Structure and Metallicity of Phase V of Hydrogen

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Bartomeu Monserrat,[1,2,*] Neil D. Drummond,[3] Philip Dalladay-Simpson,[4] Ross T. Howie,[4] Pablo López Ríos,[2,5]
Eugene Gregoryanz,[4,6,7] Chris J. Pickard,[8,9] and Richard J. Needs[2]
[1]*Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854-8019, USA*
[2]*TCM Group, Cavendish Laboratory, University of Cambridge, J. J. Thomson Avenue, Cambridge CB3 0HE, United Kingdom*
[3]*Department of Physics, Lancaster University, Lancaster LA1 4YB, United Kingdom*
[4]*Center for High Pressure Science and Technology Advanced Research, Shanghai 201203, People's Republic of China*
[5]*Max-Planck Institute for Solid State Research, Heisenbergstraße 1, 70569 Stuttgart, Germany*
[6]*Centre for Science at Extreme Conditions and School of Physics and Astronomy,*
University of Edinburgh, Edinburgh EH9 3JZ, United Kingdom
[7]*Key Laboratory of Materials Physics, Institute of Solid State Physics,*
Chinese Academy of Sciences, Hefei 230031, People's Republic of China
[8]*Department of Materials Science and Metallurgy, University of Cambridge,*
27 Charles Babbage Road, Cambridge CB3 0FS, United Kingdom
[9]*Advanced Institute for Materials Research, Tohoku University 2-1-1 Katahira, Aoba, Sendai 980-8577, Japan*

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A new phase V of hydrogen was recently claimed in experiments above 325 GPa and 300 K. Because of the extremely small sample size at such record pressures the measurements were limited to Raman spectroscopy. The experimental data on increase of pressure show decreasing Raman activity and darkening of the sample, which suggests band gap closure and impending molecular dissociation, but no definite conclusions could be reached. Furthermore, the available data are insufficient to determine the structure of phase V, which remains unknown. Introducing saddle-point *ab initio* random structure searching, we find several new structural candidates of hydrogen which could describe the observed properties of phase V. We investigate hydrogen metallization in the proposed candidate structures, and demonstrate that smaller band gaps are associated with longer bond lengths. We conclude that phase V is a stepping stone towards metallization.

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The study of dense hydrogen is important to fundamental physics and astrophysics [1–4]. Currently the most interesting question relates to the metallization and dissociation of molecular hydrogen under pressure, which has not yet been achieved in the solid state, even though it was first proposed in 1935 [5]. The known phases I, II, III, and IV/IV′ of solid hydrogen, which have been characterized extensively experimentally [6–10] and theoretically [11–18], exhibit molecular bonds and are insulating.

Dalladay-Simpson and co-workers recently reported Raman spectroscopy experiments on H_2, D_2, and HD up to pressures of 388 GPa at 300 K [19]. In these experiments, they identified a new phase V of H_2 and HD above 325 GPa and at 300 K, which was suggested to be at the onset of dissociation and could therefore represent a stepping stone towards full metallization. Several experimental reports followed, claiming metallization of H_2 under different pressure-temperature conditions [20,21], but the validity of these experiments is yet to be confirmed [22,23]. In this Letter, we focus on phases IV, IV′, and V as described in Refs. [10,19].

On the theoretical front, a number of candidate structures have been proposed to explain the observed experimental phases of high-pressure hydrogen up to 300 GPa [11,13,24]. Of these, the monoclinic $C2/c$ structure is currently the best candidate for phase III around 300 GPa [11,24], as it exhibits Raman and infrared (IR) spectra consistent with those observed experimentally. The monoclinic Pc structure is the best candidate for phase IV [13] due to its mixed layered nature that leads to the two vibron peaks observed experimentally. Recent quantum Monte Carlo and free energy calculations have confirmed these phases to be energetically favorable in the pressure range in which phases III and IV are observed [18]. The most stable atomic hydrogen candidate structure is tetragonal and has space group $I4_1/amd$ [11,12,16,17]. Despite the large number of candidate structures known for high-pressure hydrogen, none provides a good model for the recent experimental observations at pressures above about 300 GPa.

