Perspective: Role of structure prediction in materials discovery and design

Richard J. Needs and Chris J. Pickard

Articles you may be interested in

Predicted alternative structure for tantalum metal under high pressure and high temperature
J. Appl. Phys. **114**, 073520 (2013); 10.1063/1.4818963

High pressure effect on structure, electronic structure, and thermoelectric properties of MoS 2
J. Appl. Phys. **113**, 013709 (2013); 10.1063/1.4772616

Formation, structure, and electric property of CaB 4 single crystal synthesized under high pressure
Appl. Phys. Lett. **96**, 031903 (2010); 10.1063/1.3293451

First principles simulation of a superionic phase of hydrogen fluoride (HF) at high pressures and temperatures
J. Chem. Phys. **125**, 044501 (2006); 10.1063/1.2220036

Crystal structure prediction using ab initio evolutionary techniques: Principles and applications
J. Chem. Phys. **124**, 244704 (2006); 10.1063/1.2210932

Perspective: Role of structure prediction in materials discovery and design

Richard J. Needs[1,a] and Chris J. Pickard[2,b]

[1]*Theory of Condensed Matter Group, Cavendish Laboratory, J J Thomson Avenue, Cambridge CB3 0HE, United Kingdom*
[2]*Department of Materials Science & Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge CB3 0FS, United Kingdom*

Materials informatics owes much to bioinformatics and the Materials Genome Initiative has been inspired by the Human Genome Project. But there is more to bioinformatics than genomes, and the same is true for materials informatics. Here we describe the rapidly expanding role of searching for structures of materials using first-principles electronic-structure methods. Structure searching has played an important part in unraveling structures of dense hydrogen and in identifying the record-high-temperature superconducting component in hydrogen sulfide at high pressures. We suggest that first-principles structure searching has already demonstrated its ability to determine structures of a wide range of materials and that it will play a central and increasing part in materials discovery and design. © *2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).* [http://dx.doi.org/10.1063/1.4949361]

I. INTRODUCTION

Searching for crystalline structures of materials using first-principles density-functional-theory (DFT) methods[1] has motivated, aided, questioned, or corroborated many experimental studies. One of the most exciting new discoveries motivated in part by DFT studies has been the reports by Drozdov *et al.*[2,3] of superconductivity with a transition temperature (T_c) of 203 K measured on compression of hydrogen sulfide to pressures of ~200 GPa. This exceeds the lowest temperature recorded on Earth at ground level of 184 K and smashes the previous record superconducting T_c of 164 K in HgBaCaCuO at 30 GPa.[4,5] Superconductivity was inferred from the observed sharp drop in the resistivity to zero, the decrease in T_c with applied magnetic field and the presence of a strong isotope effect of the correct sign and roughly the expected magnitude.[3]

Compressed hydrogen sulfide has been studied experimentally over many years.[6–14] However, the superconductivity that was observed in hydrogen sulfide was generally thought to arise from metallic sulfur formed at high pressures. The enormous T_c found by Drozdov *et al.*[3] in hydrogen sulfide was therefore a great surprise. The number of papers published on the theory and modelling of high T_c superconductivity in hydrogen sulfide has increased rapidly since 2014, see for example Refs. 15–27.

The high-temperature superconductivity found in hydrogen sulfide was foreshadowed by theoretical work. A DFT study by Li *et al.*[15] was the first to suggest that metallic H_2S could become a high-temperature superconductor, which they predicted to have a T_c of 80 K at 160 GPa. In the same study Li *et al.*[15] also showed that pressure-induced decomposition of H_2S into its elements was thermodynamically unfavorable. This result overturned the conclusion from a DFT study[28] that pressure-induced decomposition into the elements might occur, and suggested that new H/S compounds could be formed.

[a]rn11@cam.ac.uk
[b]cjp20@cam.ac.uk

Subsequent to the work of Li *et al.*,[15] Duan *et al.*[16] reported a DFT study of $(H_2S)_2H_2$ at high pressures. They investigated several H/S structures including H_3S-$R3m$ which is stable at lower pressures and was estimated to have a T_c of ~160 K at 130 GPa, and the higher pressure H_3S-$Im\bar{3}m$ phase that was estimated to have a T_c of around 200 K at 200 GPa. These results are in reasonable agreement with the experimental data of Drozdov *et al.*[3] These data indicated the presence of two superconducting components, with maximum T_c's of about 150 K ($R3m$) and 200 K ($Im\bar{3}m$) at pressures around 150 GPa. DFT studies by Li *et al.*[15] and Duan *et al.*[16] were cited in the experimental papers of Drozdov *et al.*,[2,3] and had clearly influenced their thinking.

Errea *et al.* performed extensive structure searches over 44 H/S stoichiometries,[17] finding the cubic H_3S-$Im\bar{3}m$ phase to be the most stable at the pressures at which the ~200 K superconductivity had been observed. Searches over a much smaller number of stoichiometries were performed by Duan *et al.*[29] Errea *et al.*[17] also showed that anharmonic vibrations significantly reduce the T_c of H_3S-$Im\bar{3}m$. The high-pressure cubic structure of H_3S of space group $Im\bar{3}m$ in which the sulfur atoms lie on a body-centered cubic (bcc) lattice has now been confirmed by X-ray diffraction experiments,[30] see Fig. 1. These results demonstrated convincingly that the very-high T_c superconducting material is not H_2S, but is instead H_3S.

Li *et al.*[18] reported theoretical and experimental studies of the products of dissociation of solid H_2S under strong compression. First-principles structure searches predicted new thermodynamically stable structures with stoichiometries H_2S_3, H_3S_2, HS_2, and H_4S_3. H_4S_3 was predicted to be thermodynamically stable over the pressure range 25–113 GPa. X-ray diffraction measurements indicated the presence of H_3S and H_4S_3.[18] The experimental conditions and the kinetics of chemical reactions clearly play an important role in determining the H/S structures that are observed.

Very recently, Errea *et al.*[19] have demonstrated that the quantum hydrogen-bond symmetrization that occurs on formation of H_3S-$Im\bar{3}m$ is responsible for the very high T_c. They have also shown that anharmonic vibrations stabilise this structure down to lower pressures than would be obtained within the harmonic approximation.

The above calculations were performed using the *ab initio* random structure searching method (AIRSS)[31,32] and the CASTEP code,[33] and the CALYPSO particle-swarm optimization method[34,35] and the VASP code.[36,37] Superconductivity was calculated using the QUANTUM ESPRESSO code.[38] The PBE density functional[39] was used for all calculations reported here.

In 2013 we performed a DFT study of H_2O up to terapascal (TPa) pressures in which we predicted its decomposition into H_2O_2 and a hydrogen-rich phase at about 5 TPa.[40] We also found a H_3O structure with the same $Im\bar{3}m$ structure as in H_3S. We moved on to consider H_2S at high pressures, which has long been considered as a proxy for H_2O at pressures beyond those currently accessible to experiments. We subsequently heard about the work of Drozdov *et al.* on superconducting hydrogen sulfide and decided to pool our expertise with groups in Europe and China to work on it (see the list of authors of Ref. 17).

