The quantum nature of the superconducting hydrogen sulfide at finite temperatures

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H2S is believed to the most possible high-temperature superconducting (Tc) phase of hydrogen sulfide at ~200 GPa. It’s isotope substitution of hydrogen (H) by deuterium (D), however, shows an anomalous Tc decrease of ~100 K at 140 to 160 GPa, much larger than the Bardeen-Cooper-Schrieffer theory prediction. Using ab initio path-integral molecular dynamics (PIMD), we show that the nuclear quantum effects (NQEs) influence the structures of H2S and D2S differently at finite temperatures and the interval when H2S possesses the symmetric high Tc structure while D2S does not is in agreement with, though their absolute values are lower than experiments. This is consistent with an earlier theoretical study using the stochastic self-consistent harmonic approximation method in descriptions of the nuclei at 0 K. The remaining discrepancy can be substantially improved when the electronic structures are calculated using a hybrid function. Our study presents a simple picture to interpret the isotope dependent of Tc and emphasizes the quantum nature in the high-pressure hydrogen sulfide system.

I. INTRODUCTION

A superconductor is a material which exhibits zero electric resistance under a transition temperature (Tc), i.e. Tc. Ever since its discovery in mercury in 1911 [1], understanding the mechanism of this behavior and seeking for high-Tc superconductor have ranked among the biggest challenges in physics. Stimulated by the isotopic dependence of Tc observed in a wide range of superconductors, Bardeen, Cooper, and Schrieffer (BCS) proposed the microscopic picture of electron-phonon coupling in their seminal work in the 1950s [2,3], which explains the mechanism of most superconductors discovered by then. In 1986, a record-high 133 K Tc was found in copper oxide at ambient pressure [4], followed by a 164 K Tc in a similar system under pressure [5], and the discovery of a series of alike superconductors [6,8]. At present, the superconducting nature for most of these later found superconductors remains unclear. Consequently, it is customary to call the superconductors whose superconducting behaviors can be explained by BCS theory as the conventional ones.

Since BCS theory gives a clear guide to design high Tc conventional superconductors, (i.e. a high density of states close to the Fermi level, a favorable combination of high-frequency phonons, and a strong electron-phonon coupling), metallic hydrogen and hydrogen-rich compounds were naturally chosen as the target [9,10]. Accordingly, a series of theoretical studies on hydrogen and hydrides had been carried out (SiH4[10], SiH4[10], GeH3[11], GeH2[12], KH6[13], CaH6[14], etc). The crystal structure searching methods had played a crucial role [14,10]. For example, a high Tc value of 98 to 107 K was predicted in SiH4(H2)2 at 250 GPa (using a Coulomb parameter µ∗ = 0.1 – 0.13, hereinafter, see references for the details) [17]. In GeH4(H2)2, a Tc value of 76 to 90 K was predicted at 250 GPa [18]. In MH3 (M= Ga, Ge, Si) hydrides, Tc values scattering from 76 K to 153 K were reported [11,19,20]. In CaH6, a record-high Tc of 220 to 235 K was reported at 150 GPa [14]. In spite of these exciting theoretical results, it is fair to say that the system which has attracted most attention resides on the recent discovered hydrogen sulfides [21,27], especially after its experimental observation of a 203 K Tc based on direct transport measurement [28].

