High temperature superconductivity in the candidate phases of solid hydrogen

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Received 4 October 2021, revised 22 December 2021
Accepted for publication 18 January 2022
Published 10 February 2022

Abstract

As the simplest element in nature, unraveling the phase diagram of hydrogen is a primary task for condensed matter physics. As conjectured many decades ago, in the low-temperature and high-pressure part of the phase diagram, solid hydrogen is expected to become metallic with a high superconducting transition temperature. The metallization may occur via band gap closure in the molecular solid or via a transition to the atomic solid. Recently, a few experimental studies pushed the achievable pressures into the 400–500 GPa range. There are strong indications that at some pressure in this range metallization via either of these mechanisms occurs, although there are disagreements between experimental reports. Furthermore, there are multiple good candidate crystal phases that have emerged from recent computational and experimental studies which may be realized in upcoming experiments. Therefore, it is crucial to determine the superconducting properties of these candidate phases.

In a recent study, we reported the superconducting properties of the $C2/c$-24 phase, which we believe to be a strong candidate for metallization via band gap closure (Dogan \textit{et al} 2022 \textit{Phys. Rev. B} \textbf{105} L020509). Here, we report the superconducting properties of the $Cmca$-12, $Cmca$-4 and $I4_1/amd$-2 phases including the anharmonic effects using a Wannier function-based dense $k$-point and $q$-point sampling. We find that the $Cmca$-12 phase has a superconducting transition temperature that rises from 86 K at 400 GPa to 212 K at 500 GPa, whereas the $Cmca$-4 and $I4_1/amd$-2 phases show a less pressure-dependent behavior with their $T_c$ in the 74–94 K and 307–343 K ranges, respectively. These properties can be used to distinguish between crystal phases in future experiments. Understanding superconductivity in pure hydrogen is also important in the study of high-$T_c$ hydrides.

Keywords: superconductivity, hydrogen, high-pressure, metallization, first-principles

Supplementary material for this article is available online
(Some figures may appear in colour only in the online journal)
of solid hydrogen. It has proven challenging to determine the crystal structures of the molecular and atomic phases both theoretically and experimentally. Also, the pressure at which the transition to the atomic phase occurs is similarly difficult to predict and turns out to be high enough to be approachable only recently after several decades of advances in diamond anvil cell techniques. To complicate matters even further, it is possible that a series of structural phase transitions occur in solid hydrogen as the pressure increases, instead of a single transition from a molecular to an atomic phase.

On the theoretical front, several candidates for the molecular and atomic phases were discovered in the early 2000s.
Figure 3. Phonons and electron-phonon coupling for Cmca-4 at 500 GPa. The phonon dispersion relations for the Cmca-4 phase of hydrogen at 500 GPa pressure (left panel). The harmonic and anharmonic calculations are shown by red dashed lines and blue solid lines, respectively. The Eliashberg function $\alpha^2F$ and the electron–phonon coupling parameter $\lambda(\omega)$ (middle panel), and the PhDOS (right panel).

Figure 4. Phonons and electron-phonon coupling for I41/amd-2 at 500 GPa. The phonon dispersion relations for the I41/amd-2 phase of hydrogen at 500 GPa pressure (left panel). The harmonic and anharmonic calculations are shown by red dashed lines and blue solid lines, respectively. The Eliashberg function $\alpha^2F$ and the electron–phonon coupling parameter $\lambda(\omega)$ (middle panel), and the PhDOS (right panel).

In the following two decades, with the usage of increasingly complex computational methods that allow for more accurate enthalpy comparisons as well as input from experiments, the number of candidates was reduced, and the three molecular phases ($C2/c$-24, Cmca-12, Cmca-4) and one atomic phase ($I41/amd$-2) emerged as the most promising candidates (number after the dash denotes the number of atoms in the unit cell) [7–16]. Solid molecular hydrogen starts out as a semiconductor, and with increasing pressure, several things may occur that would result in metallization: the same crystal phase may become semimetallic and then metallic via band gap closure, a structural phase to another molecular phase (which is semimetallic or metallic) may occur, or a structural phase to an atomic phase may occur. Because there are multiple crystal phases within a few meV of each other in enthalpy at the relevant pressures, and the choices about the treatment of the quantum nature of the light hydrogen nuclei can make a difference in these values, computational studies cannot make a definitive prediction as to which of these scenarios should occur. However, computational studies have
been able to pin down the several phases that are competitive in the 300–500 GPa range (C2/c-24, Cmca-12, Cmca-4 and I41/amd-2).

