Wide-band-gap Si in open fourfold-coordinated clathrate structures

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The energetics and band structures of the elemental semiconductor Si in two fourfold-coordinated clathrate structures have been studied. For the Si(34) and Si(46) structures we predict indirect band gaps near 1.9 eV, or 0.7 eV wider than that of Si in the well-known sp^3 diamond structure. We find that the energy differences between the clathrate structures and the diamond structure are about 0.07 eV, which is nearly three times smaller than those for more compact high-pressure structures of Si. The calculations are done using an *ab initio* tight-binding-like molecular-dynamics method, and further checked by the fully self-consistent plane-wave method. The possible origin of the small energy differences between Si in the clathrate and diamond structures is discussed in terms of strain energy. We compare the results for Si with those for similar structures involving carbon.

INTRODUCTION

The semiconductor Si is the most important semiconductor material for electronic devices. However, the relatively small and indirect band gap makes it unsuitable for many possible applications. Altering the band gap can be achieved by either changing the constituents or changing the geometry. The constituents can be changed, for instance, by alloying Si with another semiconductor. $Si_{1-x}Ge_x$ alloys have been made, but unfortunately the band gap shrinks compared to that of pure Si. Alloys of Si with C have been prepared,[1,2] but so far only a very small concentration of C has been incorporated. The band-gap properties have not yet been measured, and theories disagree[3,4] as to whether the band gap will increase or decrease.

The other route to band gap engineering has been to alter the geometry. This can be accomplished in an artificial manner, such as in superlattices, dots, or porous forms, or "naturally" by altering the actual crystal structure of the material. The band gap has recently been altered dramatically by making Si in "porous" form.[5,6] Here Si is reacted with an HF acid solution, which etches the Si into long narrow columns. The material can then be designed to emit visible light of different colors at room temperature. The band gap has surely been increased, but the origin of this increase is not yet fully understood. It has been suggested to be a confinement effect,[7] as in a superlattice, due to the narrow width of the columns, but other mechanisms have also been suggested.[8] Changing the geometry of the material thus seems to be a promising method for altering the Si band gap. The application of pressure unfortunately does not widen the band gap, since more compact structures, such as that of β-Sn, are metallic for Si. On the other hand, applying "negative pressure" to produce a more open structure has not yet been studied thoroughly. In fact, the open porous Si structures had been known for nearly

40 years[9] before they were reinvestigated to determine their optical properties.

One method of producing open structures is to incorporate large numbers of impurity atoms, around which the Si atoms nucleate. One particular class of structures that grow according to this mechanism are the clathrate hydrate structures such as Cl_2 in solid H_2O.[10-12] In the hydrates the gas molecule hollows out a space for itself, and the H_2O molecules solidify in a tetrahedral framework around this hollow. Thus, these structures are relatively open. Si compounds with the clathrate structure were characterized in 1965. In the Si clathrates, metal impurity atoms, such as Na or K, stabilize the structure, just as the guest molecules do in the hydrate structures.[13-16] Both stoichiometric phases $NaSi_6$ and nonstoichiometric phases Na_xSi ($0 \leq x \leq 0.08$) are formed. Recently these compounds have been checked for superconductivity, but with negative results.[17] Clathrate structures involving Ge with K impurities have also been prepared. It has been found that very low concentrations of metal atoms can be achieved, and with specific material processing, it should be possible that the metal atoms can be entirely removed.

Recently, Nesper, Vogel, and Blochl[18] have reported theoretical studies of pure carbon in clathrate (and other zeolite) structures. Their local density approximation calculations have shown these structures to be very low in energy – substantially lower in energy than the fullerene molecule C_{60}, and lower in energy than polybenzene, a low-energy, threefold-coordinated, sp^2-bonded, three-dimensional hypothetical network.[19]

It is the purpose of this paper to examine the energetics and band structures of the elemental semiconductor Si in two clathrate structures. We also make some comparisons of the results for Si with results for similar structures involving carbon. Unlike the case for Si, no carbon clathrate structure, to our knowledge, has ever been observed experimentally. Our goal is to determine

the relative stability of these structures in comparison with those of the ground state diamond structure, and to investigate the band-gap properties of these open systems. In the present work we estimate that the Si band gap of these open structures is indirect but widened by more than 0.7 eV compared to the diamond lattice—a result comparable to that found in porous Si.