Discovering candidate structures using searching methods has been successful in many systems, particularly at high pressure [25–29]. As an example, the lowest-enthalpy candidate structures for phases II, III, and IV of hydrogen have been found using the *ab initio* random structure searching (AIRSS) method [11,13]. The experimental discovery of phase V, for which there is no obvious candidate structure, prompts the question of whether it is necessary to go beyond current structure searching methods in this case.

Standard structure searching methods such as AIRSS are restricted to structures associated with minima of the potential energy landscape. However, thermodynamically stable structures associated with saddle points that are dynamically stabilized by anharmonic nuclear motion are known to exist [30,31]. The high-temperature cubic perovskite phase of $BaTiO_3$ provides a well-known example [30,32].

A variety of computational methods has been used to determine the dynamical stability of such structures, including Monte Carlo [32], molecular dynamics [33,34], path integral molecular dynamics [35,36], and local anharmonic vibrational methods [37–41]. These methods can determine the dynamical stability of a known saddle-point structure but they have not been used to find previously unknown saddle-point structures. The following question arises: can we devise a systematic approach to searching for previously unknown structures associated with saddle points of the energy landscape? The large nuclear effects of hydrogen make it an ideal system in which to explore this possibility.

We address these questions using saddle-point *ab initio* random structure searching (sp-AIRSS). Saddle-point structures stabilized by anharmonic nuclear motion are typically of higher symmetry than their *broken-symmetry* counterparts. Based on this observation, we use sp-AIRSS to impose high-symmetry constraints during structure searches. For example, imposing cubic symmetry on $BaTiO_3$, leads to the known cubic phase, but removing the symmetry constraints leads instead to the rhombohedral phase. The symmetry constraints bias the search towards the high-symmetry structures that are expected to be stable when the vibrational amplitudes are large. We emphasize that this strategy enables the discovery of structures which cannot be found in unconstrained searches because they correspond to minima of the free energy landscape but not of the static lattice energy landscape. We then remove the symmetry constraints and relax the reference structure using an anharmonic vibrational method. In this work we have used the vibrational self-consistent field method of Ref. [40], but any of the available anharmonic methods may be applicable at this stage of the calculation [32–41]. The structure may then relax to a minimum or saddle point of the potential energy landscape.

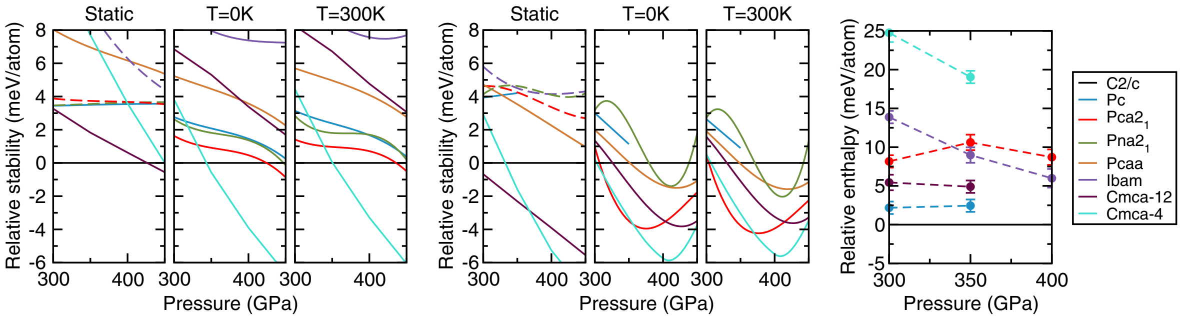
The lowest-enthalpy known hydrogen structures have monoclinic symmetry with space groups $C2/c$ (model for phase III) and Pc (model for phase IV) [11,13]. To search for new candidate structures we have therefore performed sp-AIRSS searches imposing space groups of orthorhombic or higher symmetry. The searches have led to the discovery of three new energetically competitive structures at pressures for which phase V is observed. These structures have orthorhombic symmetry with space groups $Pca2_1$, $Pna2_1$, and $Pcaa$, and 48 atoms in the primitive cell. $Pca2_1$ and $Pna2_1$ are mixed layered structures similar to Pc in which alternate layers exhibit shorter and longer molecular bond lengths, resulting in two vibron peaks in the Raman and IR spectra. $Pcaa$ has a single type of layer.

