations [10] supported this hypothesis: H$_3$S has been found stable at $P > 50$ GPa. The superconductive high pressure phases of H$_3$S found in the theoretical study of the (H$_4$S)$_2$H$_2$ system [11] have $T_c$ of $\sim 160$ K and 190 K – in agreement with our experimental values (Figures 1,2).

Further theoretical works also considered H$_3$S as responsible for the high temperature superconductivity [12-14]. Hirsch and Marsiglio proposed hole superconductivity as an alternative explanation [15]. Interestingly, metallic H$_3$S can be viewed essentially as atomic metallic hydrogen stabilized with sulfur [12].

High $T_c$ can be expected in a wide range of hydrogen-containing materials. Hydrogen atoms seem to be indispensable to provide the high frequency modes in the phonon spectrum and the strong electron-phonon coupling.
Fig. 1. Temperature dependence of resistance of sulfur hydride and sulfur deuteride measured at different pressures. Resistance was measured with four electrodes deposited on a diamond anvil. (a) Sulfur hydride as measured at the growing pressures. Plots at pressures <135 GPa were scaled (reduced in 5-10 times) for easier comparison with the higher pressure steps. (b) Data were obtained when pressure was applied in the 100-190 GPa pressure range at 100-150 K and higher temperatures at $P \sim 200$ GPa when $T_c$ sharply increased. Black points are data from Figure 1a. Blue points - other runs. Red points are measurements of D$_2$S. Dark yellow points are $T_c$'s of pure sulfur. Grey stars are calculations from [9].

Fig. 2. Pressure dependence of critical superconducting temperature $T_c$ on pressure. Comparison of the superconducting steps of sulfur deuteride and hydride at similar pressures. (b) Higher $T_c \sim 190$ K found when pressure $P > 150$ GPa was applied in combination with 220-300 K temperatures. The 190 K step is accompanied with another step with $T_c \sim 30$ K (wine points). The red point is $T_c$ for D$_2$S sample (Figure 2a).
References