On the experimental front, the challenge has been increasing the pressure while maintaining the quality of the sample and making measurements. In the 2000s and 2010s, the accessible pressure range gradually reached 400 GPa, which resulted in the observation of black hydrogen (no transmission in the visible range, indicating that the direct band gap is below ≈1.5 eV) around 310–320 GPa [17-20], and later in the observation of increased conductivity around 350–360 GPa, indicating semimetallic behavior [21, 22]. Most recently, an experiment by Loubeyre et al [23] provided the most relevant data to help us determine the crystal structure in the 150–425 GPa range. Through infrared (IR) absorption measurements which track the vibron frequency and the direct electronic band gap, it was reported that the IR-active vibron frequency linearly decreases with pressure from 150 GPa to 425 GPa, indicating that in this pressure range a single phase remains stable. It was also reported that the direct band gap gradually decreases between 360–420 GPa, but abruptly drops below the minimum experimentally observable value of ≈0.1 eV. There are disagreements between the few experimental groups that conduct high-pressure experiments on solid hydrogen. However, there are also some agreements, specifically about the increased absorption in the 425–440 GPa range, i.e. the IR measurements around 425 GPa by Dias et al [21] and the Raman measurements around 440 GPa by Erements et al [22]. Not much has been claimed about what happens beyond 440 GPa, but it is possible that a phase transition to atomic metallic hydrogen occurs around 500 GPa [24, 25].

In a previous work [26], we presented a study of the evolution of the IR-active vibron frequencies in the C2/c-24 phase calculated in the anharmonic regime, which closely agree with the observations of Loubeyre et al [23] up to 425 GPa. We also showed that the observed changes in the direct band gap can be explained as a series of changes in the band structure as the pressure increases without postulating a structural phase transition at 425 GPa. Thus, hydrogen may remain in the C2/c-24 phase beyond 425 GPa, possibly up to 500 GPa. However, it is also possible that as predicted by Dias et al [21], a structural phase transition occurs to a phase with two lower vibron frequencies with a difference of 300 cm⁻¹. Both the Cmca-12 and Cmca-4 phases have IR-active vibrons with approximately matching frequency differences [26]. Finally, the I41/amd-2 atomic phase is the strongest candidate for the atomic phase and may be the observed crystal structure around 500 GPa [15, 24, 25]. Among the four phases we have mentioned, the superconducting properties of the phases with the smaller unit cells (Cmca-4 and I41/amd-2) have been computationally investigated by others [6, 27, 28]. Because of the need for very dense k- and q-point samplings to obtain converged calculations (among other difficulties), the superconducting properties of the larger phases have remained elusive until recently. However, motivated by the developments in hydrogen-rich materials at high pressures that are breaking the records for superconducting temperatures [29-37], we recently reported an investigation into the superconducting properties of the C2/c-24 phase [38], and in this study, we focus on the Cmca-12 phase, as well as the Cmca-4 and I41/amd-2 phases.

Here, we investigate the electronic structure, vibrational properties, electron–phonon coupling and superconducting properties of solid hydrogen in the Cmca-12, Cmca-4 and I41/amd-2 phases at 400, 450 and 500 GPa using density functional theory (DFT) calculations in the generalized gradient approximation (GGA) [39-45], anharmonic corrections with the self-consistent phonon approach [46, 47] and a Wannier function-based dense k-point and q-point sampling [48] (see the supplemental material (https://stacks.iop.org/JPCM/34/15LT01/mmedia) for details).

The molecular phases Cmca-12 and Cmca-4 consist of van der Waals-bonded layers of H₂ molecules. The atomic phase consists of a highly symmetric two-atom cell. The electronic structures of the three phases differ qualitatively. Their Fermi surfaces and band structures at 500 GPa are shown in figure 1. At lower pressures, the Cmca-12 phase starts out as a semimetal, and the Fermi surface gets larger with new added sheets as the pressure increases [26]. The density of states at the Fermi energy is 0.013, 0.018 and 0.024 states/eV/atom for 400, 450 and 500 GPa respectively. By contrast, the Cmca-4 and I41/amd-2 phases have bands that cover both the valence and conduction bands, and their Fermi surfaces remain approximately fixed with increased pressure (~0.020 and ~0.036

### Table 1. Electron–phonon coupling constant and $T_c$. The electron–phonon coupling constant $\lambda$ and the superconducting transition temperature $T_c$ using both the Allen–Dynes formula and the isotropic Eliashberg theory are shown in the harmonic and anharmonic cases for 400, 450 and 500 GPa for the Cmca-12, Cmca-4 and I41/amd-2 phases. The Coulomb pseudopotential $\mu^*$ is set to 0.1 in all cases.

