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Electronic structure and metalization of a silane-hydrogen system under high pressure investigated using density functional and GW calculations

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We have computed the electronic structure and the vibrational properties of the recently discovered hydrogen-rich compound silane-hydrogen $[SiH_4(H_2)_2]$ from first principles, using density-functional theory. We have also studied the metallization under pressure of $SiH_4(H_2)_2$ by the GW approximation, and obtained that the metallization occurs around 164 GPa, whereas the standard GGA calculations predict a metallization pressure around 145 GPa. Our results are compared with the recent experiment data of Strobel *et al.* [Phys. Rev. Lett. **103**, 065701 (2009)] and Wang *et al.* [Proc. Natl. Acad. Sci. USA. **106**, 14763 (2009)] and it is found that our calculated value of the metallization pressure is higher than the proposed experimental data. Some possible reasons for such a discrepancy are discussed in the text.

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Hydrogen is a safe, environment friendly, and consistent energy carrier,[1,2] and the development of an efficient and economical hydrogen storage system is one of the main challenges of our time. Different methods have been used to find out such a material, which can store more than 6 wt % of hydrogen gravimetrically, together with a fast absorption and desorption kinetics between 60–100 °C. So far, different materials, such as metal-organic framework,[3] covalent-organic frameworks,[4] amidoboranes,[5,6] light-metal hydrides,[7–9] have been studied with the hope to meet these requirements. For instance, the properties of hydrogen-storage materials can be studied via high-pressure experiments, which can reveal much more information about these materials than standard studies. Nowadays, many researchers have emphasized on group IVa hydrides, because it contains a large amount of hydrogen, but also from a more fundamental point of view, because the metallization can possibly occur at lower pressure than for pure hydrogen, and also in view of studying superconductivity in these materials.[10–13]

Recently, Strobel *et al.*[14] have analyzed the characteristics under pressure of a new compound, namely, $SiH_4(H_2)_2$, on the basis of x-ray diffraction experiments, and found it to have a highly symmetrical, well-ordered structure, with 1 f.u./cell. Then, they have studied the phase diagram of $SiH_4(H_2)_2$, and mentioned that the H_2 bond weakening occurs at an unusual low pressure. They have also observed a darkening of the sample at a pressure around 35 GPa, which could eventually be associated with a metal-insulator transition. Roughly at the same time, Wang *et al.*[13] reported a study on the same compound and pointed out a strong interaction between the SiH_4 and the H_2 components. However, a theoretical counterpart of these experimental studies is still missing. In this publication, we analyze the electronic structure and insulator-metal transition of this hydrogen-rich material using density-functional theory (DFT) and the GW approximation (GWA) and predict the pressure of metallization.

We have performed DFT (Ref. 15) calculations with the use of projector-augmented wave (PAW) method[16] as implemented in the Vienna *ab initio* simulation package (VASP).[17,18] We have used the generalized gradient approximation (GGA) (Ref. 19) to perform the ground-state calculations. A $8\times8\times8$ k-points mesh[20] and a cutoff of 1200 eV were found to be suitable to converge the calculations. In a compound like silane-hydrogen, van der Waals interaction should be a key ingredient, which is not correctly described by a semilocal functional such as the GGA. However, the distance between SiH_4 and H_2 molecules is decreased when pressure is applied, and the correct description of this weak interaction becomes less important, as shown below by the good agreement of our calculated pressure with the experimental value (see below). Moreover, since DFT has difficulties to treat excited states, and, in particular, the band gap, which is usually underestimated by LDA or GGA, we have used the GWA (Refs. 21 and 22) to study the metallization of SiH_4-H_2 under pressure. In this case, the following quasiparticle equation is solved:

$$(T+V_{ext}+V_h)\psi_{\mathbf{k}n}(\mathbf{r})+\int d^3r'\Sigma(\mathbf{r},\mathbf{r}',E_n(\mathbf{k}))\psi_{\mathbf{k}n}(\mathbf{r}') = E_n(\mathbf{k})\psi_{\mathbf{k}n}(\mathbf{r}),$$

where T is the free-electron kinetic-energy operator, V_{ext} the external potential due to the ion cores, V_h the Hartree potential, Σ the self-energy operator, and $E_n(\mathbf{k})$ and $\psi_{\mathbf{k}n}(\mathbf{r})$ are, respectively, the quasiparticle energy and wave function. Then, the self-energy operator is approximated by the product of the Green's function and the screened Coulomb interaction W, which gives the GW approximation. Within this framework, the computation is simplified, and the DFT eigenvalues $\epsilon_n(\mathbf{k})$ are corrected by the GW approximation to give reliable excited-state properties[23]

