

Conventional Superconductivity at 190 K at High Pressures

A.P. Drozdov, M. I. Eremets, I. A. Troyan

Max-Planck Institut für Chemie, Chemistry and Physics at High Pressures Group - Postfach 3060, 55020 – Mainz - Germany.

Email: m.eremets@mpic.de

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_2S). We found that it transforms at $P \sim 90$ GPa to a metal and superconductor with T_c increasing with pressure to ~ 60 K at $P < \sim 150$ GPa (Figure 1a,b) in general agreement with recent calculations of $T_c = 80$ K for H_2S [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_2S 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 ~ 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_2S evidencing a major role of phonons in this superconductivity.

The sharp increase of T_c to ~ 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_2S to SH_n ($n > 2$) 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_3S has been found stable at $P > 50$ GPa. The superconductive high pressure phases of H_3S found in the theoretical study of the $(H_2S)_2H_2$ system [11] have T_c s of ~ 160 K and 190 K – in agreement with our experimental values (Figures 1,2).

Further theoretical works also considered H_3S as responsible for the high temperature superconductivity [12-14]. Hirsch and Marsiglio proposed hole superconductivity as an alternative explanation [15]. Interestingly, metallic H_3S 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.

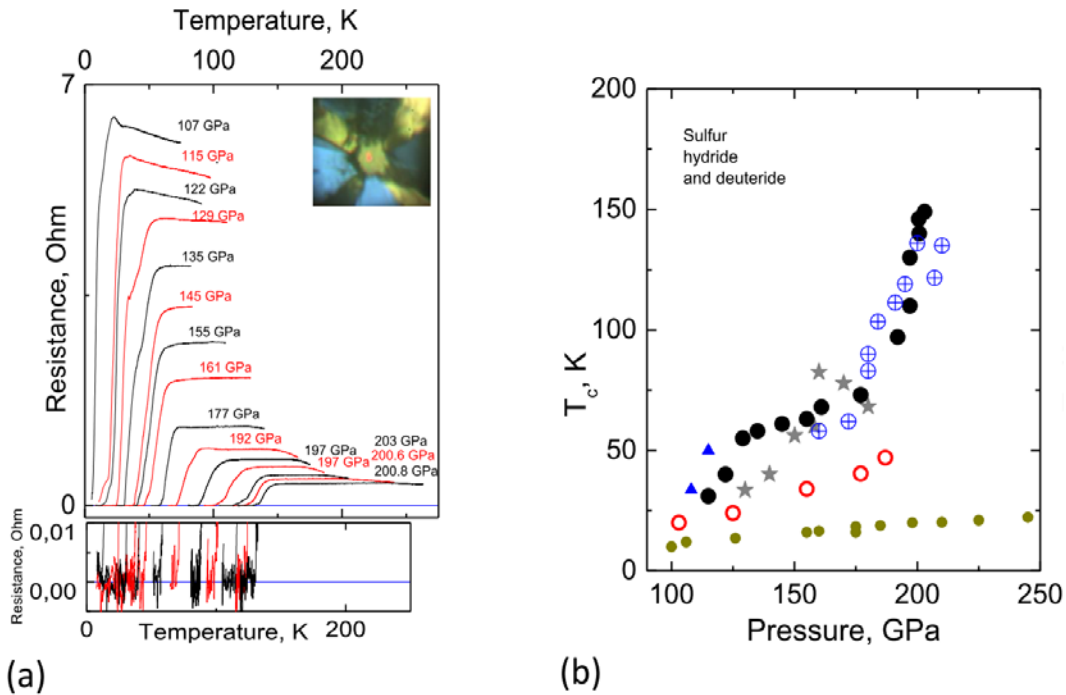


Fig. 1. Temperature dependence of resistance of sulfur hydride and sulfur deuteride measured at different pressures. Resistance was measured with four electrodes deposited on a diamond anvil. (a) Sulfur hydride as measured at the growing pressures. Plots at pressures <135 GPa were scaled (reduced in 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_2S . Dark yellow points are T_c s of pure sulfur. Grey stars are calculations from [9].