Specifically, we examine two clathrate systems, Si(34) and Si(46). In each of these systems, the Si atoms are bonded to four other Si atoms in a distorted tetrahedral arrangement. Both structures are cubic; the Si(34) structure is face-centered cubic (fcc) and the Si(46) structure is simple cubic (sc). It has been found experimentally that the Si bond length is near 2.37 Å, which is slightly expanded compared to 2.35 Å for Si in the diamond structure. These bond lengths are found not to be sensitive to the concentration of metal atoms.

These structures are the simplest of a family of structures that are derived from packing pentagonal dodecahedra and other three-valent polyhedra having hexagonal and 12 pentagonal faces. In the packings, three polyhedra meet at an edge and four meet at a vertex so that the vertices and faces define a four-connected net. The structure that we call Si(46) occurs in clathrate hydrates such as chlorine hydrate and is known as the type I hydrate structure. It is also the Si net in an impure naturally occuring form of SiO_2 known as melanophlogite, net symbol MEP.[21] The structure that we call Si(34) is also a common clathrate hydrate structure known as type II. It is the Si net in the synthetic silica zeolite ZSM-39, net symbol MTN.[21]

The Si(46) lattice is a sc lattice with a lattice constant near 10 Å and is shown in Fig. 1. At each sc lattice point, a Si_{20} icosahedral molecule is placed with another Si_{20} rotated 90° with respect to the first, placed at the body center of the cube. The Si_{20} unit is a pentagonal dodecahedron having 12 pentagonal faces. These Si_{20} units are similar to the C_{20} icosahedral fullerene. Each Si atom in the pentagonal dodecahedron is bonded to three other atoms within the same dodecahedron. The fourth bond is one of two types. The first type of bond forms along the eight $\langle 111 \rangle$ directions. These bonds connect one Si_{20} unit with another. These bonds make eight of the 20 atoms of the Si_{20} dodecahedron fourfold coordinated, leaving 12 atoms on the dodecahedron threefold coordinated. This structure is already interesting, and a very
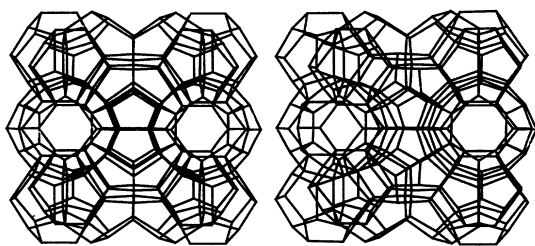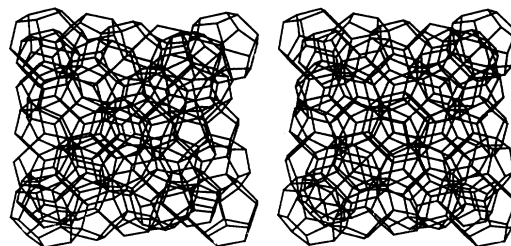

FIG. 2. The stereoscopic drawing of the Si(34) clathrate structure viewed down [100].

similar structure (with the pentagonal dodecahedron at the body center *not* rotated with respect to the first) has been studied as a solid of C_{20} fullerene.[20] To make the solid fully fourfold coordinated, a second type of bond is formed by adding twelve atoms to "interstitial" sites that surround the Si_{20} ball. These 12 additional atoms form bonds which connect to atoms on four different Si_{20} balls. Only six of these 12 additional atoms are unique to the unit cell. The addition of these atoms generates, per dodecahedron, three Si_{24} tetrakaidecahedra (14-hedra), which fill the space not occupied by the dodecahedra. These polyhedra contain two hexagons and twelve pentagons and are similar to the C_{24} fullerene molecule. The structure is labeled MEP in the zeolite atlas.[21] The 14-hedra (six per unit cell) share opposite hexagonal faces with other 14-hedra to form nonintersecting rods along $\langle 100 \rangle$ and the dodecahedra (two per unit cell) are in the interstices of the packing. There are 46 Si atoms per primitive cubic cell and the average ring size is 5.094 atoms per ring.