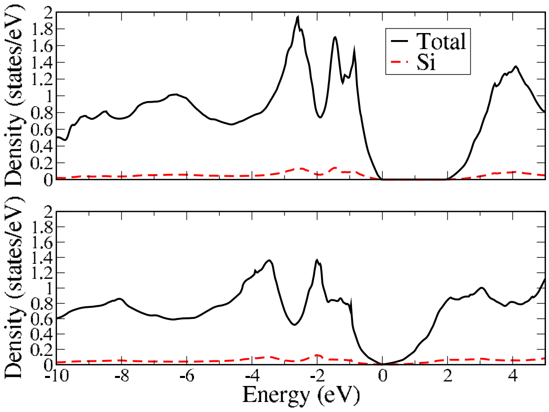

FIG. 1. (Color online) Calculated total (full line) and partial (dashed line) densities of states of $SiH_4(H_2)_2$ for 84 GPa (upper plot) and 145 GPa (lower plot).

$$\mathrm{Re}\, E_n(\mathbf{k}) = \epsilon_n^{\mathrm{DFT}}(\mathbf{k}) + Z_{n\mathbf{k}}\{\langle\Psi_{\mathbf{k}n}^{\mathrm{DFT}}|\mathrm{Re}\,\Sigma[\mathbf{r},\mathbf{r}',\epsilon_n(\mathbf{k})]|\Psi_{\mathbf{k}n}^{\mathrm{DFT}}\rangle - \langle\Psi_{\mathbf{k}n}^{\mathrm{DFT}}|V_{xc}^{\mathrm{DFT}}(r)|\Psi_{\mathbf{k}n}^{\mathrm{DFT}}\rangle\},$$

where the QP renormalization factor $Z_{n\mathbf{k}}$ is given by

$$Z_{n\mathbf{k}}^{\mathrm{DFT}} = \left\{1 - \langle\Psi_{\mathbf{k}n}^{\mathrm{DFT}}|\frac{\partial}{\partial\omega}\mathrm{Re}\,\Sigma[\mathbf{r},\mathbf{r}',\epsilon_n(\mathbf{k})]|\Psi_{\mathbf{k}n}^{\mathrm{DFT}}\rangle\right\}^{-1}.$$

We have used the GW approximation implemented in the code VASP,[18] following the method described in Ref. 24. 200 bands were used for the summation over bands in the calculation of the polarizability and the self-energy, a cutoff of 150 eV was used for the size of the polarizability matrices, together with a k-point grid of $8\times8\times8$. The implementation of the GW approximation within the PAW formalism is also reported in Refs. 25–27.

We start our investigation by using the structural information provided in Ref. 14: we setup a crystal structure with a fcc lattice containing one $SiH_4(H_2)_2$ formula per unit cell with a volume of 66.5 Å^3. After relaxation, this structure is preserved and the calculated pressure has a value of 6.5 GPa, in very good agreement with the experimental value (6.8 GPa), confirming our previous statement that a fully correct model of the van der Waals interaction is not necessary for the range of pressure that we are investigating. Then, we repeat a similar calculation for different values of the volume, until we reach metallization via an overlap of valence and conduction bands. Our calculated pressure is obtained directly from the code VASP as the trace of the stress tensor.

In Fig. 1, we present our calculated total and partial (corresponding to the Si atom) densities of states for some values of the volume of the cell of 30 Å^3 (upper plot) and 24.5 Å^3 (lower plot). The corresponding values of the calculated pressure are, respectively, 84 GPa and 145 GPa, which is the pressure of metallization (the electronic band gap is equal to zero) with the GGA. It appears that even at the pressure of 84 GPa, the system is still insulating with a sizable GGA band gap of 2 eV, and only a pressure of 145 GPa is able to make $SiH_4(H_2)_2$ to become a metal with GGA. The Si partial density of states is widely distributed in energy, indicating a strong hybridization of Si with its hydrogen neighbors. Also, the Si-derived states contribute significantly to the top of the valence band and the bottom of the conduction-band states. A large part of the total density of states weight corresponds to an energy range from 0 to −4 eV, a fact already observed for silane.[12]

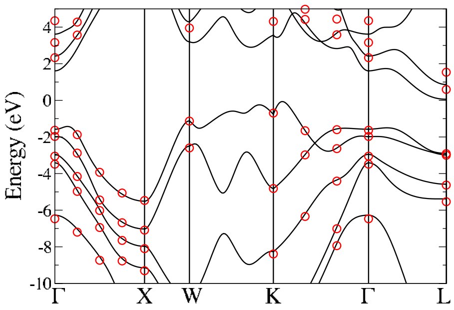

FIG. 2. (Color online) Band structure of $SiH_4(H_2)_2$ at 145 GPa computed with the GGA (full lines) and the GW approximation (red dots).