| Phase    | $P$ (GPa) | $\lambda$ (Harmonic) | $T_c$ (Allen–Dynes) (K) | $T_c$ (Eliashberg) (K) |
|----------|-----------|----------------------|-----------------------|------------------------|
|          |           | Harmonic | Anharmonic | Harmonic | Anharmonic | Harmonic | Anharmonic |
| Cmca-12  | 400       | 0.87     | 0.79       | 81       | 72         | 96       | 86         |
|          | 450       | 1.24     | 1.17       | 142      | 138        | 169      | 161        |
|          | 500       | 1.49     | 1.35       | 174      | 172        | 211      | 212        |
| Cmca-4   | 400       | 0.76     | 0.67       | 74       | 62         | 78       | 74         |
|          | 450       | 0.86     | 0.77       | 94       | 83         | 116      | 94         |
|          | 500       | 0.89     | 0.75       | 96       | 81         | 111      | 85         |
| I41/amd-2| 400       | 2.18     | 1.73       | 262      | 239        | 359      | 329        |
|          | 450       | 2.16     | 1.79       | 261      | 220        | 366      | 343        |
|          | 500       | 2.07     | 1.38       | 254      | 224        | 348      | 307        |
states/eV/atom for Cmca-4 and I4₁/amd-2, respectively). We note here that the GGA underestimates band gaps. A better treatment of excited states such as the GW approximation can increase band gaps by $\sim 1.5$ eV in this pressure range [7, 10] and should have a significant effect on the Cmca-12 phase. Nuclear quantum effects have the opposite effect reducing band gaps by smearing the positions of the potential wells, and this effect happens to be at similar magnitude [49, 50]. As a result of this accidental cancellation, we expect the computed $\lambda$ doubles from $\sim 1$ at 400 GPa to $\sim 2$ at 450 GPa [6, 51, 52]. A more recent study by Borinaga et al [27] found that $\lambda = 0.89$ in the harmonic approximation, which is close to our $\lambda = 0.86$. However, their reported anharmonic $\lambda$ is 2.00, which is much higher than our result, i.e. 0.77. This is likely due to the Fermi surface pockets around the $\Gamma$ and $R$ points found in these studies and not in the present study. Although the electronic and vibrational properties at the DFT and DFPT levels are computed to a higher precision in our study, we apply anharmonic corrections directly onto the static nuclear coordinates without attempting to modify these coordinates based on zero-point motion effects. Ultimately it is difficult to know if these Fermi surface pockets occur in the actual material, but if they do, then the superconducting properties should be enhanced as predicted by these earlier studies.

The phonon spectra of the I4₁/amd-2 phase at 500 GPa both in the harmonic and anharmonic approximations are presented in figure 4. We find that the anharmonic effects generally push up the phonon frequencies and reduce the electron–phonon coupling. The analogous plots for 400 and 450 GPa are presented in figures S5 and S6, respectively, and show the same general features. Our results for the I4₁/amd-2 phase generally agree with the previous work by McMahon and Ceperley [53], and also with Borinaga et al [28] who also found suppression of superconducting properties by anharmonicity.

All of the calculated electron–phonon coupling parameters ($\lambda$) and superconducting transition temperatures ($T_c$) resulting from the Allen–Dynes formula [54] ($\mu^* = 0.1$) are reported in table 1. We see that for the Cmca-12 phase, the $T_c$ values for harmonic and anharmonic cases are closer than the differences

Figure 5. $T_c$ and superconducting gap. (a) Superconducting transition temperature computed via isotropic Eliashberg equations for the Cmca-12, Cmca-4 and I4₁/amd-2 phases and the previously calculated C2/i-24 phase [38]. (b) Leading edge of the superconducting gap vs temperature for the Cmca-12, Cmca-4 and I4₁/amd-2 phases at 500 GPa in the harmonic and anharmonic approximations.
between harmonic and anharmonic $\lambda$, which is due to the $\omega_{\text{log}}$ values having the opposite trend. For the other two phases, the anharmonic effects reduce $\lambda$ and $T_c$ by similar amounts.

