Hypothetical low-energy chiral framework structure of group 14 elements

Chris J. Pickard

Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom
and Scottish Universities Physics Alliance, School of Physics and Astronomy, University of St. Andrews,
St. Andrews KY16 9SS, United Kingdom

R. J. Needs

Theory of Condensed Matter Group, Cavendish Laboratory, J J Thomson Avenue, Cambridge CB3 0HE, United Kingdom

We study a sp^3 bonded chiral framework structure (CFS) composed of the group 14 elements carbon (C), silicon (Si), germanium (Ge), or tin (Sn). The CFS is very simple and highly symmetric, having a six-atom primitive unit cell with all atoms being equivalent. The CFS is the elemental analog of a zeolite-type structure and is also related to clathrate structures. Density-functional theory calculations show that the CFS is only slightly higher in energy than the diamond structure, with an energy difference varying from 112 meV per atom for C to 28 meV per atom for Sn. The bulk modulus of the carbon CFS is found to be smaller than that of diamond but larger than that of the carbon clathrate II structure. The density of electronic states and band gaps of the elemental CFS materials are described and compared with those of the corresponding diamond structures.

I. INTRODUCTION

Framework structures of sp^3 bonded Si atoms with a lower density than the equilibrium diamond structure were first synthesized by Cros and co-workers.[1–4] They were named "clathrates" because their structures are analogous to those of clathrate hydrates, which occur when water molecules form cagelike structures around molecules such as methane. Framework structures have numerous commercial uses and considerable potential for new applications. Examples of such structures are the zeolites,[5] which are porous oxide structures, and the clathrates in which atoms or molecules of one substance are enclosed within the crystalline structure of another.

Clathrates have been synthesized from the group 14 elements Si and Ge in the type I, II, and III structures, and also for Sn in the type I and II structures.[6–8] Typical group 14 clathrate compounds have chemical formulas such as the type I clathrate M_8X_{46}, the type II clathrate $M_{24}X_{136}$, and the type III clathrate $M_{24}X_{100}$, where M denotes a "guest" element and X denotes the "host" element. The guest atoms are species such as Na, K, Rb, Cs, Ba, etc., which are hosted by the group 14 atoms. Clathrates composed of C host atoms and metallic guest atoms are predicted to have very interesting properties[9–11] but unfortunately no C-based clathrate has so far been synthesized.

Type I, II, and III group 14 clathrates exhibit intriguing properties such as a thermal conductivity of the form characteristic of glassy materials,[12,13] superconductivity[14] with a transition temperature as high as 8 K,[15,16] guest-atom derived magnetism,[15,17,18] tunneling of heavy guest atoms,[19] potential as useful thermoelectric materials,[20–22] and (direct) band gaps larger than the corresponding diamond structure,[23,24] suggesting possible applications as photovoltaics.

Relationships exist between zeolite and clathrate structures. For example, the cubic clathrate II framework may be derived from the ZSM-39 zeolite silicate by replacing each SiO_2 unit by a single atom. The guest species is very important in synthesizing these clathrates, as they act as a template around which the self-assembly of the nanocages occurs. In some cases it has proved possible to remove, or largely remove, the guest atoms from the clathrate, leaving a "guest-free" clathrate.[25–28] This raises the issue of the stability of guest-free clathrate structures relative to the equilibrium diamond structure of the group 14 elements. Energy differences between clathrate and diamond structures are not readily measured, and electronic-structure methods have been used to compute them instead.