DFT methods can provide quite accurate energetics for *sp*-bonded materials such as H/S compounds. The increasing availability of computational resources and developments in the methods and robustness of the codes has led to the ability to perform the numerous DFT calculations on
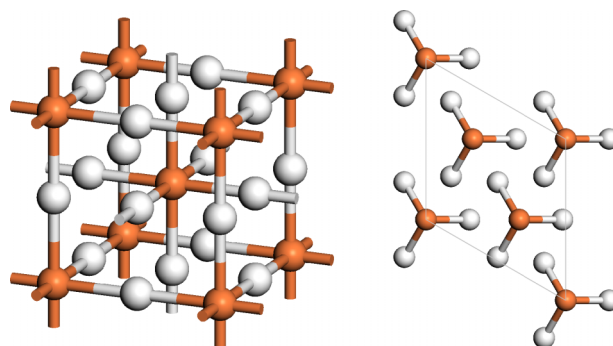

FIG. 1. The high-pressure $Im\bar{3}m$ cubic structure (left) and the lower-pressure $R3m$ trigonal structure (right) of H_3S.
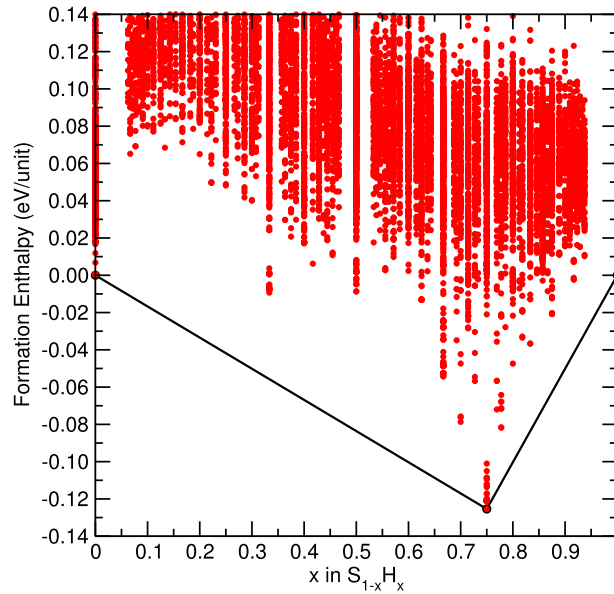
FIG. 2. Convex hull plot of the formation enthalpy of the H/S system at 200 GPa as a function of the fraction of sulfur, x, from AIRSS. The stoichiometry is $H_{(1-x)}S_x$. Each red dot corresponds to a relaxed structure. The data show that H_3S-$Im\bar{3}m$ (corresponding to $x = 0.75$) is the only thermodynamically stable compound of the H/S system at 200 GPa.

the wide range of structures required for successful searches. As an illustration we have performed additional structure searches for H/S compounds at a pressure of 200 GPa. We used the CASTEP[33] plane wave pseudopotential code with the PBE density functional,[39] ultrasoft pseudopotentials,[41] a k-point mesh of spacing $2\pi \times 0.07$ Å^{-1}, and a basis set energy cutoff of 230 eV. These computational parameters provide moderate accuracy, and higher accuracy calculations would be used to obtain converged results. The calculations were run for 24 h on 924 cores, and 17 887 structures from 3 to 16 atoms were relaxed. The results of these calculations are shown on a "Convex Hull" plot in Fig. 2.

Fig. 3 shows the electronic density of states (eDos) of cubic H_3S-$Im\bar{3}m$ calculated within DFT using the OptaDOS code.[42] Note the sharp peak in the electronic density of states at the Fermi energy. This peak has significant weight on the s-like electronic states of hydrogen atoms and the p states of sulfur atoms. Nevertheless, H_3S at high pressures is best described as a hydrogen superconductor in which the sulfur atoms stabilise the H_3S-$R3m$ and H_3S-$Im\bar{3}m$ structures, rather
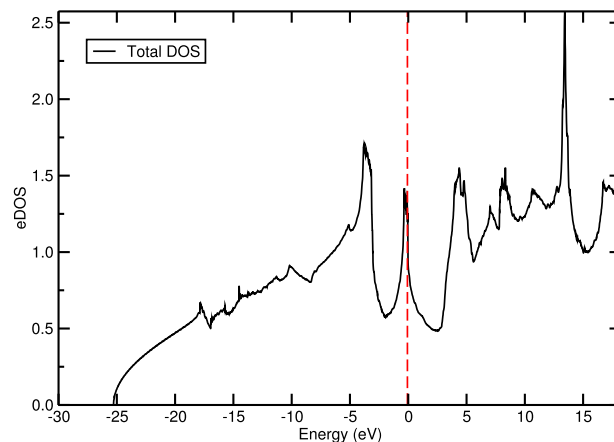

FIG. 3. Calculated electronic density of states of the cubic $Im\bar{3}m$ structure of H_3S at 200 GPa.

than playing a direct role in their superconductivity. The Van Hove singularities in the eDoS near the Fermi level may also have a significant influence on the superconducting properties.[43]

II. SUPERCONDUCTING HYDRIDES

The scientific journey that has led to the synthesis and identification of high-T_c H_3S was kick-started by work published in 1968 by Ashcroft,[44] see also Ref. [45]. This paper laid out the case for possible high-T_c superconductivity in strongly compressed hydrogen, based on the likely strong electron-phonon coupling, high vibrational frequencies, and pressure-induced metallicity. At elevated pressures the energy scales of electron-phonon coupling and vibrational frequencies are likely to be increased, as is the density of electronic states at the Fermi energy. These characteristics suggest the possibility of high-T_c superconductivity in hydrogen at high pressures. An early first-principles calculation of superconductivity in the *Cmca* phase of metallic hydrogen suggested a T_c of 107 K at 347 GPa,[46] while a more recent calculation gives a T_c of 250 K at about 450 GPa.[47] However, this phase is now known to be thermodynamically unstable, see Ref. [48]. A structure of $I4_1/amd$ symmetry found in high-pressure searches is predicted to be stable above about 400 GPa[49,50] and is the best candidate for high-T_c superconductivity in solid hydrogen found to date. Unfortunately experiments have not so far been able to test this conjecture.

The suggestion that applied pressure may enhance superconductivity is not confined to hydrogen. Ashcroft argued that hydrides might exhibit high-T_c superconductivity under sufficient pressure.[51] Feng *et al.*[52] predicted structures of silane (SiH_4) at high pressures using "chemical intuition" and DFT methods. An early form of the AIRSS structure searching method was used to find more stable structures in an overnight run on a standard single processor machine.[31] Structures that we had found of SiH_4 with $I4_1/a$ and $I\bar{4}2d$ symmetries were subsequently verified by X-ray diffraction experiments,[53,54] although the $I4_1/a$ phase is insulating, see Fig. [4]. Ashcroft's work has motivated many theoretical efforts to predict new high-temperature superconductors, and experimental studies of hydrides at high pressures.

An early application of structure searching to discovering potential high T_c superconductivity in AlH_3[55] was followed up by other studies. It was found that anharmonic vibrations suppress electron-phonon coupling in AlH_3 at high pressures which explains a significant discrepancy with earlier theoretical studies.[56] Superconductivity was recently predicted in $AlH_3(H_2)$ with a very large T_c of about 140 K at 250 GPa.[57] However, our structure searches suggest this phase to be unstable to decomposition at high pressures. High-temperature superconductivity was also predicted in a number of metallic hydrides[57–67] but most of the predicted T_c's were not realized.

