

Computer Modeling of *allo*-Si and *allo*-Ge Polymorphs

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Computer models of possible structures of the so-called *allo*-Si and *allo*-Ge phases (polymorphs of the respective elements), reported to be formed upon topotactic demetalation of the layered compounds NaLi_3Si_6 and $\text{Li}_7\text{Ge}_{12}$, are built and energy-relaxed using atomistic and periodic density functional theory (DFT) methods. The resulting clathrate-like frameworks contain straight intracrystalline tunnel-like voids with cross sections defined by seven-, eight-, or 10-atom rings. In *allo*-Si structures these tunnels are one-dimensional: the most stable and symmetric structure (as predicted by DFT), containing the widest tunnels, coincides with zeolite type TON. In most of the *allo*-Ge structures lateral seven-, eight-, or 10-member ring openings connect mutually the tunnels, leading to two-dimensional- or three-dimensional-connected intracrystalline voids which may allow easy guest atom diffusion. The possibility is discussed that these structures, potentially accessible in experimental preparations, could incorporate flexibly occluded metal atoms leading to low-dimensional metal-in-semiconductor characteristics and interesting physical or chemical properties. Comparison of the results from DFT and atomistic simulations indicate that these latter, using Stillinger–Webber potentials, may be less adequate to predict the energies of the most distorted structures.

Introduction

In recent years much attention is being paid to silicon and germanium clathrates and related compounds, which with their peculiar cage-like structures not only offer potentialities for tailoring of semiconductor properties, e.g., band gap adjustment^{1,2} but may display also, in some cases, interesting superconducting or thermoelectric properties.^{3,4}

Until now, nearly all the materials of this kind which have been experimentally prepared and studied are based on 4-fold-connected covalent frameworks which correspond to one of the so-called clathrate I or clathrate II structures. These, which are respectively isostructural with zeotypes MEP and MTN (standard nomenclature of the *Atlas of Zeolite Structures*⁵), have symmetries belonging to space groups $Pm\bar{3}n$ (standard no. 223) and $Fd\bar{3}m$ (standard no. 227), contain 46 and 34 tetrahedral atoms per primitive cell (136 atoms per standard unit cell of the nonprimitive cubic lattice in the second case) and possess internal cavities able to occlude relatively large atoms such as K or Ba, which when present confer to these solids several of their main electronic properties of interest. A number of other potentially possible structures, also with tetrahedral connectivity and internal cavities, have been proposed; one may mention here the clathrate frameworks designated III (or hex-Si40),^{1b,6} IV (or sigma),^{6b} and V⁷ or those called μ_R , μ_H , T_I , and T_P ,^{6b} as well as the frameworks, conceptually derived from known zeolite structures, which have been discussed as possible allotropic forms for carbon⁸ and silicon.^{1a} However, all those structures (some of them rather complicated; for example, the T_P structure has 920 atoms per primitive unit cell!) exist just as proposals: none of them seems to have been effectively synthesized in Si- or Ge-based compounds (except for the $\text{Eu}_4\text{Ga}_8\text{Ge}_{16}$ compound mentioned below), and no hints on possible methods for their practical synthesis have been given.

The experimentally obtained Si or Ge compounds with clathrate I and II structures have been prepared most frequently by decomposition of simple silicides or germanides such as KSi or KGe (although in some cases they have been reported to be formed also via reaction between the elements or by direct growth from the melt). Apart from these, rather few clathrate-like fully 4-fold connected frameworks have been reported; to this author's knowledge, only NaGaSn_5 ⁹ and $\text{Eu}_4\text{Ga}_8\text{Ge}_{16}$,¹⁰ both of them containing tetrahedrally connected frameworks in which Ga substitutes partially for the group IV element and is charge-compensated by the Na/Eu atom. The first compound, with chiral structure, has remarkable helicoidal 1-dimensional tunnels with cross sections defined by distorted eight-member rings, while the second one has tunnels (also one-dimensional, 1-D) with cross sections formed by more regular eight-member rings, its topology being equivalent to that of zeotype CAS (this latter relationship was not taken into account in ref 10).