First-principles electronic-structure calculations using density-functional theory (DFT) methods have shown that the energies of the guest-free type I, II, and III clathrate structures of group 14 elements are only slightly higher in energy than those of the corresponding diamond structure. For example, Dong and Sankey[29] found the type I Ge_{46} and type II Ge_{136} clathrate structures to be, respectively, 50 meV per atom and 44 meV per atom higher in energy than the Ge-diamond structure. Calculations for Sn clathrates found the type I and type II clathrate structures to be, respectively, 41 meV per atom and 38 meV per atom higher in energy than Sn-diamond.[30] Rey *et al.*[11] have recently calculated the energy of the C_{46} type I clathrate to be 90 meV per atom higher in energy than C-diamond. This energy difference is about twice those computed for the other group 14 elements. In addition, the energy penalties for deviations from the ideal tetrahedral bond angle are larger in C and it readily supports sp^2 bonding which provides many competing low-energy structures based on graphite/graphene, nanotubes, and fullerites/fullerenes. This may explain why carbon clathrates have not yet been synthesized.

Nesper *et al.*[31] studied the zeolite structures listed in the 1987 edition of the "Atlas of Zeolite Structure Types,"[32] replacing each SiO_2 unit by a C atom and neglecting those with three- and four-membered rings. The energies of the remaining six polymorphs were calculated within DFT. The
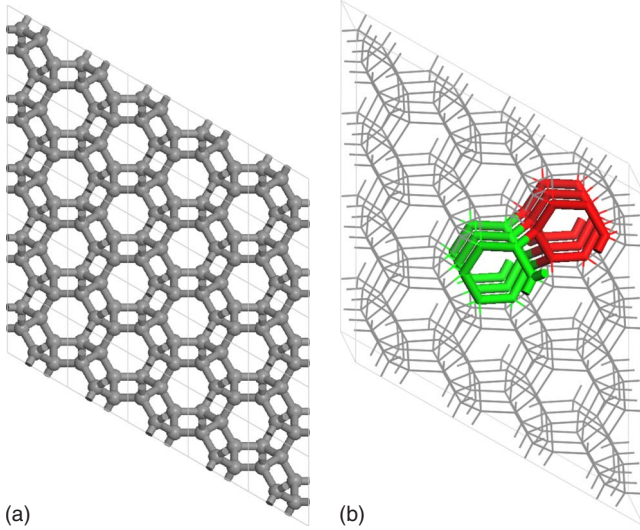
FIG. 1. (Color online) Two views of the CFS. View (a) shows the channels and the nature of the walls between them while view (b) shows the helices and the bonds between them.

lowest energy polymorph was the one derived from ZSM-39, the clathrate II structure, which they calculated to be 70 meV per atom higher in energy than C-diamond. We conclude that comparisons of the various DFT results with experiment suggest that only clathrate/zeolite-like structures of the group 14 elements which are particularly low in energy can readily be synthesized. A natural question to ask is whether other low-energy clathrate/zeolite-like structures of group 14 elements exist apart from the known clathrate I, II, and III structures.

II. SEARCHING FOR NEW STRUCTURES

We have performed a computational search for C and Si structures using first-principles DFT methods. In our approach an ensemble of random initial structures is chosen and each of them is relaxed to a minimum in the energy. This method has been successfully employed in a number of projects.[33–36] We use the CASTEP plane-wave code for our calculations,[37] with ultrasoft pseudopotentials[38] and the Perdew-Burke-Ernzerhof (PBE) (Ref. [39]) generalized gradient approximation (GGA) density functional. All of our results were obtained using plane-wave cutoff energies of 500 eV (C), 300 eV (Si), 400 eV (Ge), and 400 eV (Sn), and the Brillouin-zone integrations were performed using a k-point grid of spacing $2\pi \times 0.03$ Å^{-1}.