Si(34) is derived from a packing of dodecahedra and hexakaidecahedra (16-hedra) in the ratio 2:1 and the average ring size is 5.064 (the smallest of any such known structure). The dodecahedra (sixteen per unit cell) form intersecting face-sharing rods along $\langle 110 \rangle$ and the 16-hedra (eight per unit cell) are in the interstices of the packing. There are $4 \times 34 = 136$ Si atoms per face-centered cubic unit cell (which has the same symmetry as diamond).

The high proportion of five-membered rings (ideal angle 108°) makes the structures energetically competitve with diamond (angle 109.5°). It is not possible to make a structure with *only* five-membered rings. A stereographic[22] figure of Si(46) is shown in Fig. 1, and of Si(34) in Fig. 2.

THEORETICAL METHODS

In this section we discuss briefly the computational techniques employed in this work to obtain the ground state total energies, band structures and atomic geometries. The method is fast and particularly suitable for fairly large systems.

We use an approximate tight-binding-like molecular dynamics method,[23] which is based on density functional

FIG. 1. The stereoscopic drawing of the Si(46) clathrate structure viewed down [100].

theory within the local density approximation (LDA) and the pseudopotential approximation. To find the ground state total energy we utilize the simplified procedure introduced by Harris.[24] Here the energy functional is expressed in terms of some reference density (in our case the sum of neutral-atom spherical atomic densities) and first order changes in the output densities are included. The usual self-consistent iteration cycle is avoided.[25]

The single particle eigenstate problem is solved within a tight-binding-like formalism. A set of pseudoatomic orbitals (PAO's) is generated by solving the atomic problem within the pseudopotential approximation. We require that the single particle Hamiltonian matrix elements have a short range. This is achieved by imposing the boundary condition that the pseudoatomic orbitals vanish at a predetermined cutoff radius r_c. The linear combination of the s and p PAO's then forms a minimal set of basis functions, and the secular equation is solved. Although the method is entirely *ab initio*, the choice of r_c is somewhat important. The value of r_c should be well past the peak of the atomic wave function, but not so far that large number of neighbors overlap. The contraction of the orbital is more than a computational convenience, but simulates the contraction of the atomic charge density which has been shown to occur in solid state systems.[26,27] We have found from previous work[23,28–30] that r_c=5 Bohr is a good choice for Si. For C, we have chosen $r_c = 4.1$ Bohr so that the energy difference between the atomic levels of Si and C of the contracted atoms is the same as that of the free ($r_c \to \infty$) atoms.

We use the norm-conserving pseudopotentials of Hamman, Schluter, and Chiang[31] and the Ceperly-Alder form[32] of the exchange-correlation potential as parameterized by Perdew and Zunger.[33] The computational efficiency of this scheme enables us to use a fully converged set of k points for the integration over the Brillouin zone. The forces on each atom are calculated via the generalization of the Hellmann-Feynman theorem.[34,35,23] Molecular dynamics with a fictitious damping force is used to determine the lowest energy atomic configuration.

Because of the approximations used in this technique, we have also performed a small number of fully self-consistent plane-wave calculations. In the latter calculations, we use soft pseudopotentials of the Kerker-Martins-Troullier type.[36,37] Plane-wave energy cutoffs of 200 and 600 eV are used for Si and C, respectively. For the integration over the Brillouin zone we use two special k points in the irreducible wedge. Band structures obtained by this method are free of the limitations of the minimal local sp^3 basis.[38] The lattice constant used for the clathrate structure is estimated from the results of the local orbital calculation.

RESULTS

We have computed the total energies and band structures for the $A(34)$ and $A(46)$ clathrate structures where A is either Si or C, and have compared them to Si and C in their ground state diamond phases.

The results for the total energies for Si are given in Table I. The most important result in this table is that the energy differences between the clathrate structures and the diamond structure are of order 0.07 eV, which is surprisingly small (equivalent to less than 900 K). For comparison, the β-tin phase of Si (the first phase introduced by the application of high pressure) is approximately 0.27 eV higher in energy than the diamond phase.[25] The volume per atom of the clathrate phases is increased by about 17% compared to diamond. The crystallographic descriptions of the minimum energy configurations are given in Tables II and III. We have performed a single plane-wave calculation for the Si(34) structure at the estimated minimum energy configuration and find only a small difference in the total energy between the plane-wave and local orbital calculations, so we have confidence in our results.

