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Room-temperature superconducting in sulfur hydrides

Kwang-Hua R. Chu [a,b]

[a] *College of Mechanical and Electronic Engineering, Fujian Agriculture and Forestry University, Fuzhou 350002, PR China*
[b] *Distribution Centre, No. 120-1, Section 5, Xinhai Road, Taipei 116, Taiwan, ROC*

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With the theory of absolute reaction rate we demonstrate the possible superconducting transition in sulfur hydrides within the room-temperature regime via tuning of activation volume as well as activation energy for the first time under zero shear rates. Before we present our novel approach and numerical results we firstly verify our calculations with previous measurements [Drozdov et al. Nature 525 (2015) 73]. After successful verifications, we illustrate our novel numerical results via the enhancing transition temperature for electronic liquids in sulfur hydrides to within the room-temperature regime (after decreasing of activation volume: $\sim 10^{-27}$ m^3 decrement or increasing of activation energy under zero shear rates compared to previous Drozdov et al.'s experimental data).

1. Introduction

Hydrogen sulfide might form during hydrogen-electrode reaction on gold prepared in different ways or using the hydrogen evolution reaction (HER) in electrodes made of metal sulfides. Other formation could be traced during the processing or preparation for solid polymer electrolyte batteries as well as in searching for a promising electrode material considering high performance supercapacitors.

Recent discovery by Drozdov et al. [1] of superconducting transition (to almost zero-resistance state) temperature (T_c) = 190 K in a diamond anvil cell loaded with hydrogen sulfide (H_xS) and compressed to about 200 GPa breaks the cuprates record and overturns the conventional wisdom that such a high T_c cannot be obtained via phonon-mediated pairing. Sulfur hydride under pressure has since then been met with much excitement although the existence of almost zero-resistance states or frictionless transport of electronic fluids is yet to be confirmed by other experimental groups [2–6]. For instance, synthesis of lithium polyhydrides under high pressure around the room temperature regime (evidences of the disproportionation of LiH above 130 GPa to form lithium hydrides containing H_2 units) has just been reported quite recently [7]. Meanwhile researchers [5] suggested that optical measurements could be a useful tool to establish the existence and nature of the almost zero-resistance state in (H_xS) system. Interestingly some calculations [4,8] suggested that decomposition of the H_2S sample occurs within the diamond-anvil cell at high pressures ($3H_2S \rightarrow 2H_3S + S$ was proposed in [3]). The high-T_c material is therefore very unlikely to be H_2S as claimed in [1], while H_3S is the obvious candidate for the H-rich decomposition product (thus it is suitable still using H_xS as the detailed compound is yet not confirmed). We remind the readers that lower $T_c = 17$ K has been observed experimentally in SiH_4 (Silane) [9] and Drozdov et al. have in subsequent works [10] confirmed the existence of almost zero-resistance states by magnetic susceptibility measurements with even higher $T_c = 203$ K. Drozdov et al. mentioned that the high T_c most likely is due to H_3S which is formed from H_2S under its decomposition under pressure [10]. The above-mentioned progresses in fact are motivated by original theoretical predictions (cf. detailed cited references in [1]). The highest T_c of 203 K that Drozdov et al. [10] recently reported has been achieved most probably in H_3S having the *Im*-3m structure. We noticed that as Drozdov et al. [10] remarked that, after loading and after the initial pressure increase at 200 K, they annealed all samples by heating them to room temperature (or above) at pressures of $> \sim 150$ GPa. Changes of resistance and T_c of sulfur hydride with temperature at constant pressure—the annealing process. The sample was pressurized to 145 GPa at 220 K and then cooled to 100 K. It was then slowly warmed at $\sim$ 1 K min^{-1}; $T_c = 170$ K was determined. At temperatures above $\sim$ 250 K the resistance dropped sharply, and during the next temperature run T_c increased to $\sim$ 195 K. This T_c remained nearly the same for the next two runs.