It is therefore of interest to pay attention to other Zintl-type phases that could be possible sources for novel clathrate-like structures. In this respect one may consider the Li-containing compounds NaLi_3Si_6 and $\text{Li}_7\text{Ge}_{12}$, of known structure, which as reported by Nesper et al. can be effectively transformed by topotactic alkali atom extraction to give alkali-free polymorphs of Si and Ge, called by these authors respectively *allo*-Si¹¹ and *allo*-Ge.¹² In the case of *allo*-Si, the structure does not seem to have been determined, while for *allo*-Ge the information available (see ref 12 for a simple structure drawing, ref 13 for detailed atomic coordinates) indicates that straight tunnels with cross sections defined by seven- and eight-member Ge rings exist, similar to those present in some of the proposed zeolite-like structures,^{1a} so that other metal atoms could perhaps be inserted in them to produce clathrate-like compounds with interesting physical properties. The proposed *allo*-Ge structure,¹³ however, is a complicated one (with 128 atoms/unit cell; see below), resulting from a mixture of several possible ways of connecting to one another the bidimensionally bonded Ge_n layers

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present in the parent $\text{Li}_7\text{Ge}_{12}$ compound (in fact the structure representations given in refs 12 and 13 do not coincide), and seems to coexist in the solid with a large number of stacking faults. One may thus expect that other demetalation methods, or adequate subsequent thermal processing, might result in a simpler, better ordered structure maintaining some of the mentioned intracrystalline tunnels. Actually, in the case of *allo*-Si, although no structure could be resolved, it was observed with DTA measurements that recrystallizations could occur at intermediate temperatures which did not produce yet the thermodynamically most stable diamond-type Si form, the structure of the resulting more ordered phase remaining still unknown.¹¹

Taking into account these latter observations, one may hypothesize that relatively simple structures of *allo*-Si and *allo*-Ge type might perhaps be formed, keeping tunnels able to occlude chosen elements, if adequate demetalation methods of the said Li-containing compounds could be found. To explore the characteristics of the phases which could be formed in this way (or at least the simplest ones), starting from the known structures of these two compounds a computer modeling study has been carried out in this work to examine the different simplest and most plausible ways of connecting among themselves, during topotactical decompositions, the two-dimensional (2-D)-connected layers present in the initial NaLi_3Si_6 and $\text{Li}_7\text{Ge}_{12}$ structures. The equilibrium geometries and energies which could result are then evaluated so as to ascertain the fully saturated Ge- or Si-only lattices that most likely could appear during carefully controlled transformations of the mentioned compounds. As the results will show, several such products are potentially possible, and in one case even a Si framework could result, having 10-member ring tunnels, which coincides with one of the zeolite-derived structures previously discussed^{1a}.

Computation Methods

Geometry optimizations and lattice energy evaluations were carried out for all structures using the atomistic code GULP,¹⁴ version 1.3. Here the energy was approximated with the Stillinger–Webber-type potential, containing two- and three-body contributions;¹⁵ the parameters used for Si and Ge were those given previously.^{15,16} This potential has been shown to be useful in modeling Si, Ge and mixed structures.¹⁷ Starting from structures constructed as explained below, the corresponding unit cell dimensions and the positions of the atoms within them were simultaneously relaxed using this code until the energy minimum was obtained. In principle, full use of symmetry (when the geometry given as input specifies a space group different from P1) is made for improving computational speed. This implies that relaxations are carried out within the constraints of the specified symmetry, thus forbidding any spontaneous breaking and departure from it. Any tendency to such symmetry lowering was checked by computing subsequently phonon frequencies at the gamma point; whenever negative values were obtained, indicating that the symmetry used led to a saddle point in the energy hypersurface, the symmetry was lowered by applying atom displacements following the normal modes corresponding to those negative frequencies, and new optimizations were carried out until a true local minimum was found.

Of the thus obtained structures, several were selected for re-optimization and energy evaluation using self-consistent quantum chemical calculations within a density functional theory approach. These calculations were carried out using the total energy CASTEP code, as implemented in the Cerius² suite