The results for the total energies for C are given in Table IV. Here we find larger energy differences between the clathrate structures and the diamond structure than were found for Si, but they are still relatively small. We find that the volume has expanded by 14–18%, which is similar to the 17% expansion found for Si. Again we find that the planewave calculation gives a similar energy difference for the C(34) structure compared to the local orbital calculation, indicating that the local orbital calculations are yielding sensible results. Our energies are somewhat higher than those found by Nesper, Vogel, and Blochl,[18] who find energies relative to diamond in the 0.07–0.09 eV/atom range. We use a plane-wave method, and Nesper, Vogel, and Blochl use an augmented plane-wave method. By any measure, however, there is agreement that the energies of these structures are indeed quite low. For comparison, C_{60} is higher in energy

TABLE I. Energies and geometry of Si clathrates. The volume ratios are those obtained by taking the ratio of the volumes per atom of the clathrate and diamond (V_0) structures at their minimum energy. The cubic lattice constant a (the side of a cube edge) for the minimum volume configuration is also shown, except for the the plane-wave calculation where a full energy minimization was not done and a was estimated.

	Lattice	E_{tot} (eV/atom)	V/V_0	a (Å)
Diamond (local orbital)	fcc	0.000	1.000	5.49 (5.43 expt)
Si(34) (local orbital)	fcc	0.055	1.17	14.86
Si(34) (plane wave)	fcc	0.080		14.46
Si(46) (local orbital)	sc	0.069	1.17	10.35

TABLE II. The crystallographic description of Si(34).

Space group $Fd\bar{3}m$, $a = 14.864$ Å. Origin at $\bar{3}m$
Si(1) in 8(a): 1/8,1/8,1/8, etc.
Si(2) in 32(e): x,x,x, etc., $x=0.2174$
Si(3) in 96(g): x,x,z, etc., $x=0.1824$, $z=0.3701$
Bond length range 2.38–2.41 Å

than diamond by about 0.4 eV/atom.[19]

The most interesting result comes from an inspection of the band structure of Si in the clathrate structures. The band structure of Si in the diamond structure is compared to that of the Si(34) clathrate structure in Fig. 3. These band structures were computed using the local orbital sp^3 basis. For Si in diamond, the valence band maximum is at $\mathbf{k}=(000)$, and the conduction band minimum is along the line from $\mathbf{k}=(000)$ to $\mathbf{k}=\frac{2\pi}{a}(100)$. The band gap is indirect and equal to 1.7 eV. This is larger than the experimental band gap of 1.17 eV (0 K). The overestimate of the band gap is due to the use of a minimal sp^3 basis.[38] The band structure of Si(34) has an indirect gap of 2.4 eV, or an opening of the band gap of 0.7 eV. This is an enormous increase in the Si band gap, and makes it comparable to several III-V or II-VI compound semiconductors. It is also similar in size to the band gap observed for porous Si. We also find that the valence band maximum has moved down in energy substantially compared to the valence band maximum of Si in the diamond structure. The valence band maximum occurs at the $\frac{\pi}{a}(111)$ (L) point in the Brillouin zone and has an energy of -4.2 eV, while the maximum is at $\mathbf{k}=(000)$ (Γ) for diamond and is at -3.0 eV. The conduction band minimum also moves down, but by a smaller amount than the valence band. The conduction band minimum for Si(34) is at the $\mathbf{k}=(000)$ (Γ) point in the Brilloiun zone.

The 0.7 eV opening of the Si band gap is very significant and could well have potential applications. To check the accuracy of our results we have, therefore, repeated the band structure calculation using a converged plane-wave basis; the region near the band gap is shown in Fig. 4(b), and the near band-gap local orbital band structure is shown for comparison in Fig. 4(a). We find using plane waves that the band gap of the Si(34) clathrate is 1.40 eV; for comparison, the band gap for the diamond structure is found to be 0.70 eV. Thus from the plane-wave calculations we find that the band gap for the Si(34) clathrate has opened up by 0.70 eV compared to Si in the diamond phase, in agreement with the results for the sp^3 calculation. Also in agreement with the local orbital calculation is the fact that the valence band maximum is at L, and the conduction band minimum is at Γ. Note that the difference in energy between the valence band

TABLE III. The crystallographic description of Si(46).