The search produced many structures, including the equilibrium diamond structures of C and Si, some of the dense structures adopted by Si under high pressures,[40] and some structures which are less dense than the diamond structure. One of the low-energy less-dense structures found in both our C and Si searches is shown in Fig. 1. The atoms are fourfold coordinated and are arranged in five-membered rings. The structure consists of a hexagonal packing of helices which are crosslinked to satisfy fourfold coordination. The helices all twist to the left or all twist to the right so that the crystal is chiral and cannot be superimposed on its mirror image. The different mirror images are called "enantiomers"

or "optical isomers." The structure is simple and highly symmetrical and belongs to the space group $P6_122$ (number 178, hexagonal) or $P6_522$ (number 179, hexagonal). It has six atoms in the primitive unit cell which are all equivalent by symmetry. The details of the structure for each element are reported in Table I and we refer to it as the "chiral framework structure" or CFS. After having studied the CFS we found that it is related to the hypothetical zeolite structure "number 271" generated by mathematical methods based on "tiling theory."[41,42] The silicate structure has been studied using empirical potentials[41] but we are not aware of any previous studies of the group 14 analogs.

III. PROPERTIES OF THE CFS

We calculated the energies of the CFS for the group 14 elements C, Si, Ge, and Sn, and the differences in energy from the corresponding diamond structure are given in Table II. The energy differences from the diamond structure decrease with increasing atomic number, as has been found in calculations for clathrate II structures.[11,29,30,43] The CFS is higher in energy than the clathrate II structure for each element, by 40 meV per atom for C, but by less than 10 meV per atom for the other elements.

There has been a great deal of interest in low-energy structures of C. Under ambient conditions the diamond structure is the most stable sp^3 bonded phase of C. Polytype structures consisting of different stackings of layers along a $\langle 111 \rangle$ direction also have low energies and the highest-energy polytype (the wurtzite structure) has been calculated to be about 18 meV per atom higher in energy than diamond.[44] Wurtzite

TABLE I. The lattice parameters a, b, and c, and the parameter x of the relaxed CFS structures. The atoms occupy the $6b$ $(x, 2x, 1/4)$ Wyckoff position, where the value of x for each element is given in the table.

Element	a (Å)	b (Å)	c (Å)	x
C	3.569	3.569	3.374	0.2326
Si	5.470	5.470	5.114	0.2325
Ge	5.757	5.757	5.426	0.2332
Sn	6.628	6.628	6.232	0.2329

TABLE II. The energy difference ΔE_{CFS} between the CFS and the corresponding diamond structure, and the energy difference ΔE_{CII} between the CII (clathrate II) structure and the corresponding diamond structure, in meV per atom. The volumes V_{CFS} and V_{dia} of the CFS and diamond structures are given in Å^3 per atom.

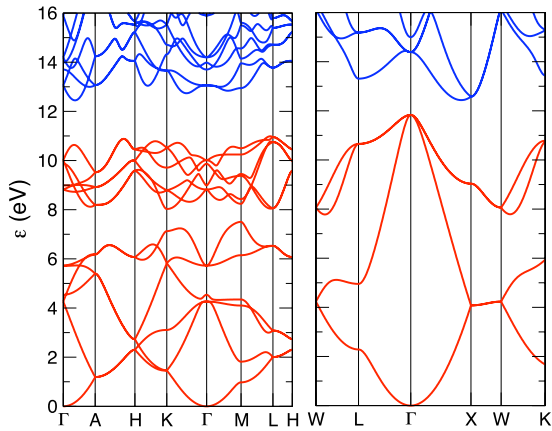| Element	ΔE_{CFS} (meV)	ΔE_{CII} (meV)	V_{CFS} (Å^3)	V_{dia} (Å^3)
C	112	72	6.20	5.68
Si	53	52	22.09	20.37
Ge	34	26	25.96	24.10
Sn	28	23	39.52	36.80