Now, a consensus has been reached that the stable compound of hydrogen and sulfur at ambient pressure, i.e. H2S, becomes unstable at high pressures. The superconducting behavior at 200 GPa is very likely due to its decomposition to H2S [22,23,25,27]. Comparisons of the ab initio static enthalpy based on density-functional theory (DFT) calculations (using the PBE functional) have shown that the stoichiometry decomposition of H2S to H2S and S happens at 43 GPa, and H2S remains stable at least up to 300 GPa [29]. Within this stability range of H2S, an orthorhombic Cccm structure dominates the group state between 43 and 112 GPa. Then, the rhombohedral R3m phase takes over and it remains most stable till 175 GPa. After 175 GPa, the cubic Im3m structure becomes the most stable phase. Calculations of the Tc based on BCS theory using this Im3m structure of H2S (D3S), in the mean time, show that this value can be as high as ~200 K (~160 K). In experiments, the Tc of H2S (D3S) was measured to be ~190 K (~150 K) at 170 GPa [28]. This agreement provides an excellent rationalization of the high Tc phase with the Im3m structure.
We note, however, that an isotope-dependence for the transition pressure to high \( T_c \) exists in experiment, i.e. \( \text{H}_2\text{S} \) enters into the high \( T_c \) region by \( \sim 20 \) GPa earlier than \( \text{D}_2\text{S} \) \[28\]. Considering the fact that these theoretical studies are mostly based on static geometry optimizations, the isotope-dependence of the experimental observation, especially the intrinsic anharmonic effects and the nuclear quantum effects (NQEs), are rarely discussed.

Recently, using the stochastic self-consistent harmonic approximation (SSCHA) method for the treatment of nuclear motion \[29, 30\], Errea et al. showed that the phonon spectra of \( \text{H}_2\text{S} \) are highly anharmonic and the anharmonic correction to the phonon spectra has a non-negligible influence on the values of \( T_c \) \[24\]. When taking into account of their contribution to the free-energy as the hydrogen (H) moves along hydrogen-bond, they further demonstrated that the hydrogen-bond symmetrization in superconducting \( \text{H}_2\text{S} \) has a strong quantum nature \[31\]. Upon replacing H by its isotope deuterium (D), which has only one extra neutron and therefore possesses less NQEs, the pressure with which the system transforms to the symmetric \( \text{Im}3\text{m} \) structure increases by 12 GPa at 0 K. Considering the fact that \( T_c \) of the asymmetric rhombohedral \( \text{R}3\text{m} \) phase has a much lower \( T_c \) than the cubic \( \text{Im}3\text{m} \) phase, this quantum symmetrization of the hydrogen position along the S-H···S axis presents a clear picture for the isotope-dependence of the transition pressure with which \( T_c \) suddenly increases in \( \text{H}_2\text{S} \) and \( \text{D}_2\text{S} \). Their absolute values are still lower than the experimental observation by \( \sim 50 \) GPa. We note that this idea of quantum symmetrization was originally proposed in studies of high-pressure \( \text{H}_2\text{O} \) \[32, 33\], and \textit{ab initio} path-integral molecular dynamics (PIMD) simulations have played an important role in their rationalization \[34\]. Confirmation of this picture and providing more physical insight to this phase transition by going to finite \( T_s \), using methods like \textit{ab initio} PIMD, are necessary. In addition to this, the PBE functional was used in descriptions of the electronic structure in Ref. \[31\] where the SSCHA method was used at 0 K. The remaining discrepancy with experiments can be substantially decreased when the electronic structures are described beyond PBE. Our study presents a simple picture to interpret the isotope-dependent of \( T_c \), rationalizes the remaining discrepancy with experimental using higher-level structures, and emphasizes the quantum nature of the high-pressure hydrogen sulfide system.

The paper is organized as follows. The computation details are given in Sec. II. In Sec. III, we presents our results on the quantum nature of the S-H···S axis symmetrization, as well as an analysis of the influence of functionals. We draw our conclusions in Sec IV.

\section{II. Computational Details}

Our simulations were preformed using the Vienna \textit{ab initio} Simulation Package (VASP) code \[37, 38\], along with our own implementation of the PIMD method \[39\] \[44\]. DFT was used to describe the electronic structure “on-the-fly” as the path of the nuclei propagates. Projector augmented wave (PAW) potentials along with a 700 eV energy cutoff were employed for the expansion of the electronic wave functions \[45, 46\]. The Perdew-Burke-Ernzerhof (PBE) functional was used to describe the electronic exchange-correlation interaction \[35\]. With a supercell containing 96 atoms and a Monkhorst-Pack k-point mesh of spacing \( 2\pi \times 0.04\text{Å}^{-1} \) to sample the Brillouin zone, we performed \textit{ab initio} PIMD simulations at 90 and 160 K. The Andersen thermostat was chosen to control the temperature of the NVT ensemble \[47\], in which the atomic velocities were periodically randomized with respect to the Maxwellian distribution every 60 fs.