Our analysis in this Letter is based on these three new structures, together with the previously reported structures $C2/c$ [11], $Cmca$-4 and $Cmca$-12 [11] (where 4 and 12 indicate the number of atoms in the primitive cell), Pc [13] and $Ibam$ [11]. The $C2/c$ and $Cmca$ structures model phase III and all theoretical methods predict that $C2/c$ is more stable at lower pressures and $Cmca$ at higher pressures, but the precise pressure above which $Cmca$ becomes stable is highly dependent on the level of theory used. An hexagonal structure of space group $P6_122$ has recently been proposed as a candidate for phase III at pressures below 200 GPa [24], but in this work we focus on higher pressures, and therefore do not include it in our analysis. The $Ibam$ structure is an extreme member of the family of mixed structures, in which the weakly bound layer is graphenelike and molecular bonds are no longer present.

Of all structures considered, $Pna2_1$ and $Pca2_1$ are dynamically unstable at the harmonic vibrational level, and their broken-symmetry counterpart is a monoclinic structure. $Ibam$ is also dynamically unstable, while the rest are dynamically stable. Note that unless sp-AIRSS had been used, $Pca2_1$ and $Pna2_1$ would have fallen into the corresponding broken-symmetry monoclinic structure, and would have gone unnoticed. The symmetry constraints prevent this and allow the potential discovery of new structures stabilised by anharmonic vibrations.

We have used first-principles methods based on density functional theory (DFT) as implemented in the CASTEP [42] code to calculate the relative stability of the eight structures under consideration. We have used both the BLYP exchange-correlation functional [43,44], which has been shown to be accurate for the description of molecular hydrogen structures [45], and the PBE exchange-correlation functional [46], which we find to favor atomic phases compared to the BLYP functional. Because of the small energy differences between competing structures of only a few meV, the resulting phase diagrams are sensitive to the level of theory used [18,45,47]. We therefore also perform selected diffusion Monte Carlo (DMC) calculations using the CASINO package [48] to establish the validity of our conclusions based on the DFT results. To calculate the vibrational contribution to the energy including anharmonic contributions we use the method of Refs. [40,49]. Further details of the first principles calculations are provided in the Supplemental Material [50].

In Figs. 1(a) and 1(b) we report static lattice enthalpies, zero-temperature enthalpies (including quantum zero-point motion), and Gibbs free energies at 300 K relative to $C2/c$ using DFT. The static lattice enthalpies of $Pca2_1$, $Pna2_1$, and $Ibam$ are shown as dashed lines to indicate dynamical



(a) BLYP functional. (b) PBE functional. (c) DMC.

FIG. 1. Relative enthalpies using the (a) BLYP and (b) PBE DFT functionals, and using (c) DMC. The DFT results are at the static lattice level, at $T = 0$ K (including zero-point motion), and at $T = 300$ K, and the dashed lines in the static lattice diagrams indicate enthalpies corresponding to structures at saddle points of the energy landscape. The DMC results are at the static lattice level, and the dashed lines between the DMC points are a guide to the eye only.

instability at the harmonic level corresponding to saddle points of the potential energy landscape. All three structures become dynamically stable when lattice vibrations are included. We also show selected static lattice DMC calculations in Fig. 1(c).

For both BLYP and PBE calculations, we observe that the *Cmca*-4 structure is the lowest in energy at the higher pressures studied. This is consistent with earlier DFT studies, but we note that using more accurate DMC calculations destabilizes this structure and removes it from the phase diagram [see Fig. 1(c)]. The *Cmca*-12 structure is also destabilized within DMC, although to a smaller degree than the *Cmca*-4 structure.

The BLYP results show that, of the mixed layered structures, $Pca2_1$ is the most competitive energetically at both zero and 300 K, becoming more stable than $C2/c$ at pressures of about 420 GPa. The PBE results also favor $Pca2_1$ as the most stable mixed layered structure, but it becomes more stable than $C2/c$ at significantly lower pressures of about 300 GPa, consistently with the observation that PBE favours atomic phases compared to molecular phases ($Pca2_1$ has alternate layers with longer bond lengths than those observed in $C2/c$). We also note that, at the PBE level, *Pc* does not exist above about 375 GPa, as it falls into the *Cmca*-4 structure. Finally, we note that the *Pcaa* structure, which is not energetically competitive at the BLYP level, becomes more competitive at the PBE level, a fact that we again attribute to the longer bond lengths exhibited by *Pcaa* when compared to $C2/c$. Our static DMC calculations combined by the DFT vibrational energy estimates confirm that $Pca2_1$ remains energetically competitive as a candidate structure of high pressure hydrogen (see Supplemental Material [50]).