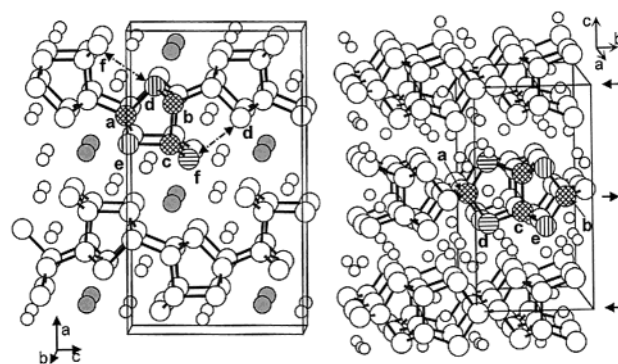


Figure 1. Crystal structures of NaLi_3Si_6 (left)¹¹ and $\text{Li}_7\text{Ge}_{12}$ (right).¹³ Connected atoms: Si or Ge; unconnected small atoms: Li; grayed atoms: Na. In each structure the basic layer building motif (consisting respectively of 6 and 8 atoms) is highlighted; 3-fold and 4-fold connected atoms are respectively indicated with vertical and crossed lines, while horizontal lines mark atoms which are coordinated respectively 2-fold and 2- or 3-fold (depending on Li content) in the Si and Ge compounds. Arrows in NaLi_3Si_6 indicate the possible formation of intralayer bonds during demetalation.

(version 4.0) of molecular and solid modeling programs.¹⁸ This code uses a plane wave description (i.e., a Fourier expansion) of the periodic single-electron wave functions,¹⁹ the atomic cores being represented by pseudopotentials of the ultrasoft Vanderbilt type.²⁰ The geometry reoptimizations were carried out within the local density approximation (LDA) with the Perdew–Zunger parametrization,²¹ and using a plane wave cutoff of moderate precision (120 eV for Si, 140 eV for Ge: the “medium” cutoff setting in CASTEP). For the thus refined structures final, more accurate energy values were then computed with the same code using a more precise cutoff value (240 eV in all cases; initial tests verified that this was enough to achieve energy convergence to within 10 meV/atom) and the generalized gradient approximation (GGA) as specified by Perdew and Wang.²² In both stages of DFT calculations, energy correction for finite plane wave basis set²³ was included, and again full use of symmetry was made to speed computation. This latter feature allows to carry out the calculations including only nonequivalent points in the \mathbf{k} -space grid used for sampling the Brillouin zone (BZ); this grid, chosen according to a Monkhorst–Pack (MP) scheme, was chosen so as to contain typically (at least) 6–8 nonequivalent points and give a BZ sampling interval not larger than 0.07 \AA^{-1} . Phonon frequency calculations are here, however, computationally too expensive, and were not carried out: it is expected that any residual tendency to symmetry breaking not foreseen by GULP will be of only marginal importance (at least for the purposes of the present work) and without severe effect on the obtained energies and basic geometric properties of the structures studied.

Where required, the maximum topological symmetry of the structures handled was determined using the Find_symmetry tools of the Cerius2 suite or the MS-DOS program KPLATE;²⁴ transformations of the specifications of crystal structures so as to conform with symmetries lower than (i.e., with subgroups of) the maximum ones were obtained when so desired using the PowderCell program.²⁵

Starting Structure Models

a. Structures Derived from $\text{Li}_7\text{Ge}_{12}$. The $\text{Li}_7\text{Ge}_{12}$ compound, from which *allo*-Ge is reported to be formed, has a layered structure (Figure 1a).¹³ It can be considered as one member of a series of structures with generic formula $\text{Li}_{4+2n}\text{Ge}_8$: all of them contain 2-D sheets, parallel to the ac plane, of intercon-

nected Ge atoms. The Ge framework can be described as repetition of a 8-atom motif (highlighted in Figure 1a). Each motif is bonded with neighboring ones in the same sheet so that some Ge atoms, marked **a**, **b**, and **c** in Figure 1a, are bonded to 4 other Ge atoms; others, marked **e** in Figure 1a, are 3-fold bonded, while of the remaining type, marked **d**, some are 2-fold and some 3-fold bonded, the relative amounts depending on the specific *n* value. Here the 3-fold bonded Ge atoms can be considered as Ge^- species carrying one lone pair, and 2-fold bonded ones as Ge^{2-} species carrying two lone pairs, with Li^+ ions compensating the charges. Upon Li extraction, the removal of electrons from the lone pairs leads to dangling bonds which couple to make new Ge–Ge bonds; ultimately these are formed also between adjacent layers so as to produce in the end a fully 4-fold connected, Li-free Ge framework (the *allo*-Ge phase). The experimental data indicate that this transformation may occur topotactically.^{12,13} As explained in more detail in the Appendix, a number of *allo*-Ge structural models have been built according to this scheme; for convenience they are labeled as GA, GB, GC, and GD types depending on the ways in which bonds between **d** and **e** atoms are established, with additional secondary labels (to give designations such as GAa1, GAa2, GCb1, etc.) to distinguish different structures resulting from different ways of mutually locating the **d**–**d** atom bonds in the lattice. On the other hand, the topology proposed for *allo*-Ge from experimental data in ref 13, which will also be considered here, is named simply GE.