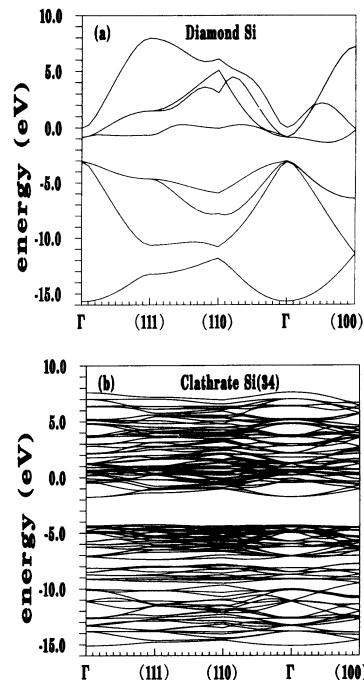| Space group $Pm\bar{3}n$, $a = 10.355$ Å |
| --- |
| Si(1) in 6(d): 0,1/4,1/2, etc. |
| Si(2) in 16(i): x,x,x, etc., $x=0.1837$ |
| Si(3) in 24(k): 0,y,z, etc., $y=0.1172$, $z=0.3077$ |
| Bond length range 2.38–2.43 Å |

FIG. 3. The band structure of Si computed using local orbitals in (a) the diamond structure and (b) in the Si(34) clathrate structure. Both structures are fcc and have the same shape for the Brillouin zone. The top of the valence band is near -3.0 eV for diamond, and near -4.2 eV for the clathrate.
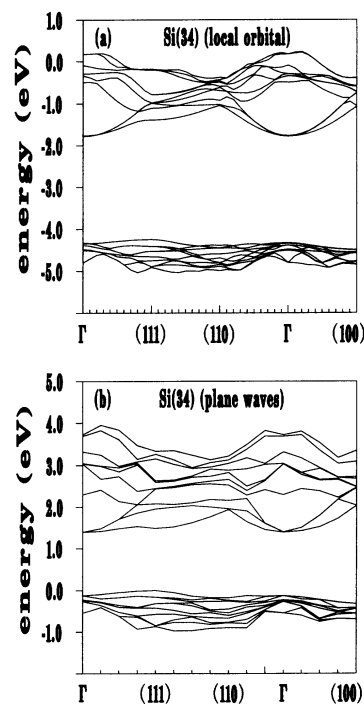

FIG. 4. The band structure in the near band-gap region for the Si(34) clathrate structure computed using (a) local orbitals and (b) plane waves. In each case only the top ten valence bands (including degeneracy) and the bottom ten conduction bands are shown.

TABLE IV. Energies and geometry of carbon clathrates. The volume ratios are those obtained by taking the ratio of the volumes per atom of the clathrate and diamond (V_0) structures at their minimum energy. The cubic lattice constant a (the side of a cube edge) for the minimum volume configuration is also shown, except for the the plane-wave calculation where a full energy minimization was not done and a was estimated.

	Lattice	E_{tot} (eV/atom)	V/V_0	a (Å)
Diamond (local orbital)	fcc	0.000	1.000	3.51 (3.57 expt)
C(34) (local orbital)	fcc	0.113	1.186	9.562
C(34) (planewave)	fcc	0.134		9.494
C(46) (local orbital)	sc	0.144	1.140	6.68

maximum at L and the valence band edge at Γ is only 0.12 eV. Thus, the band gap is indirect, but a direct band gap exists just 0.12 eV higher in energy. Thus, although this modification of Si appears not to be suitable as a light source, we do not want to exclude the possibility of further band-gap engineering, e.g., via strain, doping, or superlattices, in order to capitalize on the wide band gap for optical purposes.

All the calculations of the band gap presented here are based on the LDA. This theory is well known not to give accurate band gaps; typically (except for minimal basis set calculations) they are underestimated. Fortunately, trends in the band gaps are usually well reproduced, so we expect that the Si(34) clathrate structure band gap is significantly higher than the Si diamond structure. With these caveats in mind, our results can then be used to estimate the "true" Si(34) clathrate structure band gap to be 1.87 eV (equal to 1.17 + 0.70).