The experimental Raman spectrum of phase V is compared to the theoretical harmonic spectra of *Pc* and $Pca2_1$ calculated using the PBE functional in Fig. 2. Figure 2(a) shows a comparison of the Raman intensities at 374 GPa. In the high-frequency regime, the frequency of the experimental ν_2 vibron agrees with those of *Pc* and $Pca2_1$. The frequency of the ν_1 vibron is marginally better reproduced by *Pc* than by $Pca2_1$. We also note that Magdău and Ackland showed that anharmonic contributions push the ν_2 vibron to higher energies in *Pc* [15], and a similar behavior in $Pca2_1$ would bring the latter into better agreement with experiment. At the low-frequency regime the L_1 and L_4 modes of phase V are in better agreement with $Pca2_1$ than with *Pc*. The L_2 mode, which disappears

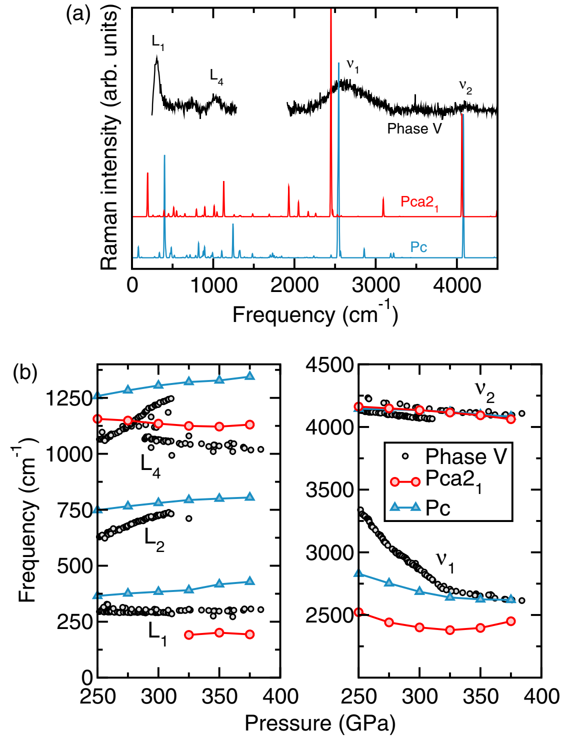


FIG. 2. (a) Raman spectra of *Pc*, $Pca2_1$, and phase V at 374 GPa. The absence of data in the range $1500 - 1900$ cm^{-1} arises from the strong signal from the diamonds at these frequencies. (b) Pressure dependence of the frequencies of the most intense Raman peaks of *Pc*, $Pca2_1$, and phase V.

upon entering phase V, is present in Pc but missing in $Pca2_1$.

The pressure dependence of the Raman peaks is shown in Fig. 2(b), with phase IV below 325 GPa, and phase V at higher pressures. The pressure dependence of the ν_2 vibron is well reproduced by both Pc and $Pca2_1$. The frequency of the low-energy vibron has a pressure dependence of $-1.4\ \mathrm{cm}^{-1}/\mathrm{GPa}$ in phase V above 325 GPa, which is much weaker than that of phase IV at lower pressures (note the change in slope for ν_1 around 325 GPa). The pressure dependence of ν_1 in Pc and $Pca2_1$ is too weak at pressures below 325 GPa, suggesting that they are not good candidates for phase IV. However, we note that, as discussed earlier, anharmonic effects significantly affect this frequency [15], and therefore we cannot discard these structures as candidates for phase IV. The pressure dependence of the low frequency part of the Raman spectrum of phase V is better reproduced by $Pca2_1$ than by Pc.

A striking feature of the experimental Raman spectrum is the dramatic increase in the width of the L_1 peak upon entering phase V, whose FWHM increases from about 70 cm^{-1} at 325 GPa to about 160 cm^{-1} at 388 GPa. The experimental data show that the increase in the peak width is strongly isotope dependent [19], suggesting a nuclear origin for this feature. Therefore, it could be attributed to a harmonic dynamical instability like the one exhibited by the $Pca2_1$ and $Pna2_1$ structures.