For the reported results, 16 beads were used. All statistics of the bond length were obtained using the centroid of the path, and we note that using the bond lengths in the individual beads gives the same results. The PBE exchange-correlation functional used in the PIMD simulations suffers from self-interaction errors, which may induce a substantial underestimation of the transition-state energy \[36\]. We investigate this effect by focusing on the transition barrier and transition distance of the hydrogen atoms as they move along the S-H···S axis between their equivalent positions, and comparing the values obtained using the PBE and the hybrid HSE06 functional \[48, 49\]. In determining these energy barriers, the climbing image nudged elastic band (cNEB) method was used \[50\], in which all force components that perpendicular to the tangent of the reaction path were reduced to less than 0.01 eV/Å.
III. RESULTS AND DISCUSSIONS

IIIa. Quantum Nature of the Phase-Transition

We start by looking at the structures of the rhombohedral R3m phase and the cubic Im3m phase at the static level. Although being rhombohedral, R3m is very close to cubic symmetry. This can be evidenced by looking at the rhombohedral angle of R3m, which is 109.5142, 109.5476, and 109.5592, respectively at 140 GPa, 150 GPa, and 160 GPa, in comparison with the value of 109.47° for a perfect bcc lattice. Therefore, we visualize the difference between the structures of these two phases in Fig. 1(a) and b), using a slightly distorted bcc cell of the R3m phase and the conventional bcc cell of the cubic Im3m phase. The S atoms stay on a slightly distorted bcc lattice in the R3m phase and the conventional bcc lattice in the Im3m phase. The difference between these two lattices is visually indistinguishable. The H atoms, however, show very different behaviors. In the R3m phase, the H atoms stay asymmetrically along the S-H···S axis, being closer to one S atom. If we label the covalent bond length S-H as d1 and the distance between the H atom and its next nearest S atom as d2, these two distances are unequal. In the Im3m phase, however, they are symmetric, with d1 = d2. Therefore, the main change happened during the phase transition from the R3m phase to the Im3m phase, lies on the symmetrization of S-H···S, instead of the rhombohedral to cubic lattice evolution. This can be clearly seen in Fig. 1(c) and d), where we show that using a rhombohedral lattice for the symmetric structure (R3m) or a cubic lattice for R3m (fixR3m) has negligible effect on enthalpy differences of these two phases, and by imposing rhombohedral or cubic lattice for R3m, the symmetrization happens at very close pressures. In Ref. 31, a cubic cell has been used in discussion of the phase transition in. Here, we adopt a rhombohedral cell in discussions of the classical and quantum nuclear effects at finite Ts. By comparing with their results, one will see that the quantum feature of hydrogen-bond symmetrization is robust with respect to this choice of the simulation cell.