Meanwhile Drozdov et al. [10] remarked that, considering the 143 GPa test, during this run the sample was clamped in the DAC at $T \approx 200$ K, and the pressure then increased to 103 GPa at this temperature; the further increase of pressure to 143 GPa was at $\sim$100 K. There were two unusual observations: (1) After next cooling to $\sim$15 K and subsequent warming, $T_c \approx 60$ K was observed,

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E-mail address: 2304343144@qq.com

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then the resistance strongly decreased with increasing temperature. Around the room-temperature regime: $275 \le T \le 296$ K the (electrical) resistance is rather small but is not zero. (2) After successive cooling and warming a kink at 185 K appeared, indicating the onset of transition. The observed transition is very broad: resistance dropped to zero only at $\sim$ 22 K. There are apparent *oscillations* on the slope. Their origin is yet not clear, though they probably reflect inhomogeneity of the sample in the transient state before complete annealing [10]. Similar *oscillations* have also been observed for other samples (see, for example, Fig. 3 in the Supplementary Information of [1]). The latter incomplete works around the room-temperature regime raise the hope for further enhancing of T_c for sulfur hydride (to room-temperature range). In fact many researchers [11–13] have explored the possibility of producing very high T_c (almost room temperature) materials in the past.

In this paper we shall adopt the verified theory of absolute reactions [14–18] and boundary perturbation method [19,20] to demonstrate the possible enhancing of T_c of sulfur hydride to room-temperature regime via tuning of activation energy and activation volume following Drozdov et al.'s incomplete works [10] (cf. the high-temperature region in extended data Fig. 2 (a) therein). Our results emphasize the importance of careful annealing and preprocessing in conventional high-power or high-performance materials should pave the way for substantially enhancing T_c by application of a high pressure and properly designed chemical substitution and suggest that in principle it is not impossible to boost the T_c to within the room-temperature regime in optimized conditions.

2. Formulations

We shall borrow from the quantum chemistry approach [14–18] considering

$$H_2S + H \leftrightarrow [TS(\text{Transition State})] \rightarrow H_3S$$

to handle the activated complex (electronic liquids) in sulfur hydride considering the almost zero (electrical) resistance states. Eyring's theory states that in order for a (liquid) particle to move, the other surrounding particles must move into the adjacent vacant sites to create a free space for the particle to enter [14–18]. The flow of any liquid can be generally regarded as a thermally activated process. At a higher temperature, the (liquid) particles have higher thermal energy so that they can more easily overcome an energy barrier and move into the adjacent vacant sites.

Under the verified Eyring's absolute reaction model or transition-state (TS) approach [14–18] (considering the stress-biased thermal activation), structural rearrangement is associated with a single energy barrier (height) ΔE that is lowered or raised linearly by a (shear) yield stress τ. If the transition rate is proportional to the shear strain rate (with a constant ratio: $K_0 \approx 2V_A/V_m$), we can calculate the shear stress [14–18] (which is proportional to the electrical resistance ρ_R [23,24])

$$\tau = 2\left[\frac{\Delta E}{V_A} + \left(\frac{k_B T}{V_A}\right)\ln\left(\frac{2\,\dot{\zeta}}{K_0 \nu_0}\right)\right], \tag{1}$$

where V_A is the activation volume, V_m is the volume of flow unit, $\dot{\zeta}$ is the shear strain rate, and ν_0 is an attempt frequency [14–18], e.g., for temperatures (T) being within the range of the order of the magnitude: O(1) K (Kelvin): $\nu_0 \approx k_B/h \sim O(10^{11})$ (1/s) with k_B being the Boltzmann constant and h the Planck constant [14–18].