Our Raman spectra analysis suggests that the $Pca2_1$ structure is consistent with phase V. The Raman spectrum of $Pna2_1$ is almost identical to that of Pc, and both give poorer agreement with experiment than $Pca2_1$. The $C2/c$, $Cmca$, and $Pcaa$ structures cannot describe phase V, as they have a unique type of bond and thus a single vibron. $Ibam$ is also an unlikely candidate for phase V, as its vibron ν_1 has a frequency below 2250 cm^{-1} in the pressure range where phase V is observed. Details of the Raman spectra of these phases are provided in the Supplemental Material [50].

Overall, $Pca2_1$ is energetically competitive at the pressures at which phase V has been observed, and crucially, of all structures considered, only its Raman spectrum is consistent with that of phase V. More generally, the known Pc structure and the new $Pna2_1$ and $Pca2_1$ structures are plausible candidates for the high pressure hydrogen structures characterized by two strong vibrons, that is, phases IV, IV$'$, and V.

Having discovered good candidate structures, we study the metallicity of phase V. The study of band gap closure and metallization in high pressure hydrogen is a challenging problem. Band gaps are typically underestimated by several electronvolts by Kohn-Sham DFT [57,58], whereas the neglect of electron-phonon coupling contributions tends to lead to an overestimation of the gap size [59,60]. These two effects alter the gap in opposite directions, canceling to some extent. We consider static lattice DFT band structures, which contain valuable insights on trends amongst the different structures, but cannot be used reliably to estimate the actual band gap values.

Metallization in layered hydrogen structures has been proposed to arise from the weakly bound layers that can be described as distorted graphene sheets [61]. Here, we extend this analysis to mixed-layered structures, where layers with short and long bond lengths coexist. In Fig. 3(a) we show the electronic densities of states at 350 GPa for the four mixed layered structures considered in this work. Pc, $Pna2_1$, and $Pca2_1$ are all insulating. Of these four structures, $Pca2_1$ has the smallest band gap by about 0.3 eV. This is a consequence of the longer bond length in the weakly bound layers, as shown in Fig. 3(b). The bond lengths of all of these structures in the strongly bound layers are comparable.

Molecular dissociation is more pronounced in $Ibam$, as the weakly bound layers are graphenelike, and the molecular character is lost. This is shown by the longer bond lengths exhibited by $Ibam$ in the graphene sheets [Fig. 3(b)]. The frequency of the ν_1 vibron in $Ibam$ increases with pressure, as expected from the decreasing bond length of the graphene sheets. In contrast, the increase in bond length with pressure in Pc, $Pna2_1$, and $Pca2_1$

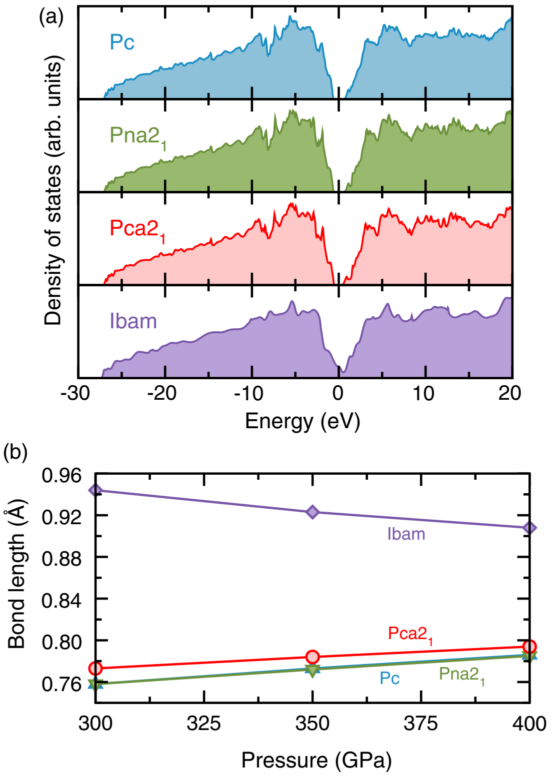


FIG. 3. (a) Electronic densities of states of hydrogen candidate mixed layered structures Pc, $Pna2_1$, $Pca2_1$, and $Ibam$ at a pressure of 350 GPa. (b) Static bond lengths of the Pc, $Pna2_1$, $Pca2_1$, and $Ibam$ structures for the layers with longer bonds. The bond lengths of Pc and $Pna2_1$ are indistinguishable.

indicates that the pressure dependence of the ν_1 vibron in these structures is qualitatively different from that of $Ibam$, and consistent with the experimental observation of phase V. $Ibam$ might become stable at higher pressures, although our DFT calculations do not support this conjecture.