We have also computed the band structure for C(34) using sp^3 orbitals, and find a less dramatic, but opposite, effect. We find that the diamond band gap is 6.18 eV while that for C(34) is 5.00 eV, and for C(46) is 5.16 eV. Corresponding results by Nesper, Vogel, and Blochl[18] using plane waves also show a shrinking of the band gap— the two structures give a 6% to 23% reduction compared with diamond.

Next we consider the band structure of the Si(46) clathrate. This is shown for the near band-gap region in Fig. 5, and was computed using sp^3 orbitals. The highest occupied state (top of the valence band) is just below −4.0 eV and the band gap is 2.5 eV, very close to the

band gap found for Si(34). We find that both the valence band maximum and the conduction band minimum have moved up slightly compared to Si(34), but again they are much lower than they were in the diamond config- uration. The valence band maximum is along the Γ to X line, with a secondary maximum along Γ to L. The conduction band minimum is at Γ.

It should be noted that the top of the valence band for these Si clathrate structures shifts down by over 1 eV compared to diamond [compare Figs. 3(a), 3(b), and 5], yet the total energy of these structures is higher than that of diamond by about 0.07 eV. In an effort to under- stand the origin of the small energy differences between Si in the clathrate and diamond structures, we have done simplified calculations of the total energy based only on the strain energy using a Keating model.[39] In the Keat- ing model, bond-stretching and bond-bending energies are included, and these are fit to the elastic constants of Si in the diamond structure.[40] No explicit chemical or electronic structure effects are included in such a model. We have completely relaxed the structure and have deter- mined the total energy versus volume using this model. In spite of its simplicity, and in spite of the large en- ergy shift of some of the electronic eigenvalues, the model using elastic energy alone seems to give a fairly accu- rate representation of the energy changes found for these structures. The total energy versus volume using this model for Si is shown in Fig. 6. The energy differences between the diamond and clathrate phases as well as min- imum energy volumes are in good agreement with those found from electronic structure calculations given in Ta-
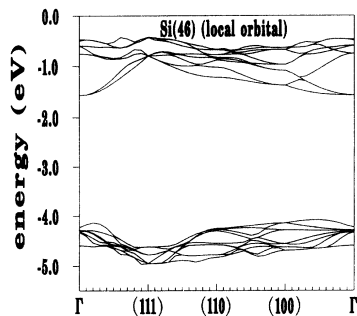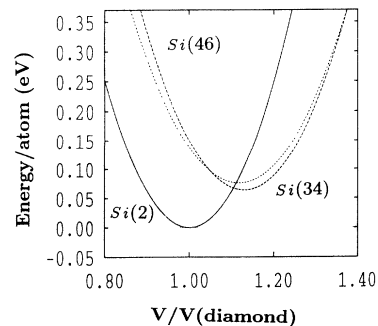

FIG. 5. The band structure in the near band-gap region for the Si(46) clathrate structure computed using local orbitals. The top of the valence band is near −4.1 eV. The band gap is 2.5 eV.

FIG. 6. The total energy of diamond (Si(2)) and two clathrate structures [Si(34) and Si(46)] as a function of re- duced volume $V/V_{diamond}$ computed using a simplified strain energy Keating model.

ble I. This calculation suggests that even though the energy bands shift considerably from those of the diamond phase, the most important contribution to the total energy is simply the angle strain on the bonds introduced by the clathrate structure.

CONCLUSIONS

We have used an approximate *ab initio* quantum molecular-dynamics method to investigate the electronic structure of the Si(34) and Si(46) clathrate solid structures. We have also determined their stability relative to the ground state Si diamond structure. We have performed similar calculations for carbon.

The most significant result is that both Si(34) and Si(46) solids have indirect band gaps significantly wider (by about 0.7 eV) than the band gap of Si in the diamond structure, which makes the band gap in these materials comparable to the band gap of porous Si. Carbon shows the opposite effect—the band gap for carbon in the clathrate structures is reduced compared to the band gap in diamond.

We find that the total energy difference between Si in the clathrate and the diamond structures is surprisingly small. The Si clathrate phases are about 0.07 eV/atom above the energy of the ground state Si diamond structure. The volume increase in the clathrate phase as compared to the diamond phase is about 17%.