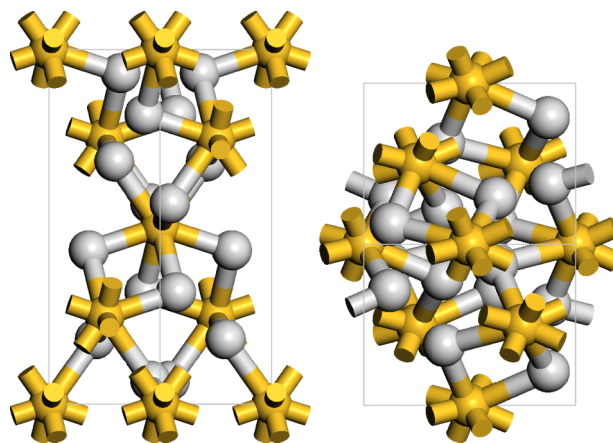FIG. 4. The $I4_1/a$ structure of SiH_4 (left) and the slightly less stable $I\bar{4}2d$ structure (right) found by AIRSS and subsequently observed experimentally. Silicon atoms are shown in gold and hydrogen atoms in white. The high symmetry insulating $I4_1/a$ structure consists entirely of equivalent Si–H–Si electron-deficient three-centre-two-electron "banana" bonds, similar to those found in diborane (B_2H_6).

The experimental observation in 2001 of high-temperature electron-phonon-based superconductivity in MgB_2 with a T_c of 39 K aroused considerable interest.[68,69] Two types of electrons were found to exist at the Fermi energy with σ bonding character leading to strong superconductivity and π bonding character giving rise to much weaker superconductivity. This T_c was the highest achieved in a conventional superconductor prior to H_3S. The jump in T_c by a factor of five from MgB_2 to H_3S is very striking.

Over the years various "rules" for guiding searches for high-temperature superconductors have been proposed, the most well-known of which are "Matthias's Rules." These rules have been modified and added to over the years as new experimental results became available. For example, the discovery of iron-based high-temperature superconductors in which magnetism plays an important role is inconsistent with Matthias's rules.[70–72] Matthias's rule that transition metals are more likely to exhibit high-temperature superconductivity than simple metals has been challenged by superconducting H_3S. In fact most of the "rules" for the occurrence of superconductivity have been broken by new discoveries, which makes the subject even more interesting.

An important idea for electron-phonon-based superconductivity that curiously was not part of Matthias's rules is that light atoms may promote superconductivity because their high phonon frequencies and large vibrational amplitudes can lead to large electron-phonon coupling. Recently we predicted that molecular water ice would show enormous electron-phonon coupling leading to a reduction in the band gap of nearly 2 eV.[73] The strong electron-phonon coupling arises from both low frequency modes and high frequency O-H stretching modes. Water ice is, of course, an insulator, but the predicted band gap renormalization illustrates that very large electron-phonon coupling can be found in materials with light atoms.

III. IMPORTANCE OF FINDING THE CORRECT STRUCTURE

The most basic and important property of a material is its structure, which determines the observed behaviour. The properties of a material normally depend very sensitively on its structure. It is therefore crucial to determine the correct structures of materials. In particular, we normally seek the thermodynamically most stable structure at a given temperature and pressure, although low-energy metastable structures are also of interest. It is often necessary to search over structures with many different stoichiometries to determine the most stable ones. In practise only a finite number of stoichiometries can be searched and only a finite number of structures with a particular stoichiometry can be calculated, whereas both the number of stoichiometries and number of structures are infinite.

It has been suggested that bias in a structure search should be avoided at all costs. However, this ignores the fact that all useful structure searches depend for their success on biases. One extremely useful type of bias is to reduce the number of possible configurations. For example, we normally choose the average densities of the initial structures to be within a factor of two or so of our best estimate. This massively reduces the structure space that needs to be searched, and is what we call a "clear bias." In the following we refer to the set of all possible structures as the "structure space." In all our searches we embrace clear and easily understood biases or constraints. However, having selected these biases we insist on a uniform, random and uncorrelated, sampling of configuration space, and abhor the potentially deleterious effects of hidden bias.

A number of different approaches to structure searching using first-principles methods have been developed, such as basin hopping,[74] evolutionary/genetic algorithms,[75–77] minima hopping,[78] *ab initio* random structure searching (AIRSS),[32] and swarm intelligence.[34] The various searching methods exhibit many similar features, and successes have been achieved using each of them.

A complete structure search on, for example, the binary hydrogen/oxygen (H/O) system would have to consider all possible H/O stoichiometries and all possible structures for each stoichiometry. The number of *locally stable* structures increases roughly exponentially with the number of atoms in the unit cell[79] and the cost of determining the lowest energy structure increases very rapidly with system size. However, for small numbers of atoms the number of locally stable structures may increase less rapidly. Given the enormity of the searching problem, how is it possible that searches for structures containing several tens of atoms could be successful?

In fact searching for low energy structures is often not as difficult as the above discussion might imply. Choosing a suitable set of initial structures for a search is very important. If we know that H and O react to form water (H_2O) then it is unhelpful to start a search with all the H atoms at one end of the cell and all the O atoms at the other end. It is also unhelpful to start a search with atoms almost on top of one another. Taking the latter point further, we can choose different minimum initial separations for H–H, H–O, and O–O nearest neighbours. We may allow nearest neighbour distances to be somewhat smaller than the physical bond lengths, so as not to impede structural relaxation. This approach is useful because it eliminates the structure space in regions where low-lying minima are highly unlikely to be found. Note that only two atomic types are present in H/O, and the presence of additional atomic types would make the searching considerably more costly.

Low-energy structures tend to have large "basins of attraction" so that they occupy a large part of the structure space[80] and are therefore relatively easy to find in searches. Monte Carlo methods have been developed for measuring volumes of basins of attraction associated with minima in the potential energy surface.[81] Wide and deep basins of attraction tend to be found near other low-energy basins, and the barriers between such basins tend to be relatively low. Empirically, we find that the difficulty in discovering the most stable structure tends to decrease with pressure, which suggests that the structure space becomes simpler under pressure. Also, we find that some empirical potentials have many more minima than those obtained from first-principles calculations.

High-symmetry structures are expected to have unit cells containing rather few atoms, and therefore they may be readily found in inexpensive searches. Pauling's principle that low-energy structures tend to possess symmetry is relevant here.[82] These ideas suggest that constraining searches to conform to high-symmetry space groups could be a useful strategy, although clearly it makes it impossible to find very low symmetry structures which are sometimes the most stable. The use of symmetry constraints can lead to enormous reductions in the size of the structure space to be searched, although such constraints break up the structure space into disconnected regions that prevent some structures from relaxing fully. Imposing symmetry constraints can be a very efficient strategy for finding some very-low-energy structures.

Another very useful approach is to use "chemical units." In the H/O system we are justified in searching only the H_2O stoichiometry because chemistry tells us that only structures of this stoichiometry are thermodynamically stable (unless the pressure is extremely high, see Ref. 40). For example, we could place H_2O "units" randomly within the cell, instead of placing the atoms randomly, in conjunction with minimum distance constraints.

Many other ideas can readily be incorporated in the searches. For example, one can concentrate searches on particular space groups that have been found by experiment or previous searches to be common in certain types of structure, such as in inorganic or organic crystals.[83] Structure searching is also very flexible and can readily be adapted for discovering point defect structures,[84,85] surface and interface structures,[86–88] etc. The most important aspects of searching are illustrated in Fig. 5.