For completeness, we emphasize that at 0 K, the metallic atomic $I4_1/amd$ structure is predicted to become thermodynamically stable at a pressure of around 400 GPa [16,17]. It would be interesting to assess the relative stability of $I4_1/amd$ with respect to the mixed structures around room temperature, but this is beyond the scope of the present work.

Overall, our energetic and spectroscopic results show that $Pca2_1$ is a promising model structure for hydrogen phase V. It exhibits longer bond lengths compared to those of other similar structures, suggesting that phase V is a stepping stone towards the metallization of hydrogen.

Supporting research data may be freely accessed following the link in Ref. [62].

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*bm418@cam.ac.uk

[1] N. W. Ashcroft, Metallic Hydrogen: A High-Temperature Superconductor?, Phys. Rev. Lett. **21**, 1748 (1968).

[2] I. F. Silvera, The solid molecular hydrogens in the condensed phase: Fundamentals and static properties, Rev. Mod. Phys. **52**, 393 (1980).

[3] J. M. McMahon, M. A. Morales, C. Pierleoni, and D. M. Ceperley, The properties of hydrogen and helium under extreme conditions, Rev. Mod. Phys. **84**, 1607 (2012).

[4] A. F. Goncharov, R. T. Howie, and E. Gregoryanz, Hydrogen at extreme pressures, Low Temp. Phys. **39**, 402 (2013).

[5] E. Wigner and H. B. Huntington, On the possibility of a metallic modification of hydrogen, J. Chem. Phys. **3**, 764 (1935).

[6] I. F. Silvera and R. J. Wijngaarden, New Low-Temperature Phase of Molecular Deuterium at Ultrahigh Pressure, Phys. Rev. Lett. **47**, 39 (1981).

[7] R. J. Hemley and H. K. Mao, Phase Transition in Solid Molecular Hydrogen at Ultrahigh Pressures, Phys. Rev. Lett. **61**, 857 (1988).

[8] M. I. Eremets and I. A. Troyan, Conductive dense hydrogen, Nat. Mater. **10**, 927 (2011).

[9] R. T. Howie, C. L. Guillaume, T. Scheler, A. F. Goncharov, and E. Gregoryanz, Mixed Molecular and Atomic Phase of Dense Hydrogen, Phys. Rev. Lett. **108**, 125501 (2012).

[10] R. T. Howie, T. Scheler, C. L. Guillaume, and E. Gregoryanz, Proton tunneling in phase IV of hydrogen and deuterium, Phys. Rev. B **86**, 214104 (2012).

[11] C. J. Pickard and R. J. Needs, Structure of phase III of solid hydrogen, Nat. Phys. **3**, 473 (2007).

[12] J. M. McMahon and D. M. Ceperley, High-temperature superconductivity in atomic metallic hydrogen, Phys. Rev. B **84**, 144515 (2011).

[13] C. J. Pickard, M. Martinez-Canales, and R. J. Needs, Density functional theory study of phase IV of solid hydrogen, Phys. Rev. B **85**, 214114 (2012); Erratum **86**, 059902(E) (2012).

[14] H. Liu, L. Zhu, W. Cui, and Y. Ma, Room-temperature structures of solid hydrogen at high pressures, J. Chem. Phys. **137**, 074501 (2012).

[15] I. B. Magdău and G. J. Ackland, Identification of high-pressure phases III and IV in hydrogen: Simulating Raman spectra using molecular dynamics, Phys. Rev. B **87**, 174110 (2013).

[16] S. Azadi, B. Monserrat, W. M. C. Foulkes, and R. J. Needs, Dissociation of High-Pressure Solid Molecular Hydrogen: A Quantum Monte Carlo and Anharmonic Vibrational Study, Phys. Rev. Lett. **112**, 165501 (2014).

[17] J. McMinis, R. C. Clay, D. Lee, and M. A. Morales, Molecular to Atomic Phase Transition in Hydrogen under High Pressure, Phys. Rev. Lett. **114**, 105305 (2015).