In conclusion, our results show that Si in the clathrate structures has very low energy and a large band gap. The implications of these results suggest that this material should be studied further for possible new electronic applications.

ACKNOWLEDGMENTS

[1] J.B. Posthill, R.A. Rudder, S.V. Hattangady, G.G. Fountain, and R.J. Mazkunas, Appl. Phys. Lett. **56**, 743 (1990).

[2] S.S. Iyer, K. Eberl, M.S. Gorsky, F.K. Legoues, F. Cardone, and B.A. Ek, in *Silicon Molecular Beam Epitaxy*, edited by J.C. Beam, S. Iyer, and K. Wung, MRS Symposium Proceedings No. 220 (Materials Research Society, Pittsburgh, 1991), p. 581.

[3] R.A. Soref, J. Appl. Phys. **70**, 2470 (1991).

[4] A.A. Demkov and O.F. Sankey, Phys. Rev. B **48**, 2207 (1993).

[5] L.T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).

[6] A.G. Cullis and L.T. Canham, Nature (London) **353**, 335 (1991).

[7] F. Buda, J. Kohanott, and M. Parrinello, Phys. Rev. Lett **69**, 1272 (1992).

[8] M.S. Brandt, M.D. Fuchs, M. Stutzmann, J. Weber, and M. Cardona, Solid State Commun. **81**, 307 (1992).

[9] For a review of some of the history, see L. Canham, Physics World, March 1992, p. 41.

[10] W.F. Claussen, J. Chem. Phys. **19**, 259 (1951).

[11] W.F. Claussen, J. Chem. Phys. **19**, 1425 (1951).

[12] L. Pauling and R.E. Marsh, Proc. Natl. Acad. Sci. USA **38**, 112 (1952).

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

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

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

[16] C. Cros, M. Pouchard, P. Hagenmuller, Bull. Soc. Chim. France **2**, 379 (1971).

[17] S.B. Roy, K.E. Sim, and A.D. Caplin, Philos. Mag. B **65**, 1445 (1992).

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

[19] M. O'Keeffe, G.B. Adams, and O.F. Sankey, Phys. Rev. Lett. **68**, 2325 (1992).

[20] G.B. Adams, O.F. Sankey, J.P. Page, and M. O'Keeffe, Chem. Phys. **176**, 61 (1993).

[21] W.M. Meier and D.H. Olson, *Atlas of Zeolite Structure Types*, 3rd ed. (Butterworth-Heineman, London, 1992).

[22] The figures are readily seen with stereo glasses, which can be obtained from any chemistry supply house.

[23] O.F. Sankey and D.J. Niklewski, Phys. Rev. B **40**, 3979 (1989).

[24] J. Harris, Phys. Rev. B **31**, 1770 (1985).

[25] M.T. Yin, and M.L. Cohen, Phys. Rev. B **26**, 5668 (1982).

[26] M.W. Finnis, J.Phys. Condens. Matter **2**, 331 (1990).

[27] N. Chetty, K.W. Jacobsen, and J.K. Norskov, Phys. Rev. B **46**, 3798 (1992).

[28] D.A. Drabold, P.A. Fedders, O.F. Sankey, and J.D. Dow, Phys. Rev. B **42**, 5135 (1990).

[29] D.A. Drabold, J.D. Dow, P.A. Fedders, A.E. Carlsson, and O.F. Sankey, Phys. Rev. B **42**, 5345 (1990).

[30] G.B. Adams and O.F. Sankey, Phys. Rev. Lett. **67**, 867 (1991).

[31] D.R. Hamann, M. Schluter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

[32] D.M. Ceperly and G.L. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[33] J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[34] H. Hellmann, *Einfuhrung in die Quantumchemie* (Franz Deutsche, Leipzig, 1937).

[35] R.P. Feynman, Phys. Rev. **56**, 340 (1939).

[36] G. Kerker, J. Phys. C **13**, 189 (1980).

[37] M. Troullier and J.L. Martins, Phys. Rev. B **43**, 1993 (1991).

[38] R.W. Jansen and O.F. Sankey, Phys. Rev. B **36**, 6520 (1987).

[39] P.N. Keating, Phys. Rev. **145**, 637 (1966).

[40] R.M. Martin, Phys. Rev. B **1**, 4005 (1970).