IV. STRUCTURES OF SOLID HYDROGEN AT HIGH PRESSURES

Experimental determination of high-pressure structures of solid hydrogen is extremely challenging because of its low X-ray scattering and the small sample sizes obtained at the pressures of interest of up to above 350 GPa.[89] X-ray diffraction experiments have provided useful data,[90] but most of the experimental data has been provided by infra-red and particularly Raman vibrational spectroscopy. Unfortunately it has not proved possible to determine high pressure structures of hydrogen from the available experimental information alone, apart from that of the low pressure phase I whose hexagonal structure was solved over two decades ago. The structure of phase II is unknown, but the lowest energy candidate from structure searching[91] is in plausible agreement with the experimental vibrational data. The high pressure phase III represents a triumph for structure searching in that the lowest energy structure from the AIRSS searches of $C2/c$ symmetry gives a good account of the experimental vibrational data,[49] see Fig. 6.

Energetically competitive "mixed structures" of *Ibam* and *Pbcn* symmetries consisting of alternate layers of molecules with short bonds and considerably longer bonds were reported in the
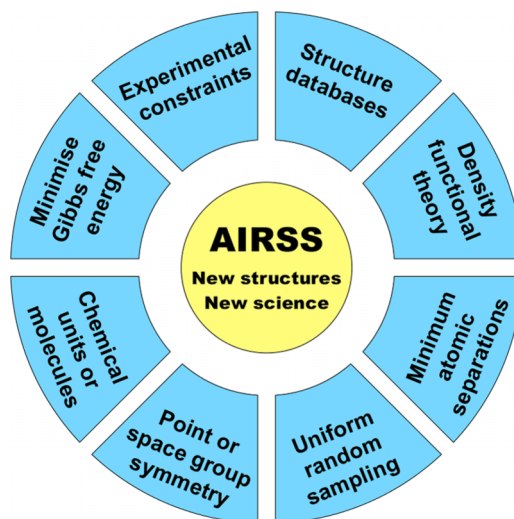
FIG. 5. The AIRSS wheel of good fortune for finding new low-energy structures. The main elements of successful searching are presented. Elements from the wheel can be combined in different ways in a particular search. For example, in searching for superconductors we might consider only high-symmetry structures. We could also choose that the initial structures be composed of chemically relevant units. Experimental constraints can also be applied. The use of minimum initial separations reduces the size of the structure space to be studied and speeds up the relaxation procedure. Although we consider structures from databases for comparison, our most interesting and important results have arisen from AIRSS calculations.

AIRSS study of Ref. 49. In 2011 Eremets *et al.*[92] reported the experimental discovery of a new phase IV of hydrogen, see also Ref. 93. We immediately saw that the *Ibam* and *Pbcn* structures might explain features of the new phase IV. Additional AIRSS calculations identified a structure of *Pc* symmetry that was similar to *Ibam* and *Pbcn*, but more energetically stable.[94] It seems very unlikely that such a strange structure-type would have been conceived without the aid of first-principles structure searches. It is clear that structure searching has played a crucial role in determining the structures of high-pressure phases of hydrogen. The *Pc* structure that we use to model phase IV is shown in Fig. 6.

An experimental paper has recently appeared on a new high-pressure phase V of solid hydrogen.[95] This could be a step on the route to finding metallic solid hydrogen, with implications for potential high temperature superconductivity. A very recent preprint[96] questions some of the conclusions of Ref. 95. Studying solid hydrogen at high pressures remains a very active field.

V. A GLIMPSE OF THE FUTURE

Developments in diamond-anvil-cell (DAC) techniques are making it possible to compress materials to ever higher pressures. The record high pressure for hydrogen in a "standard" DAC is currently about 350 GPa. Two-stage DACs have recently reached pressures of up to 750 GPa with an osmium sample,[97] although the stress showed significant anisotropy. This breakthrough will open new vistas in high-pressure experimental research that will stimulate further structure searches. "Ramped compression" techniques are being developed in which the precise control of strong laser pulses generates enormous pressures far beyond those accessible in static diamond anvil cells, but at much lower temperatures than in shock wave studies. Compression of diamond to 5 terapascals (TPa) was recently achieved at the National Ignition Facility (NIF) in the USA, which is 14 times the pressure at the centre of the Earth,[98] see also Refs. 99 and 100. It is therefore now possible to investigate experimentally the conditions found deep within giant planets. One of the great challenges will be to retrieve high-quality experimental data gathered under extreme conditions from X-ray diffraction experiments, and extended X-ray absorption fine structure (EXAFS) measurements for probing local quantities. This will allow identification of structures and measurement of
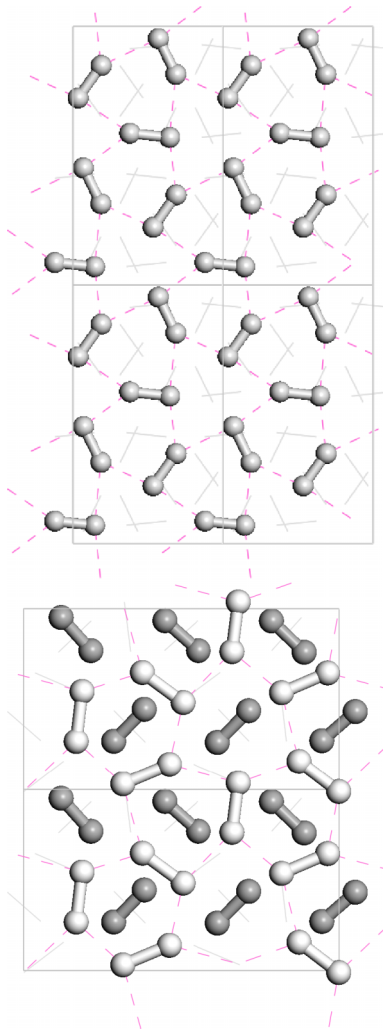
FIG. 6. Top: The $C2/c$ layered structure of solid hydrogen shown at 300 GPa provides a good model of the observed phase III. Note that in fact a $B2/n$ space group setting was used to produce a more orthorhombic cell. Bottom: The Pc layered structure of solid hydrogen at 250 GPa which models phase IV of hydrogen. Light pink dashed lines indicate close contacts between molecules and light grey solid lines indicate molecules in lower layers. Molecules in the Pc structure with short bonds have dark shading. The $C2/c$ and Pc structures are the most stable found by AIRSS at high pressures, and they provide good accounts of the experimental vibrational signals of phases III and IV. The $C2/c$ structure reproduces the large infrared vibronic response observed in phase III, which accords with the fact that the two ends of the molecules have different environments. Phase IV exhibits a vibronic mode with an almost constant high frequency and a second vibronic mode whose frequency declines rapidly with pressure. AIRSS finds structures in this pressure regime consisting of alternate layers of strong and weakly bonded molecules which can account for the experimentally observed vibrational data for phase IV.

properties.[101] These experimental developments will further stimulate first-principles DFT calculations of solids at extreme pressures and temperatures. For example, there has been much interest in predicting the stability of "electride" structures at high pressures in which some of the higher energy electrons occupy interstitial regions within the crystal and behave as anions,[40,100,102–105] see Fig. 7. However, very different results might be obtained if the effects of (anharmonic) vibrations were included at the high pressures and temperatures that occur within giant planets.