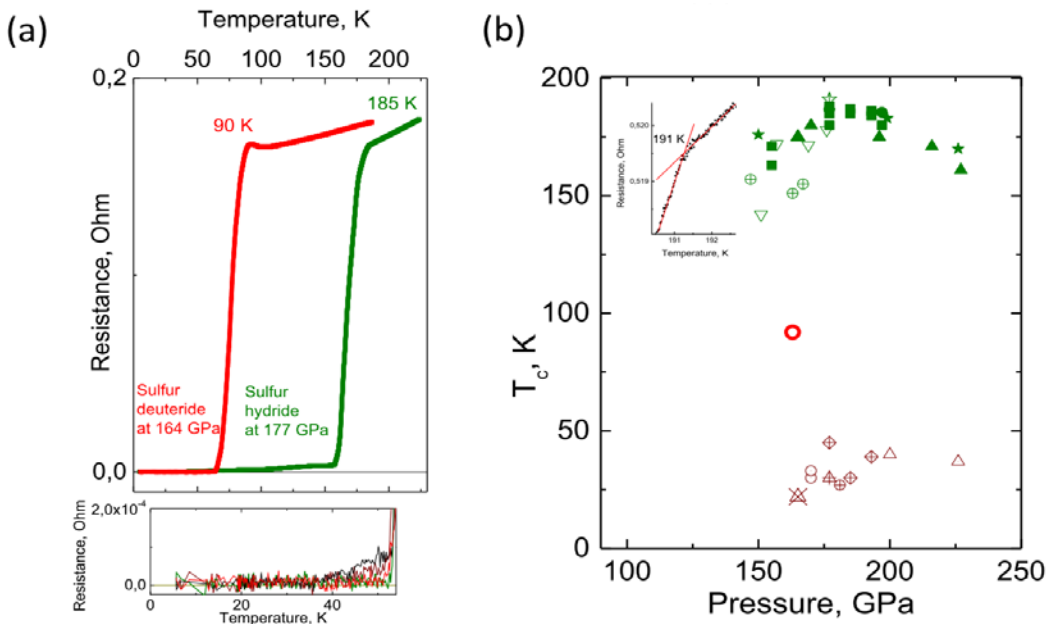


Fig. 2. Pressure dependence of critical superconducting temperature T_c on pressure. Comparison of the superconducting steps of sulfur deuteride and hydride at similar pressures. (b) Higher $T_c \sim 190$ K found when pressure $P > 150$ GPa was applied in combination with 220-300 K temperatures. The 190 K step is accompanied with another step with $T_c \sim 30$ K (wine points). The red point is T_c for D_2S sample (Figure 2a).

References

- [1] J. G. Bednorz, K. A. Mueller, Possible high TC superconductivity in the Ba-La-Cu-O system. *Zeitschrift für Physik B* **64**, 189–193 (1986).
- [2] A. Schilling, M. Cantoni, J. D. Guo, O. H. R., Superconductivity above 130-K in the Hg-BaA-Ca-Cu-O system. *Nature* **363**, 56-58 (1993).
- [3] L. Gao, Y. Y. Xue, F. Chen, Q. Xiong, R. L. Meng, D. Ramirez, C. W. Chu, J. H. Eggert, H. K. Mao, Superconductivity up to 164 K in HgBa₂Cam-lCum_{0.2m+2+6} (m=1, 2, and 3) under quasihydrostatic pressures. *Phys. Rev. B* **50**, 4260-4263 (1994).
- [4] N. W. Ashcroft, Metallic hydrogen: A high-temperature superconductor? *Phys. Rev. Lett.* **21**, 1748-1750 (1968).
- [5] N. W. Ashcroft, Hydrogen Dominant Metallic Alloys: High Temperature Superconductors? *Phys. Rev. Lett.* **92**, 187002-187001-187004 (2004).
- [6] Y. Wang, Y. Ma, Perspective: Crystal structure prediction at high pressures. *J. Chem. Phys.* **140**, 040901 (2014).
- [7] M. I. Eremets, I. A. Trojan, S. A. Medvedev, J. S. Tse, Y. Yao, Superconductivity in Hydrogen Dominant Materials: Silane. *Science* **319**, 1506-1509 (2008).
- [8] M. I. Eremets, A.P. Drozdov, I. A. Troyan, Conventional superconductivity at 190 K at high pressures. *arXiv:1412.0460*, (2014).
- [9] Y. Li, J. Hao, Y. Li, Y. Ma, The metallization and superconductivity of dense hydrogen sulfide. *J. Chem. Phys.* **140**, 174712 (2014).
- [10] Defang Duan, Xiaoli Huang, Fubo Tian, Da Li, Hongyu Yu, Yunxian Liu, Yanbin Ma, Bingbing Liu, T. Cui, Pressure-induced decomposition of solid hydrogen sulfide *arXiv:1501.01784*, (2015).
- [11] D. Duan, Y. Liu, F. Tian, D. Li, X. Huang, Z. Zhao, H. Yu, B. Liu, W. Tian, T. Cui, Pressure-induced metallization of dense (H₂S)₂H₂ with high-T_c superconductivity. *Sci. Reports* **4**, 6968 (2014).
- [12] D. A. Papaconstantopoulos, B. M. Klein, M. J. Mehl, W. E. Pickett, Cubic H₃S around 200 GPa: an atomic hydrogen superconductor stabilized by sulfur *arXiv:1501.03950*, (2015).
- [13] N. Bernstein, C. S. Hellberg, M. D. Johannes, I. I. Mazin, M. J. Mehl, What superconducts in sulfur hydrides under pressure, and why *arXiv: 1501.00196* (2015).
- [14] A. P. Durajski, R. Szczesniak, Y. Li, Eliashberg analysis of the superconducting state in hydrogen sulfide near the structural phase transition point. *arXiv: 1412.8640* (2014).
- [15] J. E. Hirsch, F. Marsiglio, Hole superconductivity in H₂S and other sulfides under high pressure *arXiv:1412.6251*, (2014).