Additionally, we have calculated the vibrational modes (at the Γ point) of $SiH_4(H_2)_2$, in order to compare them with the available experimental values. For a calculated pressure of 6.5 GPa, our calculated H_2 vibron has a frequency of 4290 cm^{-1}, which is in good agreement with the experimental values (around 4200 cm^{-1} in Refs. 13 and 14). The modes related to silane are calculated to have values around 2220 cm^{-1} for $\nu_1(A_1)$ and $\nu_3(F_2)$ which corresponds to the experimental value of 2280 cm^{-1} (Ref. 14) and around 2200 cm^{-1} (Ref. 13). The mode $\nu_2(E)$ is calculated to be 960 cm^{-1} in good agreement with the value of 935 cm^{-1} (Strobel *et al.*[14]) and 900 cm^{-1} (Wang *et al.*[13]). We have also performed a similar calculation for a pressure of 84 GPa, in order to observe how these frequencies are modified by pressure. We found that while the frequencies of the modes related to silane are increased [$\nu_1(A_1)$ and $\nu_3(F_2)$ ≈ 2450 cm^{-1}; $\nu_2(E) \approx 1370$ cm^{-1}], the frequency associated to H_2 is decreased to a value of 3690 cm^{-1}. This is also what is observed in the experiments,[14] and fully confirms the particular behavior of the H_2 vibron in $SiH_4(H_2)_2$ under pressure.

However, as we mentioned above, common approximations to the exchange-correlation potential used in DFT are not able to describe correctly the band gap. This is exemplified by Fig. 2, where we plot the band structure of $SiH_4(H_2)_2$ at 145 GPa using both the GGA (full lines) and the GW approximation (red dots). As expected, most of the bands show a large dispersion, indicating an important interaction between the different components of this material. While the top of the valence band (near the high-symmetry point K) and the bottom of the conduction band (at the high-symmetry point L) have the same energy with the GGA (indicating metallization), the GW approximation still shows a sizable band gap of roughly 1.0 eV.

This fact highlights the importance of using an adapted tool (the GW approximation) in order to study insulator to metal transitions. Therefore, we have performed a series of GW calculations in order to obtain the value of the true pressure of metallization, the corresponding results are presented in Fig. 3. The band gap decreases almost linearly with the

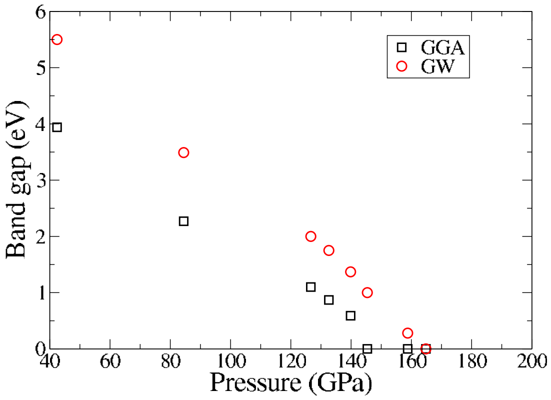

FIG. 3. (Color online) Pressure variation in the minimum electronic band gap computed with the GGA (black squares) and the GWA (red circles). Using the GGA, the insulator-metal transition is found to occur at 145 GPa while with the GWA the corresponding pressure is 164 GPa.

pressure, and it is found that the pressure of transition is about 164 GPa, which is almost 20 GPa more than the pressure given by the GGA (145 GPa). From this study, it could appear that the calculated pressure of metallization is much higher than the one noticed in Ref. 14, who observed a darkening of the sample around 35 GPa.

However, as mentioned in their paper, Strobel *et al.*[14] cannot exclude a possible interaction between silane, hydrogen, and the gasket material to explain the darkening of the sample (which is a general difficulty not only related to the present study), and indeed our calculations seems to favor such a scenario. Moreover, whether the stoichiometry of $2H_2:1SiH_4$ is exactly fulfilled or not is also a delicate question since a different chemical composition can also change significantly the electronic structure. To further explore this possibility, we have performed some calculations for the $1H_2:1SiH_4$ composition. To setup the system, we have simply removed a H_2 molecule in the $2H_2:1SiH_4$ cell and then relaxed the system for various values of the volume, reaching at maximum a pressure of 53 GPa. The corresponding density of states, obtained from DFT, are presented in Fig. 4. Even at this relatively high pressure, the SiH_6 system is still insulating, with a band gap of 2.1 eV, and therefore the darkening of the sample cannot be explained by a different chemical composition such as SiH_6. An other fact that was not mentioned in the experimental papers is the possibility to have one or several phase transitions under pressure, as it was observed for silane.[12] This was also not considered in our calculations because we did not notice any sign of a possible destabilization of the lattice. In any case, the current understanding of the physics behind the behavior of this material is only at the beginning and further experiments are needed. An other approach to be pursued as well is the study of materials with a higher concentration of hydrogen, like SiH_{12}.[28] Such a study would give more valuable information about the whole family of Si-H materials with ultimately a better understanding of pure hydrogen.