DFT calculations are relatively cheap, and the cost of a particular calculation falls rapidly, year-on-year. This leads to a dynamic field in which improvements in accuracy and breadth of applicability occur rapidly, motivating even more ambitious studies. Many of the most limiting aspects of experimental studies do not exist in calculations, for example, in DFT studies the stoichiometry is known precisely, the system is pure so there are no unwanted materials that can induce chemical
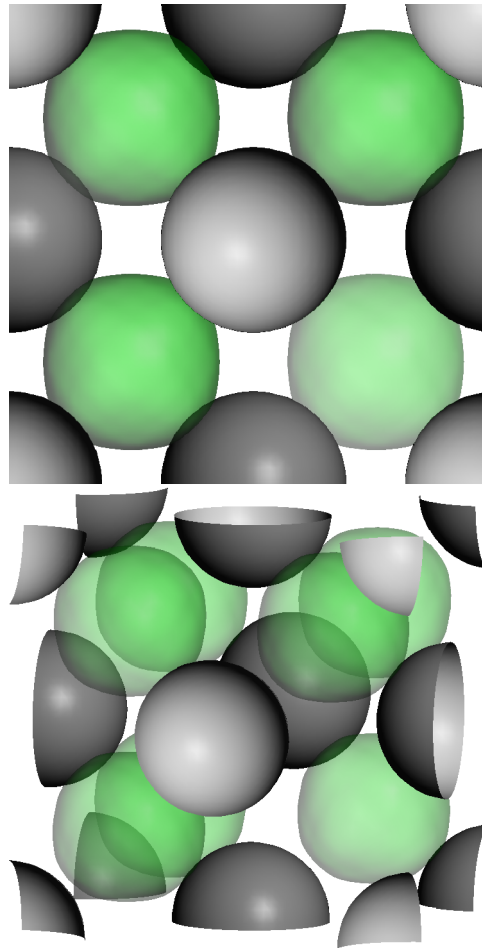
FIG. 7. Two views of face centered cubic carbon at a pressure of 50 TPa. An electride structure is formed in which the valence electrons (green) are spatially separated from the $1s$ core electrons of the carbon atoms (grey). There is competition between the attraction of the valence electrons to the positively charged core and the reduction in the kinetic energy achieved by the valence electrons moving away from the $1s$ cores so that they are not subject to Pauli repulsion from the $1s$ electrons.

reactions, the presence of large kinetic barriers does not hinder most structure searches, calculations can identify both stable and metastable phases, and signals are not blocked by the diamonds used in high-pressure studies as of course no diamonds are present (and therefore none are broken), etc. Hooking up experiments directly to DFT calculations should accelerate progress. There is practically no limit to the range of pressures that can be explored in DFT structure searching (individual calculations and searches generally get easier as the pressure is increased), and therefore it should be possible to make fundamental progress in materials under extreme pressures.

The agreement between the calculated structures and superconducting properties of H_3S and the experimental data is very good. This strongly suggests that superconducting H_3S has indeed been synthesized, and engenders confidence in both theory and experiment. It would be very interesting to return to experimental and theoretical studies of metallic hydrides to try and determine why theory gave values of T_c that were much larger than those found experimentally. One likely reason for these discrepancies could be the substantial difficulties involved in such experimental studies, particularly in sample preparation. Another problem was that some early structure searches were poor and tended to produce rather unstable structures with substantial eDoS at the Fermi energy (E_F). A structure with a low eDoS at E_F normally corresponds to complete or nearly complete filling of the bonding orbitals, which leads to greater thermodynamic stability than in strongly metallic structures. The true ground state structure tended to have a lower eDoS at E_F, and therefore

a lower propensity for superconductivity. It is worth mentioning that our recent structure searches for hydrogen sulfide at high pressures involved relaxing around one million structures, see Refs. 17 and 18. The use of approximate density functionals is also a significant issue. The neglect of anharmonicity in earlier calculations could also have been problematic in some cases. However, here there is much room for optimism because methods for performing accurate vibrational calculations within DFT are being actively developed.[106,107]

We conclude that experiments on hydrogen sulfide vindicate Ashcroft's ideas on superconducting hydrides. It is, however, still unclear whether high-T_c superconductivity will be observed in pure hydrogen.

Is H_3S the highest-T_c material that will be found? We see no reason why this must be the case. The eDoS of H_3S has a sharp peak at E_F that is similar in height to that of a homogeneous electron gas of the same density, and the highest vibrational frequencies are much lower than in solid hydrogen. The superconductivity in H_3S therefore arises in circumstances that could occur in other metallic hydrides. Only a fraction of potential superconducting compounds have been studied under ambient conditions, and an even smaller fraction at high pressures. For example, the number of structure searches and experimental studies for ternary hydrides performed with the aim of finding high temperature superconductors is small. Further experimental and theoretical studies will undoubtedly uncover new high-T_c superconductors. For example, Drozdov *et al.* have recently reported superconductivity at high pressures in PH_3 above 100 K.[108,109] There is every reason to be optimistic about finding new metallic hydrides with even higher superconducting T_c's than H_3S.

It should be noted that the structure prototypes predicted for phases III and IV of solid hydrogen do not appear in databases such as the Inorganic Crystal Structure Database (ICSD) of experimental structures.[110] In fact databases of experimental structures are currently very small. The various efforts currently underway to construct databases of DFT structures will help to provide much larger amounts of structural data.

Structure searching can be combined successfully with X-ray or neutron diffraction data, and other techniques such as X-ray absorption spectroscopy. This is particularly synergetic in the case of diffraction because, even if the structure cannot be solved directly from the experimental data, the cell vectors may often be deduced from experiment, which makes searching for the correct structure enormously easier. (Space group or other structural data might also be available to further reduce the searching task.) A few successful calculations of this type have already been performed,[111,112] and we look forward to them becoming a routine part of structure determination.

Some structures may be stabilized by anharmonic nuclear vibrations at saddle points of the Born-Oppenheimer surface. For example, at low temperatures elemental lithium adopts a rhombohedral structure, but upon heating above ~100 K it adopts the high-symmetry bcc structure.[113] As mentioned above, the cubic $Im\bar{3}m$ structure of H_3S responsible for the very high T_c in H_3S is stabilized down to considerably lower pressures when anharmonic quantum nuclear zero-point motion is included.[19] Both lithium at low pressures and H_3S-$Im\bar{3}m$ at high pressures are close to structural instabilities. Matthias emphasised the importance of structural symmetry in determining superconducting T_c's,[114] and empirical observations suggest that cubic symmetry is particularly efficacious. It is well-known that superconductivity can arise in the vicinity of soft vibrational modes, charge transfer instabilities, quantum critical points, etc. We are currently developing an approach based on first-principles structure searching that should enable the discovery of structures stabilised by anharmonic nuclear motion. Such searches might lead us to new superconducting hydrides and other structures of interest.[115]

We have emphasised the overriding importance of determining the correct structure of a material, which arises from the very strong dependence of properties on structure. Structures may be discovered by experiment and/or structure searching using first-principles or empirical methods, backed up by the available databases. At the moment the human directing the structure searching plays a very important role, but we expect that this can be reduced and eventually eliminated using expert systems and machine learning that can emulate the decision making of a trained human. Structure prediction should benefit from these developments. The success of first-principles structure searching will promote the prediction of new materials, interpretation of experimental data, identification of stable and metastable structures, and the design of materials.

ACKNOWLEDGMENTS

[1] R. O. Jones, "Density functional theory: Its origins, rise to prominence, and future," Rev. Mod. Phys. **87**, 897 (2015).

[2] A. P. Drozdov, M. I. Eremets, and I. A. Troyan, "Conventional superconductivity at 190 K at high pressures," e-print arXiv:1412.0460 (2014).

[3] A. P. Drozdov, M. I. Eremets, I. A. Troyan, V. Ksenofontov, and S. I. Shylin, "Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system," Nature **525**, 73 (2015).