It is well known that the Allen–Dynes formula underestimates $T_c$ in this class of materials [38, 55]. We thus proceed to the isotropic Eliashberg calculations to determine the leading edge of the superconducting gap ($\Delta_0$) vs. temperature. Our resulting $T_c$ values are presented in Table 1 and figure 5(a) and a representative calculation at 500 GPa is presented in figure 5(b). In figure 5(a), the Eliashberg $T_c$ values taken from our previous study of the $C2/c$-24 are also presented for completeness. $T_c$ rapidly increases with pressure for the phases where the electronic density of states at the Fermi level also increases with pressure. These values and their pressure dependence can be used in experiments to distinguish between crystal phases.

Recently, theoretical efforts have been focused on proposing formulae that can predict superconducting properties from simple calculations. In this vein, a parameter called the networking value ($\phi$) based on the electron localization function (ELF) was proposed as highly correlated with $T_c$ in hydrides [55]. The parameter $\phi$ is obtained by finding the largest value of ELF for which the isosurface of ELF creates a connected network in all three spatial directions. In figures 6(a)–(c), we present the plot of the ELF isosurface at the networking value for the three phases in question at 500 GPa. Plotting all the anharmonic Eliashberg $T_c$ and $\phi$ values for the three phases plus the $C2/c$-24 phase [38], we arrive at figure 6(d). The linear fit results in a weak correlation with an $R^2$ value of 0.58. However, when we plot $T_c$ vs DOS@Ef (figure 6(e)), the correlation significantly improves to an $R^2$ value to 0.89. When many hydrides are compared (177 hydrides in ref [55]), $\phi$ provides a better correlation with $T_c$ than DOS@Ef, but we conclude that this measure cannot be used in a smaller sample, in particular, to compare the different crystal structures of the same hydride (in this case, hydrogen). As a final note, we present the dielectric function and reflectivity of the $Cmca$-12, $Cmca$-4 and $I4_1/amd$-2 phases at 500 GPa calculated in the random phase approximation in figure S7. Because it is very challenging to characterize these crystal structures using other methods, these additional data points may be useful for experiments that measure optical properties of high-pressure hydrogen samples.

In summary, we have found that the predicted superconducting transition temperatures for the $Cmca$-12 phase at 400, 450 and 500 GPa are 86, 161 and 212 K, respectively. This rise of $T_c$ with pressure is explained by the increase in the density of states at the Fermi level, which parallels the previously reported $C2/c$-24 phase [38]. On the other hand, $T_c$ has a more modest dependence on pressure for the $Cmca$-4 and $I4_1/amd$-2 phases.

Figure 6. Atomic structures, ELF isosurfaces taken at the networking values and dependence of $T_c$ on networking value. (a)–(c) The atomic structures of the $Cmca$-12, $Cmca$-4 and $I4_1/amd$-2 phases at 500 GPa, respectively. The unit cell is also shown as a frame. The ELF is plotted in the figures as isosurfaces with the networking value $\Phi$ (see main text for details). (d) $T_c$ vs $\Phi$ for the calculated phases as well as the previously reported $C2/c$-24 phase. (e) $T_c$ vs the density of states at the Fermi energy for the calculated phases as well as the previously reported $C2/c$-24 phase.
phases. We have also found that anharmonic corrections cause a slight to moderate reduction in the electron–phonon coupling and $T_c$ for all the studied phases. The current status of the theoretical and experimental research on solid hydrogen requires us to take all of these four crystal phases seriously as candidates in the 300–500 GPa range, with special attention given to the C2/c-24 and Cmc-12 phases. Our results indicate that by measuring superconducting properties on high-pressure hydrogen, experimental researchers can also determine the crystal structure, bringing us one step closer to elucidating the properties of the simplest material in nature under extreme conditions.

Acknowledgments

This work was supported primarily by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division, of the US Department of Energy under Contract No. DE-AC02-05-CH11231, within the Theory of Materials program (KC2301), which supported the structure optimization and calculation of vibrational properties. Further support was provided by the NSF Grant No. DMR-1926004 which supported the determination of electron–phonon interactions. Computational resources used were Cori at National Energy Research Scientific Computing Center (NERSC), which is supported by the Office of Science of the US Department of Energy under Contract No. DE-AC02-05-CH11231, Stampede2 at the Texas Advanced Computing Center (TACC) through Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation (NSF) under Grant No. ACI-1053575, Frontera at TACC, which is supported by NSF Grant No. OAC-1818253, and Bridges-2 at the Pittsburgh Supercomputing Center (PSC), which is supported by NSF Award Number ACI-1928147. We thank Hyungjun Lee for technical assistance with the EPW code.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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References