[18] N. D. Drummond, B. Monserrat, J. H. Lloyd-Williams, P. López Ríos, C. J. Pickard, and R. J. Needs, Quantum Monte Carlo study of the phase diagram of solid molecular hydrogen at extreme pressures, Nat. Commun. **6**, 7794 (2015).

[19] P. Dalladay-Simpson, R. T. Howie, and E. Gregoryanz, Evidence for a new phase of dense hydrogen above 325 gigapascals, Nature (London) **529**, 63 (2016).

[20] R. P. Dias and I. F. Silvera, Observation of the Wigner-Huntington transition to metallic hydrogen, Science **355**, 715 (2017).

[21] M. I. Eremets, A. P. Drozdov, P. P. Kong, and H. Wang, Molecular semimetallic hydrogen, arXiv:1708.05217.

[22] X.-D. Liu, P. Dalladay-Simpson, R. T. Howie, B. Li, and E. Gregoryanz, Comment on Observation of the Wigner-Huntington transition to metallic hydrogen, Science **357**, eaan2286 (2017).

[23] A. F. Goncharov and V. V. Struzhkin, Comment on Observation of the Wigner-Huntington transition to metallic hydrogen, Science **357**, eaam9736 (2017).

[24] B. Monserrat, R. J. Needs, E. Gregoryanz, and C. J. Pickard, Hexagonal structure of phase III of solid hydrogen, Phys. Rev. B **94**, 134101 (2016).

[25] C. J. Pickard and R. J. Needs, High-Pressure Phases of Silane, Phys. Rev. Lett. **97**, 045504 (2006).

[26] A. R. Oganov and C. W. Glass, Crystal structure prediction using *ab initio* evolutionary techniques: Principles and applications, J. Chem. Phys. **124**, 244704 (2006).

[27] Y. Wang, J. Lv, L. Zhu, and Y. Ma, Crystal structure prediction via particle-swarm optimization, Phys. Rev. B **82**, 094116 (2010).

[28] C. J. Pickard and R. J. Needs, *Ab initio* random structure searching, J. Phys. Condens. Matter **23**, 053201 (2011).

[29] D. C. Lonie and E. Zurek, Xtalopt: An open-source evolutionary algorithm for crystal structure prediction, Comput. Phys. Commun. **182**, 372 (2011).

[30] M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Oxford University Press, New York, 2001).

[31] G. Grimvall, B. Magyari-Köpe, V. Ozoliņš, and K. A. Persson, Lattice instabilities in metallic elements, Rev. Mod. Phys. **84**, 945 (2012).

[32] W. Zhong, D. Vanderbilt, and K. M. Rabe, Phase Transitions in $BaTiO_3$ from First Principles, Phys. Rev. Lett. **73**, 1861 (1994).

[33] B. J. Alder and T. E. Wainwright, Studies in molecular dynamics. I. General method, J. Chem. Phys. **31**, 459 (1959).

[34] R. Car and M. Parrinello, Unified Approach for Molecular Dynamics and Density-Functional Theory, Phys. Rev. Lett. **55**, 2471 (1985).

[35] J. Cao and G. A. Voth, The formulation of quantum statistical mechanics based on the Feynman path centroid density. I. Equilibrium properties, J. Chem. Phys. **100**, 5093 (1994).

[36] J. Cao and G. A. Voth, The formulation of quantum statistical mechanics based on the Feynman path centroid density. II. Dynamical properties, J. Chem. Phys. **100**, 5106 (1994).

[37] P. Souvatzis, O. Eriksson, M. I. Katsnelson, and S. P. Rudin, Entropy Driven Stabilization of Energetically Unstable Crystal Structures Explained from First Principles Theory, Phys. Rev. Lett. **100**, 095901 (2008).

[38] O. Hellman, I. A. Abrikosov, and S. I. Simak, Lattice dynamics of anharmonic solids from first principles, Phys. Rev. B **84**, 180301 (2011).

[39] N. Antolin, O. D. Restrepo, and W. Windl, Fast free-energy calculations for unstable high-temperature phases, Phys. Rev. B **86**, 054119 (2012).

[40] B. Monserrat, N. D. Drummond, and R. J. Needs, Anharmonic vibrational properties in periodic systems: Energy, electron-phonon coupling, and stress, Phys. Rev. B **87**, 144302 (2013).