FIG. 2. (Color online) Band structures of (left) Si-CFS and (right) Si-diamond. The zeros of energy are aligned on the lowest-energy valence-band states.
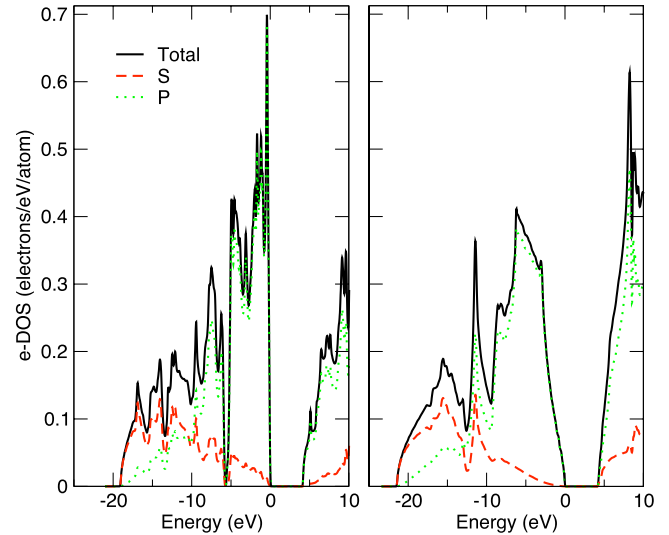

FIG. 3. (Color online) Electronic density of states of (left) the C-CFS and (right) C-diamond. The solid line shows the total density of states while the dashed and dotted lines show the s and p components, respectively.

and the other polytypes are clearly substantially lower in energy than either the CFS or clathrate II structure. Recently, Li et al.[45] performed a DFT study of a low-energy sp^3 bonded monoclinic structure of C with $C2/m$ symmetry. This structure also turned up in our searches and we calculate it to be 161 meV per atom higher in energy than the C-diamond structure so that it is less stable than our C-CFS. Li et al.[45] showed that calculated x-ray diffraction and near K-edge spectroscopy data for mixtures of graphite and their $C2/m$ structure are consistent with experimental data for over-compressed graphite,[46] although it seems likely that mixtures of graphite and many other sp^3 bonded structures would also be consistent with the available experimental data.

Table II also gives the volumes of the CFS and those of the corresponding diamond structures. The CFS is less dense in each case, by 8.4%, 7.8%, 7.2%, and 6.9% for C, Si, Ge, and Sn, respectively, so that the percentage density difference from the corresponding diamond structure decreases with atomic number. The C-CFS has a density intermediate between diamond and graphite. The CFS has three bond angles which are a little smaller than the perfect tetrahedral angle of 109.5° and one bond angle which is substantially larger. For example, the bond angles of the C-CFS are 105.2°, 106.3°, 107.2°, and 124.5°, and those for the other elements are very similar. We calculated the bulk modulus of the C-CFS to be $B_0 = 390$ GPa and its pressure derivative to be $B_0' = 3.6$. These may be compared with the values calculated for C-diamond of $B_0 = 435$ GPa and $B_0' = 3.6$, which are in good agreement with experiment[47,48] while we find $B_0 = 373$ GPa and $B_0' = 3.6$ for the C-clathrate II structure. We calculated the volume of the C-clathrate II structure to be 6.57 Å per atom, which is larger than that of the C-CFS. The bulk moduli of the C-clathrate II, C-CFS, and C-diamond phases therefore follow the usual trend; the bulk modulus increases with the density of the material.

The band structures of Si-CFS and Si-diamond are shown in Fig. 2. The valence-band maximum (VBM) of Si-CFS is close to the L point in the Brillouin zone while the conduction-band minimum (CBM) is about 0.4 of the way along the Γ-A line. The minimum band gap of 1.46 eV is substantially larger than the minimum band gap of Si-

diamond, which we calculated to be 0.6 eV. The experimental band gap of Si-diamond is about 1.2 eV and the underestimation of the Si-diamond band gap in our calculations is typical of the results obtained with the PBE-GGA density functional. We expect all of the calculated band gaps reported here to be underestimates but the differences in the calculated band gaps between the CFS and diamond structures are likely to be more accurate than the band-gap values themselves. The valence bands of Si-CFS are divided into two parts (each accommodating two valence electrons per atom) separated by an energy gap of about 0.5 eV. The total valence-band width of Si-CFS is calculated to be 11.0 eV while that of Si-diamond is somewhat larger at 11.8 eV.