[4] L. Gao, Y. Y. Xue, F. Chen, Q. Xiong, R. L. Meng, D. Ramirez, C. W. Chu, J. H. Eggert, and H. K. Mao, "Superconductivity up to 164 K in $HgBa_2Ca_{m-1}Cu_mO_{2m+2+\delta}$ ($m = 1, 2$, and 3) under quasihydrostatic pressures," Phys. Rev. B **50**, 4260 (1994).

[5] J. G. Bednorz and K. A. Muller, "Possible high T_c superconductivity in the Ba-La-Cu-O system," Z. Phys. B: Condens. Matter **64**, 180 (1986).

[6] H. Shimizu, Y. Nakamichi, and S. Sasaki, "Pressure-induced phase transition in solid hydrogen sulfide at 11 GPa," J. Chem. Phys. **95**, 2036 (1991).

[7] H. Shimizu and S. Sasaki, "High-pressure Brillouin studies and elastic properties of single-crystal H_2S grown in a diamond cell," Science **257**, 514 (1992).

[8] S. Endo, N. Ichimiya, K. Koto, S. Sasaki, and H. Shimizu, "X-ray-diffraction study of solid hydrogen sulfide under high pressure," Phys. Rev. B **50**, 5865 (1994).

[9] H. Shimizu, T. Ushida, S. Sasaki, M. Sakashita, H. Yamawaki, and K. Aoki, "High-pressure phase transitions of solid H_2S probed by Fourier-transform infrared spectroscopy," Phys. Rev. B **55**, 5538 (1997).

[10] M. Sakashita, H. Yamawaki, H. Fujihisa, K. Aoki, S. Sasaki, and H. Shimizu, "Pressure-induced molecular dissociation and metallization in hydrogen-bonded H_2S solid," Phys. Rev. Lett. **79**, 1082 (1997).

[11] S. Endo, A. Honda, K. Koto, O. Shimomura, T. Kikegawa, and N. Hamaya, "Crystal structure of high-pressure phase-IV solid hydrogen sulfide," Phys. Rev. B **57**, 5699 (1998).

[12] M. Sakashita, H. Fujihisa, H. Yamawaki, and K. Aoki, "Molecular dissociation in deuterium sulfide under high pressure: Infrared and Raman study," J. Phys. Chem. A **104**, 8838 (2000).

[13] H. Fujihisa, H. Yamawaki, M. Sakashita, A. Nakayama, T. Yamada, and K. Aoki, "Molecular dissociation and two low-temperature high-pressure phases of H_2S," Phys. Rev. B **69**, 214102 (2004).

[14] T. A. Strobel, P. Ganesh, M. Somayazulu, P. R. C. Kent, and R. J. Hemley, "Novel cooperative interactions and structural ordering in H_2S–H_2," Phys. Rev. Lett. **107**, 255503 (2011).

[15] Y. Li, J. Hao, H. Liu, Y. Li, and Y. Ma, "The metallization and superconductivity of dense hydrogen sulfide," J. Chem. Phys. **140**, 174712 (2014).

[16] D. Duan, Y. Liu, F. Tian, D. Li, X. Huang, Z. Zhao, H. Yu, B. Liu, W. Tian, and T. Cui, "Pressure-induced metallization of dense $(H_2S)_2H_2$ with high-Tc superconductivity," Sci. Rep. **4**, 6968 (2014).

[17] I. Errea, M. Calandra, C. J. Pickard, J. R. Nelson, R. J. Needs, Y. Li, H. Liu, Y. Zhang, Y. Ma, and F. Mauri, "High-pressure hydrogen sulfide from first principles: A strongly anharmonic phonon-mediated superconductor," Phys. Rev. Lett. **114**, 157004 (2015).

[18] Y. Li, L. Wang, H. Liu, Y. Zhang, J. Hao, C. J. Pickard, J. R. Nelson, R. J. Needs, W. Li, Y. Huang, I. Errea, M. Calandra, F. Mauri, and Y. Ma, "Dissociation products and structures of solid H_2S at strong compression," Phys. Rev. B **93**, 020103 (2016).

[19] I. Errea, M. Calandra, C. J. Pickard, J. R. Nelson, R. J. Needs, Y. Li, H. Liu, Y. Zhang, Y. Ma, and F. Mauri, "Quantum hydrogen-bond symmetrization in the superconducting hydrogen sulfide system," Nature **532**, 81 (2016).

[20] A. Bianconi and T. Jarlborg, "Superconductivity above the lowest Earth temperature in pressurized sulfur hydride," EPL **112**, 37001 (2015).

[21] M. Komelj and H. Krakauer, "Electron-phonon coupling and exchange-correlation effects in superconducting H_3S under high pressure," Phys. Rev. B **92**, 205125 (2015).

[22] N. Bernstein, C. S. Hellberg, M. D. Johannes, I. I. Mazin, and M. J. Mehl, "What superconducts in sulfur hydrides under pressure and why," Phys. Rev. B **91**, 060511 (2015).

[23] E. J. Nicol and J. P. Carbotte, "Comparison of pressurized sulfur hydride with conventional superconductors," Phys. Rev. B **91**, 220507 (2015).

[24] D. A. Papaconstantopoulos, B. M. Klein, M. J. Mehl, and W. E. Pickett, "Cubic H_3S around 200 GPa: An atomic hydrogen superconductor stabilized by sulfur," Phys. Rev. B **91**, 184511 (2015).

[25] R. Akashi, M. Kawamura, S. Tsuneyuki, Y. Nomura, and R. Arita, "First-principles study of the pressure and crystal-structure dependences of the superconducting transition temperature in compressed sulfur hydrides," Phys. Rev. B **91**, 224513 (2015).

[26] C. Heil and L. Boeri, "Influence of bonding on superconductivity in high-pressure hydrides," Phys. Rev. B **92**, 060508 (2015).

[27] J. A. Flores-Livas, A. Sanna, and E. K. U. Gross, "High temperature superconductivity in sulfur and selenium hydrides at high pressure," Eur. Phys. J. B **89**, 63 (2016).

[28] R. Rousseau, M. Boero, M. Bernasconi, M. Parrinello, and K. Terakura, "*Ab initio* simulation of phase transitions and dissociation of H_2S at high pressure," Phys. Rev. Lett. **85**, 1254 (2000).

[29] D. Duan, X. Huang, F. Tian, D. Li, H. Yu, Y. Liu, Y. Ma, B. Liu, and T. Cui, "Pressure-induced decomposition of solid hydrogen sulfide," Phys. Rev. B **91**, 180502 (2015).

[30] M. Einaga, M. Sakata, T. Ishikawa, K. Shimizu, M. Eremets, A. Drozdov, I. Troyan, N. Hirao, and Y. Ohishi, "Crystal structure of 200 K-superconducting phase of sulfur hydride system," e-print arXiv:1412.0460 (2015).

[31] C. J. Pickard and R. J. Needs, "High-pressure phases of silane," Phys. Rev. Lett. **97**, 045504 (2006).

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

[33] 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).

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

[35] Y. Wang, J. Lv, L. Zhu, and Y. Ma, "CALYPSO: A method for crystal structure prediction," Comput. Phys. Commun. **183**, 2063 (2012).

[36] G. Kresse and J. Furthmüller, "Efficiency of *ab-initio* total energy calculations for metals and semiconductors using a plane-wave basis set," Comput. Mater. Sci. **6**, 15 (1996).