b. Structures Derived from NaLi_3Si_6 . As reported in the literature,¹¹ this compound has also a layered structure (Figure 1b). It can be described as resulting from the repetition of Si_6 motifs (one pentagonal ring and one additional atom), highlighted in Figure 1b, mutually connected by simple bonds or bridges to produce corrugated layers which lie (in the average) parallel to the *bc* plane and contain again atoms coordinated 4-fold (those marked **a**, **b** and **c** in Figure 1b), 3-fold (marked **d** and **e**) and 2-fold (marked **f**), thus describable respectively as Si^0 , Si^- , (with one lone pair) and Si^{2-} (with two lone pairs); the alkali atoms are located mainly between these layers. As in the *allo*-Ge case, upon extraction of the alkali atoms (achieved by reaction with protic solvents or benzophenone, or by electrochemical procedures¹¹) new bonds involving atoms of types **d**, **e**, and **f** will appear. As described in the Appendix, different ways of pairing these atoms are designated as types SA, SB, SC and SD, additional numbers (i.e., resulting in structure labels SA1, SA2, ...; SB1, SB2, ...) being used to distinguish different spatial distributions of the interlayer bonds.

Results and Discussion

a. Overview of Results. Si and Ge structures with all the above-described connectivities were relaxed to their energy minima in atomistic computations with GULP. For comparative purposes, the same procedures were carried out also for the thermodynamically stable structure (diamond type, designated as DI; deviations of +0.04% and –0.15% from the experimental values at room temperature were found here for the cell constants of Si and Ge, respectively) and for other 4-fold connected, open frameworks experimentally known for group IV compounds: those of the clathrate I and II polymorphs (zeotypes MEP and MTN) and those of the above-mentioned compounds NaGaSn_5 (here called NGS) and $\text{Eu}_4\text{Ga}_8\text{Ge}_{16}$ (zeotype CAS). Results of the energies obtained for the thus relaxed structures, referred to that of the DI lattice taken as zero, are represented in Figure 2a,b. As it was done in ref 1a for the case of zeolite-like structures, the volume per atom (relative to

that of the DI structure determined by the same procedure) is taken as a convenient abscissa in the plot. For completeness of the comparisons, results have been obtained, and are given in these plots, also for structures of G-class (i.e., derived from the Ge compound topology) formed by Si atoms only and for structures of S-class (derived from the Si compound) formed by Ge atoms, even though it is not expected that they can be obtained from the experimentally known Li-containing precursors.

It is worth noting that, for both elements, structure DI is effectively predicted to be the most stable one, and that the experimentally known MEP and MTN frameworks appear next in stability, being followed by the NGS structure. It can be noted also that dopant metal-free clathrate structure has been prepared only, to this author's knowledge, for the Si-MTN case, in which the relative atomic volume is found to be 1.156;²⁶ this value is rather close to the GULP result obtained here (1.1496). Finally, it was observed that, in these GULP calculations, some of the S-class structures, which when built with Si show rather high energies (indicating that they are rather strained), are not stable for Ge in these GULP calculations, and reconstruct to give one of the other structures; for these latter cases no data are given.

For a number of the thus obtained structures and geometries involving different connectivity types and energies (the experimentally known frameworks except GE, all those of S-class and a selection of the G-class ones) additional geometry optimizations and energy evaluations were carried out with CASTEP. The results are displayed in Figure 2c,d, again plotted against the atomic volume relative to that computed for the DI structure (for which the cell constant obtained now differs from the experimental one by –0.9% and –2.0% for Si and Ge, respectively). These results indicate that the volumes per atom (relative to that of DI) predicted by both programs are very similar for Si-formed structures (note that the value given by CASTEP for Si-MTN, 1.1585, is even closer to the experimental one than that given by GULP); the concordance is somewhat less good for Ge, where CASTEP predicts volumes lower than GULP (ca. 3% in the average). In the case of the excess energies, however, GULP predicts significantly higher values, and a more or less good correlation is observed only for the G-type structures, as shown by the comparison plots given in Figure 3. Also, in the case of the experimentally known clathrate structures (MEP and MTN) the excess energy per atom predicted by CASTEP is clearly higher than that given by GULP, in particular for the Si frameworks; although both clathrates still appear as more stable than nearly all the other structures, now the energy of the NGS framework appears as roughly equal or even lower. This difference between both methods in the stability prediction for the MEP and MTN structures might be due to the fact that in these latter the conformations around the bonds present are in all cases of eclipsed type, while in the S and G structures they are more frequently (at least 50% of them) close to the more stable staggered type; since the Stillinger–Webber potential does not contain bond torsion terms, this factor of instability, which due to the exclusive presence of eclipsed configurations is more important in the MEP and MTN structures, is not reflected in the atomistic calculations.