The electronic densities of states of C-diamond and C-CFS shown in Fig. 3 are quite similar, with the s components lying mostly in the lower half of the valence band and the p components in the upper half. In C-CFS the upper and lower halves of the valence band overlap slightly resulting in a strong pseudogap at −5.7 eV in Fig. 3. The total valence-band width of C-CFS is calculated to be 19.0 eV while that of C-diamond is somewhat larger at 21.4 eV. The VBM of C-CFS is close to the L point and the CBM is about 0.4 of the way along the Γ-A line. The minimum band gap of 4.12 eV is almost the same as the calculated value for C-diamond of 4.14 eV, although this is smaller than the experimental gap of C-diamond of 5.5 eV.

The VBM of Ge-CFS is close to the L point while the CBM is about 0.4 of the way along the H-K line. The minimum band gap of Ge-CFS is 0.80 eV while the calculations give no gap for Ge-diamond, although experimental measurements give a gap of 0.66 eV. The valence band of Ge-CFS is divided into two halves separated by 1.3 eV. The VBM of Sn-CFS is close to the L point while the CBM is about 0.4 of the way along the H-K line. The minimum band gap of Sn-CFS is 0.44 eV while the calculations give no gap for Sn-diamond and experimentally it is a zero-band-gap

semiconductor. The two halves of the valence band of Sn-CFS are separated by a gap of 1.5 eV.

We have investigated the possibility of incorporating hydrogen (H) atoms within the CFS. We performed a number of searches by inserting two H atoms or an H_2 molecule at random positions within the CFS and then relaxing the structures. We found the lowest energy configuration for two H atoms within the Si-CFS to consist of a H_2 molecule which is not bonded to the Si framework and sits within one of the "channels" apparent in Fig. 1. The most favorable structure of two H atoms in C-CFS consists of a broken C-C bond with each dangling bond saturated by a H atom, which is roughly 1 eV more stable than molecular H_2 configurations. These structures mirror those found for H defects in the respective diamond structures. The most favorable defect for two H atoms in bulk diamond-structure Si is an interstitial H_2 molecule[49] while in bulk C-diamond the H_2 molecule dissociates with one H atom sitting at a bond center and the other occupying an antibonding site in a configuration known as the H_2^* defect.[50] Our calculations show that it costs energy for a gas-phase H_2 molecule to enter the channels of the Si-CFS and C-CFS, as it does for the bulk diamond structures, and therefore the Si-CFS and C-CFS are not useful hydrogen storage materials.

IV. CONCLUSIONS

We have studied a simple and highly symmetric framework structure of group 14 elements which is comparable in energy to the clathrate I and II structures, which have been synthesized in Si, Ge, and Sn. Synthesis of the CFS might be possible because it is low in energy but a suitable template would have to be found to facilitate its self-assembly. The bulk modulus of the C-CFS is larger than that of the C-clathrate II structure but smaller than that of C-diamond.

The band structures of the C-, Si-, Ge-, and Sn-CFS show similar features. They are indirect band-gap semiconductors with minimum band gaps substantially larger than those of the corresponding diamond structures, except for C where the band gaps are almost the same. The indirect band gaps of the CFS make them less useful for optoelectronic applications than the clathrate I, II, and III structures, which have direct band gaps. The occupied valence-band widths of the CFS are narrower than for the corresponding diamond structure. The valence bands are separated into two halves by an energy gap which is approximately zero in C but which increases with atomic number.

The CFS is less dense than the equilibrium diamond structures of the group 14 elements and it contains channels which could accommodate guest atoms, although the C and Si forms are not useful hydrogen storage materials. The CFS is a microporous chiral structure so that it might be used to selectively bind enantiomers and act as an enantioselective solid catalyst.[51] We are unable to suggest a synthesis route for the CFS but we hope that our study will motivate theoretical and experimental work on new group 14 framework structures.