[37] G. Kresse and J. Furthmüller, "Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set," Phys. Rev. B **54**, 11169 (1966).

[38] P. Gianozzi *et al.*, "QUANTUM ESPRESO: A modular and open source software project for quantum simulations of materials," J. Phys.: Condens. Matter **21**, 395502 (2009).

[39] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," Phys. Rev. Lett. **77**, 3865 (1996).

[40] C. J. Pickard, M. Martinez-Canales, and R. J. Needs, "Decomposition and terapascal phases of water ice," Phys. Rev. Lett. **110**, 245701 (2013).

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

[42] A. J. Morris, R. J. Nicholls, C. J. Pickard, and J. R. Yates, "A tool for obtaining density of states, core-level and optical spectra from electronic structure codes," Comput. Phys. Commun. **185**, 1477 (2014).

[43] A. Bianconi and T. Jarlborg, Novel Superconducting Materials **1**(1), 2299 (2015).

[44] N. W. Ashcroft, "Metallic hydrogen: A high-temperature superconductor?," Phys. Rev. Lett. **21**, 1748 (1968).

[45] C. F. Richardson and N. W. Ashcroft, "High temperature superconductivity in metallic hydrogen: Electron-electron enhancements," Phys. Rev. Lett. **78**, 118 (1997).

[46] L. Zhang, Y. Niu, Q. Li, T. Cui, Y. Wang, Y. Ma, Z. He, and G. Zou, "*Ab initio* prediction of superconductivity in molecular metallic hydrogen under high pressure," Solid State Commun. **141**, 610 (2007).

[47] P. Cudazzo, G. Profeta, A. Sanna, A. Flores, A. Continenza, S. Massidda, and E. K. U. Gross, "Electron-phonon interaction and superconductivity in metallic molecular hydrogen. II. Superconductivity under pressure," Phys. Rev. B **81**, 134505 (2010).

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

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

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

[51] N. W. Ashcroft, "Hydrogen dominant metallic alloys: High temperature superconductors?," Phys. Rev. Lett. **92**, 187002 (2004).

[52] J. Feng, W. Grochala, T. Jaron, R. Hoffmann, A. Bergara, and N. W. Ashcroft, "Structures and potential superconductivity in SiH$_4$ at high pressure: En route to 'metallic hydrogen,'" Phys. Rev. Lett. **96**, 017006 (2006).

[53] M. I. Eremets, I. A. Trojan, S. A. Medvedev, J. S. Tse, and Y. Yao, "Superconductivity in hydrogen dominant materials: Silane," Science **319**, 1506 (2008).

[54] O. Degtyareva, J. E. Proctor, C. L. Guillaume, E. Gregoryanz, and M. Hanfland, "Formation of transition metal hydrides at high pressures," Solid State Commun. **149**, 1583 (2009).

[55] C. J. Pickard and R. J. Needs, "Metallization of aluminum hydride at high pressures: A first-principles study," Phys. Rev. B **76**, 144114 (2007).

[56] B. Rousseau and A. Bergara, "Giant anharmonicity suppresses superconductivity in AlH$_3$ under pressure," Phys. Rev. B **82**, 104504 (2010).

[57] P. Hou, X. Zhao, F. Tian, D. Li, D. Duan, Z. Zhao, B. Chu, B. Liu, and T. Cui, "High pressure structures and superconductivity of AlH$_3$(H$_2$) predicted by first principles," RSC Adv. **5**, 5096 (2015).

[58] G. Gao, H. Wang, A. Bergara, Y. Li, G. Liu, and Y. Ma, "Metallic and superconducting gallane under high pressure," Phys. Rev. B **84**, 064118 (2011).

[59] G. Gao, A. R. Oganov, A. Bergara, M. Martinez-Canales, T. Cui, T. Iitaka, Y. Ma, and G. Zou, "Superconducting high pressure phase of germane," Phys. Rev. Lett. **101**, 107002 (2008).

[60] X. Jin, X. Meng, Z. He, Y. Ma, B. Liu, T. Cui, G. Zou, and H. Mao, "Superconducting high-pressure phases of disilane," Proc. Natl. Acad. Sci. U. S. A. **107**, 9969 (2010).

[61] Y. Li, G. Gao, Y. Xie, Y. Ma, T. Cui, and G. Zou, "Superconductivity at ~100 K in dense SiH$_4$(H$_2$)$_2$ predicted by first principles," Proc. Natl. Acad. Sci. U. S. A. **107**, 15708 (2010).

[62] H. Wang, S. T. John, K. Tanaka, T. Iitaka, and Y. Ma, "Superconductive sodalite-like clathrate calcium hydride at high pressures," Proc. Natl. Acad. Sci. U. S. A. **109**, 6463 (2012).

[63] D. Y. Kim, R. H. Scheicher, and R. Ahuja, "Predicted high-temperature superconducting state in the hydrogen-dense transition-metal hydride YH$_3$ at 40 K and 17.7 GPa," Phys. Rev. Lett. **103**, 077002 (2009).

[64] Y. Li, J. Hao, H. Liu, S. T. John, Y. Wang, and Y. Ma, "Pressure-stabilized superconductive yttrium hydrides," Sci. Rep. **5**, 09948 (2015).

[65] D. Y. Kim, R. H. Scheicher, C. J. Pickard, R. J. Needs, and R. Ahuja, "Predicted formation of superconducting platinum-hydride crystals under pressure in the presence of molecular hydrogen," Phys. Rev. Lett. **107**, 117002 (2011).

66 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).

67 T. Kaewmaraya, D. Y. Kim, S. Lebegue, C. J. Pickard, R. J. Needs, and R. Ahuja, "Theoretical investigation of xenon-hydrogen solids under pressure using *ab initio* DFT and GW calculations," Phys. Rev. B **84**, 092101 (2011).

68 J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, "Superconductivity at 39 K in magnesium diboride," Nature **410**, 63 (2001).

69 S. L. Bud'ko, G. Lapertot, C. Petrovic, C. E. Cunningham, N. Anderson, and P. C. Canfield, "Boron isotope effect in superconducting MgB_2," Phys. Rev. Lett. **86**, 1877 (2001).

70 Y. Kamihara, H. Hiramatsu, M. Hirano, R. Kawamura, H. Yanagi, T. Kamiya, and H. Hosono, "Iron-based layered superconductor: LaOFeP," J. Am. Chem. Soc. **128**, 10012 (2006).

71 Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, "Iron-based layered superconductor La[$O_{1-x}F_x$]FeAs ($x =$ 0.05–0.12) with $T_c =$ 26 K," J. Am. Chem. Soc. **130**, 3296 (2008).

72 Z. P. Yin, K. Haule, and G. Kotliar, "Magnetism and charge dynamics in iron pnictides," Nat. Phys. **7**, 294 (2011).

73 B. Monserrat, E. A. Engel, and R. J. Needs, "Giant electron-phonon interactions in molecular crystals and the importance of nonquadratic coupling," Phys. Rev. B **92**, 140302 (2015).

74 D. J. Wales and J. P. K. Doye, "Global optimization by basin-hopping and the lowest energy structures of Lennard-Jones clusters containing up to 110 atoms," J. Phys. Chem. A **101**, 5111 (1997).

75 A. R. Oganov and C. W. Glass, "Crystal structure prediction using evolutionary algorithms: Principles and applications," J. Chem. Phys. **124**, 244704 (2006).