Now we include the nuclear statistical effects at the classical level. This is done by carrying out the ab initio molecular dynamics (MD) simulations at 90 K for a supercell of the R3m phase. We define a H transfer coordinate δ = d1 − d2. When it is zero, the hydrogen bond is symmetric and the H atom is equally shared by the two S atoms. When it is large in magnitude on both positive and negative sides, the H belongs to one S atom. The results are shown in Fig. 2(a) and b). It is clear that although the hydrogen bond symmetrization happens at ~170 GPa at the static level, this transition pressure is substantially decreased at a finite T upon including the nuclear classical statistical effects. At 140 GPa, the probability distribution (P(δ)) has two clear peaks at δ equals ±0.2 Å, indicating that the hydrogen bonds are still asymmetric. At 150 GPa, it has a single peak at δ = 0, a clear indication of hydrogen bond symmetrization. Therefore, the symmetrization of the hydrogen bond happens in between 140 and 150 GPa, when the nuclear classical statistical effects are included at 90 K. This symmetrization is also confirmed by the corresponding single-peak (double-well) structure, indicating that the hydrogen bonds are still not symmetric. At 100 GPa, however, the single-peak (single-well) structure already appeared, meaning that the hydrogen bond symmetrization happened. Therefore, the transi-
FIG. 2. Symmetrization of the hydrogen bonds. Using the H transfer coordinate (defined as $\delta = d_1 - d_2$), the probability distribution $P(\delta)$ and the free-energy profile $\Delta F(\delta)$ are plotted to the left and right scales based on *ab initio* MD and *ab initio* PIMD simulations at 90 K. Panels a) and b) correspond to results using classical nuclei, where the upper bound for the asymmetric structure and lower bound for the symmetric structure are reported within numerical resolution of 10 GPa. Panels c) and d) correspond to results obtained using quantum nuclei for D$_3$S. And panels e) and f) correspond to results obtained using quantum nuclei for H$_3$S.

We note that these values for H$_3$S and D$_3$S are lower than the transition pressures of 103 and 115 GPa when quantum nuclei are used at 0 K. To investigate in more detail the T-dependence of this transition pressure, we carried out a separate series of *ab initio* MD and *ab initio* PIMD simulations at 160 K. Using right- and left-solid triangles, we label the upper and lower bound for the asymmetric structure and lower bond for the symmetric structure in Fig. 3 along with results discussed earlier for the 90 K simulations. The results reported for classical nuclei and quantum nuclei (both D$_3$S and H$_3$S) at 0 K in Ref. 31 were also labelled using diamond, solid circle, and open circle respectively. From these figure, it is clear that while being consistent with the isotope-dependence of the symmetrization pressure as reported in Ref. 31 our simulations also show that the symmetrization happens at lower pressures upon increasing T. This is also in agreement with a series of earlier hydrogen bond symmetrization study of ice under pressure 32, 34, 51. Considering the fact that symmetric Im3m phase exhibits a much higher $T_c$ than the asymmetric R3m phase when calculations based on BCS theory is used 22, this presents a clear picture for the isotope-dependence of the transition pressure of H$_3$S and D$_3$S to the high $T_c$ phase 28. In comparison with the results obtained using classical nuclei, the hydrogen bonds in H$_3$S are strongly quantum in nature.

FIG. 3. T-dependence of the hydrogen bond symmetrization using classical nuclei, and quantum nuclei for D$_3$S and H$_3$S. The upper (lower) bounds of the asymmetric (symmetric) hydrogen bonds are labelled using left-(right-)oriented triangles respectively. Two series of *ab initio* MD and *ab initio* PIMD simulations are reported. The results from Ref. 31 for classical nuclei and quantum nuclei (D$_3$S and H$_3$S) at 0 K were labelled using blue upward triangle, green half square, and black half circle.

IIIb. Deficiency of PBE Functional

In spite of the qualitatively excellent agreement between the theoretical and experimental results, as reported above and in Ref. 31 a large discrepancy still exists. The predicted symmetrization happens at a pressure ~60 GPa lower than the experimental observation. Considering the fact that the proton-transfer energy barriers and the distance of proton transfer play an important role for such a symmetrization 31, and the PBE functional used here and in Ref. 31 is well-known to underestimate the transition state (TS) energy in description of the chemical reactions 36, it is reasonable to expect that the deficiency of the PBE functional plays a key role on the underestimation of this transition pressure. Based on this consideration, we investigate the functional-dependence of the symmetrization pressure.