[1] J. S. Kasper, P. Hagenmuller, M. Pouchard, and C. Cros, Science **150**, 1713 (1965).

[2] C. Cros, M. Pouchard, and P. Hagenmuller, C. R. Acad. Sci. URSS **260**, 4764 (1965).

[3] C. Cros, M. Pouchard, P. Hagenmuller, and J. S. Kasper, Bull. Soc. Chim. Fr. **7**, 2737 (1968).

[4] C. Cros, M. Pouchard, and P. Hagenmuller, J. Solid State Chem. **2**, 570 (1970).

[5] C. Baerlocher, L. B. McCusker, and D. H. Olson, *Atlas of Zeolite Framework Types*, 6th ed. (Elsevier, New York, 2007). See also http://www.iza-structure.org/databases/

[6] A. San-Miguel, P. Kéghélian, X. Blase, P. Mélinon, A. Perez, J. P. Itié, A. Polian, E. Reny, C. Cros, and M. Pouchard, Phys. Rev. Lett. **83**, 5290 (1999).

[7] A. San-Miguel and P. Toulemonde, High Press. Res. **25**, 159 (2005).

[8] M. Beekman and G. S. Nolas, J. Mater. Chem. **18**, 842 (2008).

[9] X. Blase, P. Gillet, A. San Miguel, and P. Mélinon, Phys. Rev. Lett. **92**, 215505 (2004).

[10] F. Zipoli, M. Bernasconi, and G. Benedek, Phys. Rev. B **74**, 205408 (2006).

[11] N. Rey, A. Muñoz, P. Rodriguez-Hernandez, and A. San Miguel, J. Phys.: Condens. Matter **20**, 215218 (2008).

[12] J. L. Cohn, G. S. Nolas, V. Fessatidis, T. H. Metcalf, and G. A. Slack, Phys. Rev. Lett. **82**, 779 (1999).

[13] J. Martin, H. Wang, and G. S. Nolas, Appl. Phys. Lett. **92**, 222110 (2008).

[14] H. Kawaji, H. O. Horie, S. Yamanaka, and M. Ishikawa, Phys. Rev. Lett. **74**, 1427 (1995).

[15] K. Tanigaki, T. Shimizu, K. M. Itoh, J. Teraokai, Y. Moritomo, and S. Yamanaka, Nature Mater. **2**, 653 (2003).

[16] R. Lortz, R. Viennois, A. Petrovic, Y. Wang, P. Toulemonde, C. Meingast, M. M. Koza, H. Mutka, A. Bossak, and A. San Miguel, Phys. Rev. B **77**, 224507 (2008).

[17] S. Paschen, W. Carrillo-Cabrera, A. Bentien, V. H. Tran, M. Baenitz, Y. Grin, and F. Steglich, Phys. Rev. B **64**, 214404 (2001).

[18] G. T. Woods, J. Martin, M. Beekman, R. P. Hermann, F. Grandjean, V. Keppens, O. Leupold, G. J. Long, and G. S. Nolas, Phys. Rev. B **73**, 174403 (2006).

[19] R. P. Hermann, V. Keppens, P. Bonville, G. S. Nolas, F. Grandjean, G. J. Long, H. M. Christen, B. C. Chakoumakos, B. C. Sales, and D. Mandrus, Phys. Rev. Lett. **97**, 017401 (2006).

[20] G. A. Slack, Mater. Res. Soc. Symp. Proc. **478**, 47 (1997).

[21] B. B. Iversen, A. E. C. Palmqvist, D. E. Cox, G. S. Nolas, G. D. Stucky, N. P. Blake, and H. Metiuf, J. Solid State Chem. **149**, 455 (2000).

[22] X. F. Tang, P. Li, S. K. Deng, and Q. J. Zhang, J. Appl. Phys. **104**, 013706 (2008).

[23] G. B. Adams, M. O'Keeffe, A. A. Demkov, O. F. Sankey, and

Y.-M. Huang, Phys. Rev. B **49**, 8048 (1994).