76 N. L. Abraham and M. I. J. Probert, "A periodic genetic algorithm with real-space representation for crystal structure and polymorph prediction," Phys. Rev. B **73**, 224104 (2006).

77 Z. Falls, D. C. Lonie, P. Avery, A. Shamp, and E. Zurek, "XtalOpt Version r9: An open-source evolutionary algorithm for crystal structure prediction," Comput. Phys. Commun. **199**, 178 (2016).

78 S. Goedecker, "Minima hopping: An efficient search method for the global minimum of the potential energy surface of complex molecular systems," J. Chem. Phys. **120**, 9911 (2004).

79 F. H. Stillinger, "Exponential multiplicity of inherent structures," Phys. Rev. E **59**, 48 (1999).

80 J. P. K. Doye and C. P. Massen, "Characterizing the network topology of the energy landscapes of atomic clusters," J. Chem. Phys. **122**, 084105 (2005).

81 N. Xu, D. Frenkel, and A. J. Liu, "Direct determination of the size of basins of attraction of jammed solids," Phys. Rev. Lett. **106**, 245502 (2011).

82 L. Pauling, "The principles determining the structure of complex ionic crystals," J. Am. Chem. Soc. **51**, 1010 (1929).

83 V. S. Urusov and T. N. Nadezhina, "Frequency distribution and selection of space groups in inorganic crystal chemistry," J. Struct. Chem. **50**, 22 (2010).

84 A. J. Morris, C. J. Pickard, and R. J. Needs, "Hydrogen/silicon complexes in silicon from computational searches," Phys. Rev. B **78**, 184102 (2008).

85 A. J. Morris, C. P. Grey, R. J. Needs, and C. J. Pickard, "Energetics of hydrogen/lithium complexes in silicon analyzed using the Maxwell construction," Phys. Rev. B **84**, 224106 (2011).

86 G. Schusteritsch, S. P. Hepplestone, and C. J. Pickard, "First-principles structure determination of interface materials: The Ni_xInAs nickelides," Phys. Rev. B **92**, 054105 (2015).

87 G. Schusteritsch and C. J. Pickard, "Predicting interface structures: From $SrTiO_3$ to graphene," Phys. Rev. B **90**, 035424 (2014).

88 J. Chen, G. Schusteritsch, C. J. Pickard, C. G. Saltzmann, and A. Michaelides, "Two dimensional ice from first-principles: Structures and phase transitions," Phys. Rev. Lett. **116**, 025501 (2016).

89 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).

90 Y. Akahama, M. Nishimura, H. Kawamura, N. Hirao, Y. Ohishi, and K. Takemura, "Evidence from x-ray diffraction of orientational ordering in phase III of solid hydrogen at pressures up to 183 GPa," Phys. Rev. B **82**, 060101 (2010).

91 C. J. Pickard and R. J. Needs, "Structures at high pressure from random searching," Phys. Status Solidi B **246**, 536 (2009).

92 M. I. Eremets and I. A. Troyan, "Conductive dense hydrogen," Nat. Mater. **10**, 927 (2011).

93 R. T. Howie, C. L. Guillaume, T. Scheler, A. F. Goncharof, and E. Gregoryanz, "Mixed molecular and atomic phase of dense hydrogen," Phys. Rev. Lett. **108**, 125501 (2012).

94 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, *ibid.* **86**, 059902 (2012).

95 P. Dalladay-Simpson, R. T. Howie, and E. Gregoryanz, "Evidence for a new phase of dense hydrogens above 325 gigapascals," Nature **529**, 63 (2016).

96 M. I. Eremets, I. A. Troyan, and A. P. Drozdov, "Low temperature phase diagram of hydrogen at pressures up to 380 GPa. A possible metallic phase at 360 GPa and 200 K," preprint arXiv:1601.04479 (2016).

97 L. Dubrovinsky, N. Dubrovinskaia, E. Bykova, M. Bykov, V. Prakapenka, C. Prescher, K. Glazyrin, H.-P. Liermann, M. Hanfland, M. Ekholm, Q. Feng, V. L. Pourovskii, M. I. Katsnelson, J. M. Wills, and I. A. Abrikosov, "The most incompressible metal osmium at static pressures above 750 gigapascals," Nature **525**, 226 (2015).

98 R. F. Smith *et al.*, "Ramp compression of diamond to five terapascals," Nature **511**, 330 (2014).

99 C. J. Pickard and R. J. Needs, "High-pressure physics: Piling up the pressure," Nature **511**, 294 (2014).

100 M. Martinez-Canales, C. J. Pickard, and R. J. Needs, "Thermodynamically stable phases of carbon at multiterapascal pressures," Phys. Rev. Lett. **108**, 045704 (2012).

101 B. A. Remington, R. E. Rudd, and J. S. Wark, "From microjoules to megajoules and kilobars to gigabars: Probing matter at extreme states of deformation," Phys. Plasmas **22**, 090501 (2015).

102 M.-S. Miao and R. Hoffmann, "High pressure electrides: A predictive chemical and physical theory," Acc. Chem. Res. **47**, 1311 (2014).

[103] C. J. Pickard and R. J. Needs, "Aluminium at terapascal pressures," Nat. Mater. **9**, 624 (2010).

[104] J. Sun, M. Martinez-Canales, D. D. Klug, C. J. Pickard, and R. J. Needs, "Stable all-nitrogen metallic salt at terapascal pressures," Phys. Rev. Lett. **111**, 175502 (2013).

[105] Y. Li, Y. Wang, C. J. Pickard, R. J. Needs, Y. Wang, and Y. Ma, "Metallic icosahedron phase of sodium at terapascal pressures," Phys. Rev. Lett. **114**, 5501 (2015).

[106] 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).

[107] E. A. Engel, B. Monserrat, and R. J. Needs, "Anharmonic nuclear motion and the relative stability of hexagonal and cubic ice," Phys. Rev. X **5**, 021033 (2015).

[108] A. P. Drozdov, M. I. Eremets, and I. A. Troyan, "Superconductivity above 100 K in PH_3 at high pressures," e-print arXiv:1508.06224 (2015).

[109] Y. Fu, X. Du, L. Zhang, F. Peng, M. Zhang, C. J. Pickard, R. J. Needs, D. J. Singh, W. Zheng, and Y. Ma, "High-pressure phase stability and superconductivity of pnictogen hydrides and chemical trends for compressed hydrides," Chem. Mater. **28**, 1746 (2016).

[110] See https://icsd.fiz-karlsruhe.de/ for information about the ICSD database which reports experimentally verified inorganic crystal structures.

[111] A. D. Fortes, E. Suard, M.-H. Lemee-Cailleau, C. J. Pickard, and R. J. Needs, "Crystal structure of ammonia monohydrate II," J. Am. Chem. Soc. **131**, 13508 (2009).

[112] G. I. G. Griffiths, A. D. Fortes, C. J. Pickard, and R. J. Needs, "Crystal structure of ammonia dihydrate II," J. Chem. Phys. **136**, 174512 (2012).

[113] A. M. Schaeffer, W. Cai, E. Olejnik, J. J. Molaison, S. Sinogeikin, A. M. dos Santos, and S. Deemyad, "Boundaries for martensitic transition of ^{7}Li under pressure," Nat. Commun. **6**, 8030 (2015).

[114] B. T. Matthias, "Symmetries of superconducting sulfides," Int. J. Quantum Chem. **10**, 435 (1976).

[115] B. Monserrat, C. J. Pickard, and R. J. Needs (unpublished).