[41] I. Errea, M. Calandra, and F. Mauri, Anharmonic free energies and phonon dispersions from the stochastic self-consistent harmonic approximation: Application to platinum and palladium hydrides, Phys. Rev. B **89**, 064302 (2014).

[42] S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. Probert, K. Refson, and M. C. Payne, First principles methods using CASTEP, Z. Kristallogr. **220**, 567 (2005).

[43] A. D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior, Phys. Rev. A **38**, 3098 (1988).

[44] C. Lee, W. Yang, and R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, Phys. Rev. B **37**, 785 (1988).

[45] R. C. Clay, J. Mcminis, J. M. McMahon, C. Pierleoni, D. M. Ceperley, and M. A. Morales, Benchmarking exchange-correlation functionals for hydrogen at high pressures using quantum Monte Carlo, Phys. Rev. B **89**, 184106 (2014).

[46] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized Gradient Approximation made Simple, Phys. Rev. Lett. **77**, 3865 (1996).

[47] S. Azadi and W. M. C. Foulkes, Fate of density functional theory in the study of high-pressure solid hydrogen, Phys. Rev. B **88**, 014115 (2013).

[48] R. J. Needs, M. D. Towler, N. D. Drummond, and P. López Ríos, Continuum variational and diffusion quantum Monte Carlo calculations, J. Phys. Condens. Matter **22**, 023201 (2010).

[49] J. H. Lloyd-Williams and B. Monserrat, Lattice dynamics and electron-phonon coupling calculations using nondiagonal supercells, Phys. Rev. B **92**, 184301 (2015).

[50] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.120.255701 for numerical details of the sp-AIRSS searches, of the anharmonic vibrational calculations, of the quantum Monte Carlo calculations, the Raman spectra of candidate structures, and cif files for the $Pca2_1$, $Pna2_1$, and $Pcaa$ structures relaxed within PBE at 350 GPa. It includes Refs. [51–56].

[51] D. Vanderbilt, Soft self-consistent pseudopotentials in a generalized eigenvalue formalism Phys. Rev. B **41**, 7892 (1990).

[52] J. O. Jung and R. B. Gerber, Vibrational wave functions and spectroscopy of $(H_2O)_n$, $n = 2, 3, 4, 5$: Vibrational self-consistent field with correlation corrections, J. Chem. Phys. **105**, 10332 (1996).

[53] J. M. Bowman, Self-consistent field energies and wave functions for coupled oscillators, J. Chem. Phys. **68**, 608 (1978).

[54] W. M. C. Foulkes, L. Mitas, R. J. Needs, and G. Rajagopal, Quantum Monte Carlo simulations of solids, Rev. Mod. Phys. **73**, 33 (2001).

[55] C. Lin, F. H. Zong, and D. M. Ceperley, Twist-averaged boundary conditions in continuum quantum Monte Carlo algorithms, Phys. Rev. E **64**, 016702 (2001).

[56] H. Kwee, S. Zhang, and H. Krakauer, Finite-Size Correction in Many-Body Electronic Structure Calculations, Phys. Rev. Lett. **100**, 126404 (2008).

[57] S. Azadi, W. M. C. Foulkes, and T. D. Kühne, Quantum Monte Carlo study of high pressure solid molecular hydrogen, New J. Phys. **15**, 113005 (2013).

[58] S. Azadi, N. D. Drummond, and W. M. C. Foulkes, Nature of the metallization transition in solid hydrogen, Phys. Rev. B **95**, 035142 (2017).

[59] M. A. Morales, J. M. McMahon, C. Pierleoni, and D. M. Ceperley, Towards a predictive first-principles description of

solid molecular hydrogen with density functional theory, Phys. Rev. B **87**, 184107 (2013).

[60] S. Azadi, R. Singh, and T. D. Kühne, Nuclear quantum effects induce metallization of dense solid molecular hydrogen, J. Comput. Chem. **39**, 262 (2018).

[61] R. E. Cohen, I. I. Naumov, and R. J. Hemley, Electronic excitations and metallization of dense solid hydrogen, Proc. Natl. Acad. Sci. U.S.A. **110**, 13757 (2013).

[62] https://doi.org/10.17863/CAM.23386.