We consider a steady, fully developed transport of the electronic liquids under high pressure loading (together with an initial electric field) along a wavy-rough nanotube of r_o (in mean-averaged outer radius) with the outer interface or wall being a fixed wavy-rough surface : $r = r_o + \epsilon \sin(k_w \theta)$ where ϵ is the amplitude of the (wavy) roughness and k_w is the wave number: $k_w = 2\pi/L$ (L is the wavelength). Our interest is to calculate the (electrical) resistance along the shell-like microscopic interface or boundary. We can have (via the boundary perturbation series method [19,20]), after using the forcing parameter (as the force balance gives the shear stress at a radius r as $\tau = -r\delta(F)/2$ with $\delta(F)$ being the net external forcing)

$$\psi = -\left(\frac{r_o}{2\tau_0}\right)\delta(F), \quad \delta(F) = \left[\delta(F_e) \equiv \delta(\rho_e E_z) + \left(\frac{dp}{dz}\right)\right] \tag{2}$$

($\tau_0 = 2k_B T/V_A$ and $|-\delta(\rho_e E_z)|$ is the net electric force along the axis of the cylindrical domain or the transport direction, ρ_e is the net charge density, and E_z (the only electric field) is presumed to be a constant or uniform, δF being composed of $\delta(F_e)$ and dp/dz which is the pressure gradient along the axis of the cylindrical domain or the transport direction) $\dot{\zeta} = \dot{\zeta}_0 \sinh(\psi) + \text{HOT}$ with the small wavy-roughness effect being the first order perturbation which is rather small and thus neglected (HOT means the higher order contributions [19,20]). Here the shear rate ($\dot{\zeta}$) is obtained by $|\dot{\zeta}| = |(dv/dn)| = |\nabla v \cdot \mathbf{n}| = |\nabla v \cdot [\nabla(r - r_o - \epsilon \sin(k_w\theta))/|\nabla(r - r_o - \epsilon \sin(k_w\theta))|]|$, with v being the rate of deformation (or velocity) in the longitudinal (z-) direction of the nanotube [19,20]. $K_0\nu_0$ in Eq. (1) is temperature dependent and the value could be traced before [19,20]. We noticed that the above flow law is highly nonlinear. There are difficulties in selecting parameters for experimental condition or process, such as dp/dz and V_A. Nevertheless, once the approximate shear stresses or shear rates and activation energies were tabled together with the (electrical) resistances in previous experiments, we can fix all necessary parameters for corresponding temperature (T). The main task is to fix the value of ψ by prescribing r_o and $|\delta(\rho_e E_z)|$ (as well as $|dp/dz|$) with different temperatures. The shear viscosity is calculated via $\tau/\dot{\zeta}$. After all these, the remaining in Eq. (1) is the unique relationship between V_A and T for a fixed τ (which is proportional to the electrical resistance ρ_R [19,20]). Note that r_o is of the order of magnitude around 0.2 μm here considering the sample size in [10] and most of the mathematical derivations could be found before [19,20].

3. Numerical results and discussion

We first verify our approach by comparing our numerical results with previous measurements considering normalized (electrical) resistances. As shown in Fig. 1, we select an activation energy 6×10^{-20} J (symbol: circles and squares) considering (electrical) resistances measured by Drozdov et al. [1] (cf. Fig. 1 (b) therein). Drozdov et al.'s (electrical) resistance measurements (symbol: upper triangles for sulfur deuteride at 164 GPa, symbol: lower triangles for sulfur hydride at 177 GPa [1]) were normalized with respect to that at temperature (T): 200 K. Our numerical data were also normalized with respect to that at temperature (T): 200 K. To let the readers easily capture the physical trend of our calculated normalized (electrical) resistances between different temperatures, we connect each symbol via a dashed line. T_c for sulfur deuteride at 164 GPa and sulfur hydride at 177 GPa are $\approx$ 90 and 185 K, respectively. We can observe that the comparison of temperature-dependent normalized (electrical) resistances ($\rho_R/\rho_R(200\text{ K})$) between Drozdov et al.'s and ours show rather good fit and thus confirms our present approach. To make comparison with Drozdov et al.'s newest measurements [10] we firstly show in Fig. 2 our calculations after selecting an activation energy 1.5×10^{-20} J (symbol: circles) considering (electrical) resistances measured by Drozdov et al. [10] (cf. extended data Fig. 2 (a) therein). Drozdov et al.'s (electrical) resistance measurements [10] (symbol: lower triangles for