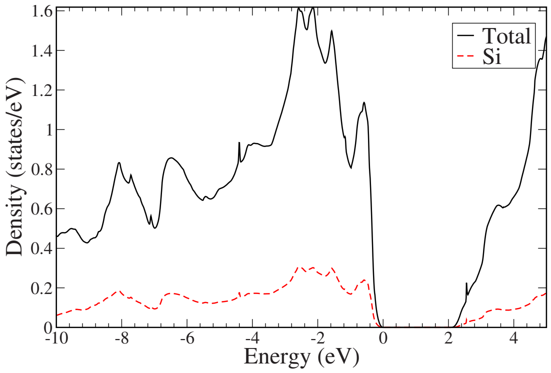

FIG. 4. (Color online) Calculated total (full line) and partial (dashed line) densities of states of SiH_4-H_2 at 53 GPa. The system has a band gap of 2.1 eV.

In summary, we have studied the electronic structure of $SiH_4(H_2)_2$. We have found this material to be a large band-gap insulator, which becomes a metal only for a pressure as high as 164 GPa when using the GW approximation. Our calculated value being higher than the experimental one, we have proposed several explanations to understand this difference, such as phase transitions or an interaction between the sample and the gasket material during the experiment. Then, the vibrational properties were calculated, and a good agreement with experiments was found. In particular, the decrease in the vibrational mode associated to H_2 in function of pressure is confirmed by our calculations. We expect that our work will stimulate further experimental and theoretical work on silane-hydrogen and on related materials.

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[1] L. Schlapbach and A. Zuttel, Nature Mater. **414**, 353 (2001).
[2] M. S. Dresselhaus and I. L. Thomas, Nature Mater. **414**, 332 (2001).
[3] A. Blomqvist, C. M. Araujo, P. Srepusharawoot, and R. Ahuja, Proc. Natl. Acad. Sci. U.S.A. **104**, 20173 (2007).
[4] P. Srepusharawoot, R. H. Scheicher, C. M. Araujo, A. Blomqvist, U. Pinsook, and R. Ahuja, J. Phys. Chem. C **113**, 8498 (2009).
[5] Z. Xiong, C. K. Yong, G. Wu, P. Chen, W. Shaw, A. Karkamkar, T. Autrey, M. O. Jones, S. R. Johnson, P. P. Edwards, and W. I. F. David, Nature Mater. **7**, 138 (2008).
[6] M. Ramzan, F. Silvearv, A. Blomqvist, R. H. Scheicher, S. Leb-

ègue, and R. Ahuja, Phys. Rev. B **79**, 132102 (2009).

[7] M. Ramzan and R. Ahuja, Appl. Phys. Lett. **94**, 141903 (2009).

[8] M. Ramzan, T. Hussain, and R. Ahuja, Appl. Phys. Lett. **94**, 221910 (2009).

[9] M. Ramzan and R. Ahuja, J. Appl. Phys. **106**, 016104 (2009).

[10] K. A. Johnson and N. W. Ascroft, Nature (London) **403**, 632 (2000).

[11] N. W. Ashcroft, Phys. Rev. Lett. **92**, 187002 (2004).

[12] D. Y. Kim, R. H. Scheicher, S. Lebègue, J. Prasongkit, B. Arnaud, M. Alouani, and R. Ahuja, Proc. Natl. Acad. Sci. U.S.A. **105**, 16454 (2008).

[13] S. Wang, H. Mao, X. Chen, and W. L. Mao, Proc. Natl. Acad. Sci. U.S.A. **106**, 14763 (2009).

[14] T. A. Strobel, M. Somayazulu, and R. J. Hemley, Phys. Rev. Lett. **103**, 065701 (2009).

[15] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

[16] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[17] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).

[18] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[19] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).

[20] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[21] L. Hedin, Phys. Rev. **139**, A796 (1965).

[22] L. Hedin and S. Lundquist, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1969), Vol. 23, p. 1.

[23] G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).

[24] M. Shishkin and G. Kresse, Phys. Rev. B **74**, 035101 (2006).

[25] B. Arnaud and M. Alouani, Phys. Rev. B **62**, 4464 (2000).

[26] S. Lebègue, B. Arnaud, M. Alouani, and P. E. Blöechl, Phys. Rev. B **67**, 155208 (2003).

[27] S. Lebègue, M. Alouani, B. Arnaud, and W. E. Pickett, Europhys. Lett. **63**, 562 (2003).

[28] N. W. Ashcroft, Phys. **2**, 65 (2009).