[1] Wigner E and Huntington H B 1935 On the possibility of a metallic modification of hydrogen J. Chem. Phys. 3 764
[2] Ashcroft N W 1968 Metallic hydrogen: a high-temperature superconductor? Phys. Rev. Lett. 21 1748
[3] Johnson K A and Ashcroft N W 2000 Structure and bandgap closure in dense hydrogen Nature 403 632
[4] Städele M and Martin R M 2000 Metallization of molecular hydrogen: predictions from exact-exchange calculations Phys. Rev. Lett. 84 6070
[5] Pickard C J and Needs R J 2007 Structure of phase III of solid hydrogen Nat. Phys. 3 473
[6] Cudazzo P, Profeta G, Sanna A, Floris A, Continenza A, Massidda S and Gross E K U 2008 Ab initio description of high-temperature superconductivity in dense molecular hydrogen Phys. Rev. Lett. 100 257001
[7] Lebègue S, Araujo C M, Kim D Y, Ramzan M, Mao H and Ahuja R 2012 Semimetallic dense hydrogen above 260 GPa Proc. Natl Acad. Sci. 109 9766
[8] Pickard C J, Martinez-Canales M and Needs R J 2012 Density functional theory study of phase IV of solid hydrogen Phys. Rev. B 85 214114
[9] Morales M A, McMahon J M, Pierleoni C and Ceperley D M 2013 Towards a predictive first-principles description of solid molecular hydrogen with density functional theory Phys. Rev. B 87 184107
[10] McMinis J, Clay R C, Lee D and Morales M A 2015 Molecular to atomic phase transition in hydrogen under high pressure Phys. Rev. Lett. 114 105050
[11] Drummond N D, Monserrat B, Lloyd-Williams J H, Rios P L, Pickard C J and Needs R J 2015 Quantum Monte Carlo study of the phase diagram of solid molecular hydrogen at extreme pressures Nat. Commun. 6 7794
[12] Monserrat B, Needs R J, Gregorzyan E and Pickard C J 2016 Hexagonal structure of phase III of solid hydrogen Phys. Rev. B 94 134101
[13] Azadi S, Drummond N D and Foulkes W M C 2017 Nature of the metallization transition in solid hydrogen Phys. Rev. B 95 035142
[14] Monserrat B, Drummond N D, Dalladay-Simpson P, Howie R T, López Ríos P, Gregorzyan E, Pickard C J and Needs R J 2018 Structure and metallicity of phase V of hydrogen Phys. Rev. Lett. 120 255701
[15] Zhang X-W, Wang E-G and Li X-Z 2018 Ab initio investigation on the experimental observation of metallic hydrogen Phys. Rev. B 98 134110
[16] Zhang C, Zhang C, Chen M, Kang W, Gu Z, Zhao J, Liu C, Sun C and Zhang P 2018 Finite-temperature infrared and Raman spectra of high-pressure hydrogen from first-principles molecular dynamics Phys. Rev. B 98 144301
[17] Loubye P, Occelli F and LeToullec R 2002 Optical studies of solid hydrogen to 320 GPa and evidence for black hydrogen Nature 416 613
[18] Howie R T, Guillaume C L, Scheler T, Goncharov A F and Gregorzyan E 2012 Mixed molecular and atomic phase of dense hydrogen Phys. Rev. Lett. 108 125501
[19] Eremets M I, Troyan I A, Lerch P and Drozdov A 2013 Study of hydrogen up to 310 GPa at room temperature Nat. Phys. 9 134110
[20] Loubye P, Occelli F and Dumas P 2013 Hydrogen phase IV revisited via synchrotron infrared measurements in H2 and D2 up to 290 GPa at 296 K Phys. Rev. B 87 144301
[21] Dias R P, Noked O and Silvera I F 2019 Quantum phase transition in solid hydrogen at high pressure Phys. Rev. B 100 184112
[22] Eremets M I, Drozdov A P, Kong P P and Wang H 2019 Semimetallic molecular hydrogen at pressure above 350 GPa Nat. Phys. 15 12
[23] Loubye P, Occelli F and Dumas P 2020 Synchrotron infrared spectroscopic evidence of the probable transition to metal hydrogen Nature 577 7792
[24] Dias R P and Silvera I F 2017 Observation of the Wigner–Huntington transition to metallic hydrogen Science 355 aea1579
[25] Silvera I F and Dias R 2018 Metallic hydrogen J. Phys.: Condens. Matter 30 254003
[26] Dogan M, Oh S and Cohen M L 2020 Observed metallization of hydrogen interpreted as a band structure effect J. Phys.: Condens. Matter 33 03LT01