[24] K. Kishimoto, T. Koyanagi, K. Akai, and M. Matsuura, Jpn. J. Appl. Phys. **46**, L746 (2007).

[25] J. Gryko, P. F. McMillan, R. F. Marzke, G. K. Ramachandran, D. Patton, S. K. Deb, and O. F. Sankey, Phys. Rev. B **62**, R7707 (2000).

[26] A. Ammar, C. Cros, M. Pouchard, N. Jaussaud, J. M. Bassat, G. Villeneuve, M. Duttine, M. Ménétrier, and E. Reny, Solid State Sci. **6**, 393 (2004).

[27] A. M. Guloy, R. Ramlau, Z. Tang, W. Schnelle, M. Baitinger, and Y. Grin, Nature (London) **443**, 320 (2006).

[28] T. F. Fässler, Angew. Chem., Int. Ed. **46**, 2572 (2007).

[29] J. Dong and O. F. Sankey, J. Phys.: Condens. Matter **11**, 6129 (1999).

[30] C. W. Myles, J. Dong, and O. F. Sankey, Phys. Rev. B **64**, 165202 (2001).

[31] R. Nesper, K. Vogel, and P. E. Blochl, Angew. Chem. **32**, 701 (1993).

[32] W. M. Meier and D. H. Olson, *Atlas of Zeolite Structure Types* (Butterworths, London, 1987).

[33] C. J. Pickard and R. J. Needs, Phys. Rev. Lett. **97**, 045504 (2006).

[34] C. J. Pickard and R. J. Needs, Nat. Phys. **3**, 473 (2007).

[35] C. J. Pickard and R. J. Needs, Phys. Rev. B **76**, 144114 (2007).

[36] C. J. Pickard and R. J. Needs, Nature Mater. **10**, 757 (2008).

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

[38] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[39] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[40] A. Mujica, A. Rubio, A. Muñoz, and R. J. Needs, Rev. Mod. Phys. **75**, 863 (2003).

[41] M. D. Foster, O. D. Friedrichs, R. G. Bell, F. A. Almeida Paz, and J. Klinowski, J. Am. Chem. Soc. **126**, 9769 (2004). Note that the caption to Fig. 8 of this paper states that zeolite number 271 contains five- and six-membered rings but in fact it consists entirely of five-membered rings.

[42] O. D. Friedrichs, A. W. M. Dress, D. H. Huson, J. Klinowski, and A. L. Mackay, Nature (London) **400**, 644 (1999).

[43] J. Dong, O. F. Sankey, and G. Kern, Phys. Rev. B **60**, 950 (1999).

[44] Z. Wang, Y. Zhao, C.-s. Zha, Q. Xue, R. T. Downs, R.-G. Duan, R. Caracas, and X. Liao, Adv. Mater. (Weinheim, Ger.) **20**, 3303 (2008).

[45] Q. Li, Y. Ma, A. R. Oganov, H. Wang, H. Wang, Y. Xu, T. Cui, H.-k. Mao, and G. Zou, Phys. Rev. Lett. **102**, 175506 (2009).

[46] W. L. Mao, H.-k. Mao, P. J. Eng, T. P. Trainor, M. Newville, C.-c. Kao, D. L. Heinz, J. Shu, Y. Meng, and R. J. Hemley, Science **302**, 425 (2003).

[47] H. J. McSkimin and P. Andreatch, Jr., J. Appl. Phys. **43**, 2944 (1972).

[48] R. Maezono, A. Ma, M. D. Towler, and R. J. Needs, Phys. Rev. Lett. **98**, 025701 (2007).

[49] K. J. Chang and D. J. Chadi, Phys. Rev. B **40**, 11644 (1989).

[50] P. Briddon, R. Jones, and G. M. S. Lister, J. Phys. C **21**, L1027 (1988).

[51] M. E. Davis, Top. Catal. **25**, 3 (2003).