For periodic system, the easiest way to check this underestimation of the TS energy, mostly due to the delocalization error 36, is to compare the results obtained from the hybrid-functional calculations with those obtained from the standard local-density approximation (LAD) or generalized-gradient approximation (GGA) calculations. However, considering the fact that the com-
computational cost of performing a hybrid-functional based PIMD simulation is beyond what we can afford, we carried out such an analysis at the static level. The cNEB method is used to find the TS for the H atom transfer from one S atom to the other. The energy-profiles are shown in Fig. 4 for the simulation at 100 GPa. From this figure, it is clear that the PBE functional has underestimated the proton transfer energy barrier by 50% in comparison with the HSE06 based results. Considering the fact that partial exact-exchanges are included in this hybrid-functional, which helps to cure the artificial electron charge delocalization induced by self-interaction [36], this is a clear indication that PBE has underestimated the proton transfer energy barrier. Consequently, when the ab initio PIMD simulations are performed using electronic structures provided by the DFT calculations using PBE functional, a systematic underestimation of the symmetrization pressure occurs. We note that a similar underestimation of the transition pressure also happens in the molecular liquid dissociation to the atomic liquid phase in high-pressure hydrogen, as pointed out in Ref. [40]. Upon including more exact-exchange interaction in this HSE-based functional, this underestimation is even more serious. Therefore, we believe that the right answer for proton transfer energy barrier must lie somewhere much higher than the PBE result. A quantitative determination of this value requires more sophisticated electronic structure methods, which is beyond the scope of the present paper.

Finally, despite hybrid-functional based ab initio PIMD simulations are beyond the computational cost we can afford, due to the fact that extend of proton delocalization is sensitive to the area below the proton transfer energy profile, an estimation of the symmetrization pressure can be provided. An estimator $\Delta S = d \times \Delta E$, as the descriptor. The upper horizontal line at $\Delta S \sim 5$ indicates the situation when $H_3S$ symmetrization is confirmed. The upper horizontal line at $\Delta S \sim 2$ indicates the situation when $D_3S$ symmetrization is confirmed. Based on this extrapolation, we estimate that using the HSE function will increase the symmetrization pressure of $H_3S$ ($D_3S$) by 21 (25) GPa, toward the experimental results.

FIG. 4. TS searching based on the cNEB method for the proton transfer process. The red squares are obtained using HSE06. The black triangles are obtained using PBE. Upon including partial exact exchange, the proton transfer barrier and the proton transfer distance increase. This is a clear indication that self-interaction substantially underestimates these quantities, and consequently underestimates the symmetrization pressure.

FIG. 5. Estimation of the symmetrization pressure, using $\Delta S = d \times \Delta E$, as the descriptor. The upper horizontal line at $\Delta S \sim 5$ indicates the situation when $H_3S$ symmetrization is confirmed. The upper horizontal line at $\Delta S \sim 2$ indicates the situation when $D_3S$ symmetrization is confirmed. Based on this extrapolation, we estimate that using the HSE function will increase the symmetrization pressure of $H_3S$ ($D_3S$) by 21 (25) GPa, toward the experimental results.
the PBE functional, so that further theoretical studies could be aware of in such simulations.

CONCLUSIONS

Based on ab initio MD and ab initio PIMD simulations, we systematically investigate the influence of nuclear statistical effects on the symmetrization of H$_3$S and D$_3$S with classical and quantum nuclei at finite $T_c$. The accuracy of standard GGA functional was analyzed by comparing the PES of the hydrogen along the S-H···S axis with the hybrid ones. Our simulations show that NQEs influence the structures of H$_3$S and D$_3$S differently and the interval when H$_3$S possesses the symmetric high $T_c$ structure while D$_3$S does not is in agreement with, though their absolute values are lower than the experimental observations. These results at 90 and 160 K are consistent with a earlier theoretical study in Ref. [31] where the SSCHA method was used at 0 K. The remaining discrepancy with experiments can be substantially decreased when the hybrid-functional is used. This study presents a simply picture to interpret the isotope-dependent of $T_c$. In the meantime, it also rationalizes the remaining discrepancy with experiments by pointing out the deficiency of the PBE functional, and emphasizes the quantum nature of the high-pressure hydrogen sulfide system.

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