Full description of all these relaxed structures (cell dimensions, space groups and fractional atomic coordinates), and tables with their excess energies and relative atomic volumes, are available as Supporting Information. The structure data given there for the known “experimental” and the S-class frameworks are those predicted by CASTEP; for G-class frameworks, those derived from GULP are given, as their set is more complete.

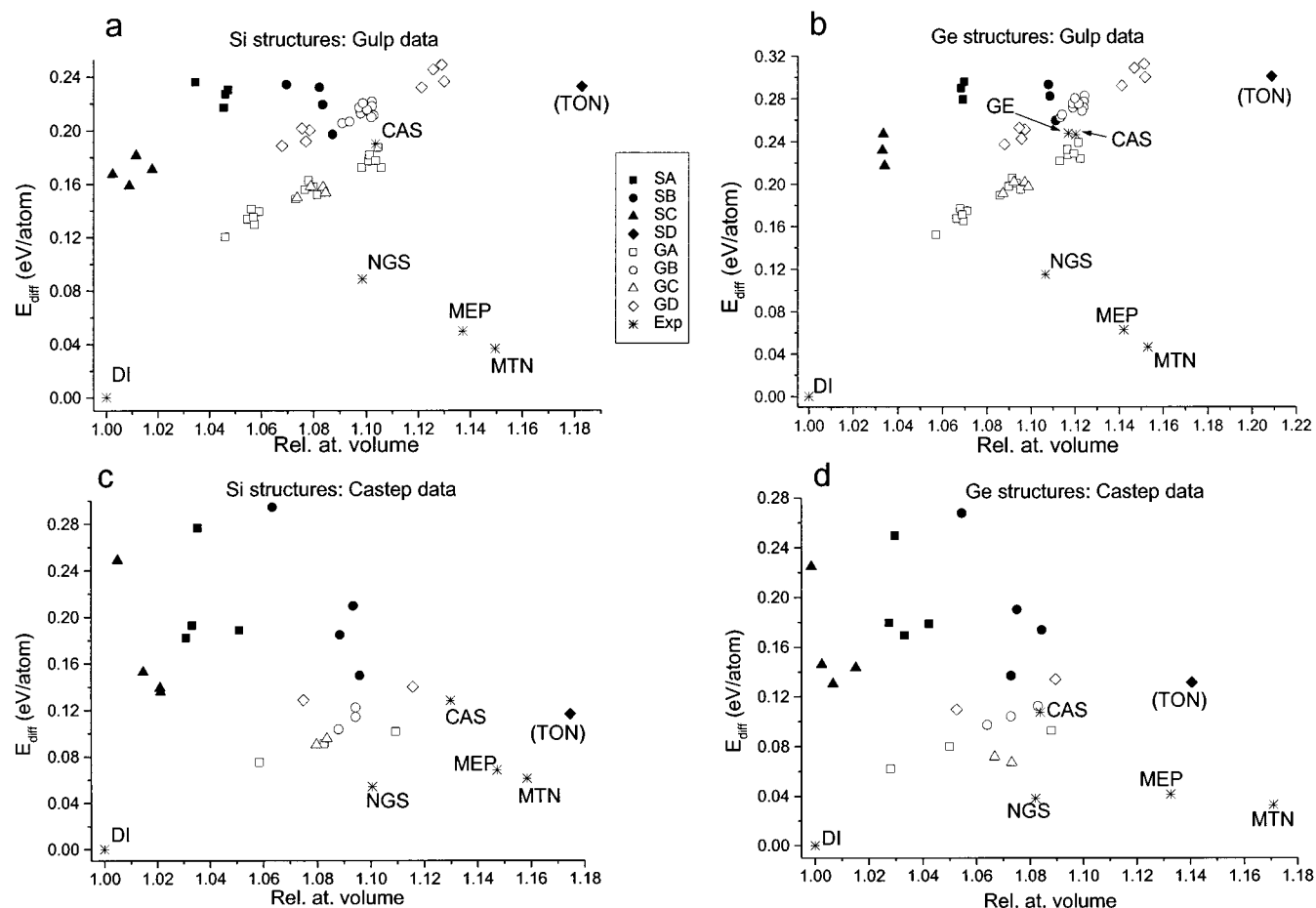


Figure 2. Excess cohesive energy per atom (over that obtained for the diamond structure) computed for Si (a, c) and Ge (b, d) structures with atomistic (a, b) and DFT (c, d) codes. Open symbols indicate structures derived from the structure of $\text{Li}_7\text{Ge}_{12}$; filled symbols those derived from the structure of NaLi_3Si_6 . Stars refer to “experimental” frameworks: the diamond lattice and others which have been reported to appear in clathrate-type structures, each one with the corresponding label (see text).

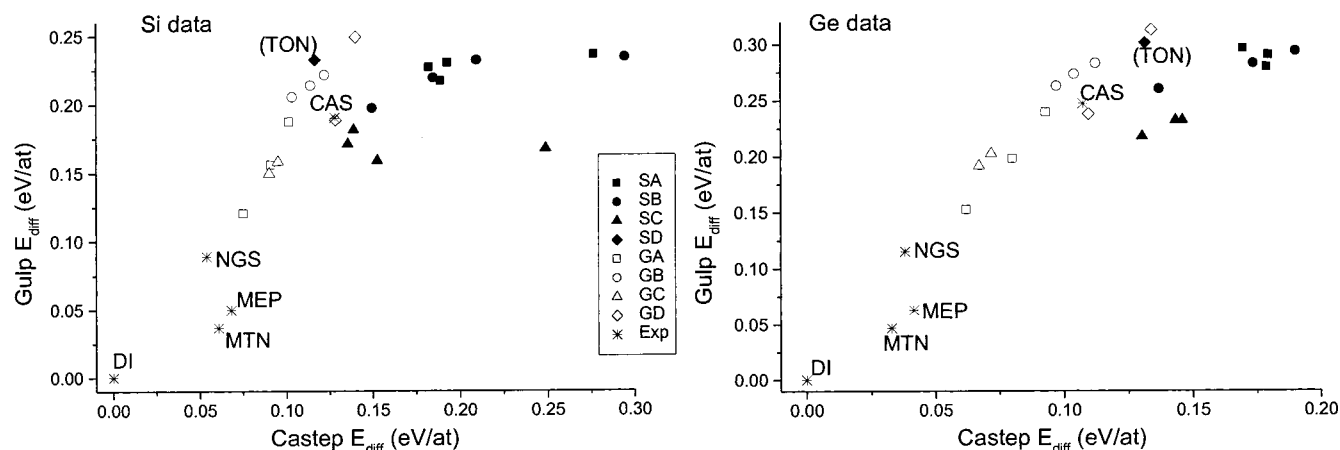


Figure 3. Comparison of atomistic and DFT calculations results for excess energies of Si and Ge frameworks. Symbol meanings as in Figure 2.

Relevant examples of the structure types obtained are depicted in Figures 4 and 5. In the latter, dashed lines are drawn crossing (and thus highlighting) the bonds which are formed upon demetalation, since the relationship of these topologies with the parent layered structure is not visually obvious. It can be observed that in both classes of structures the formation of bonds between the layers leads to the appearance of voids in the shape of straight tunnels, directly visible nearly perpendicular to the drawing plane in the Figures, which run parallel to the planes corresponding to the layers present in the parent Li-containing compounds. These tunnels, which appear with similar sizes

within each of the A, B, C, and D structure types in each one of the S- and G-class frameworks, will be called here primary tunnels. It is pertinent to analyze the mutual connectivity and size of these voids, as they will presumably determine the possibilities for diffusion of occluded atoms (primarily Li and Na during the preparation, but maybe also others in ulterior processings) and therefore may be important for the obtention and use of these Si and Ge polymorphs. In this sense, one can probably consider that apertures delimited by five- and six-member rings, which appear throughout these structures, will represent a more important barrier than larger rings for an easy

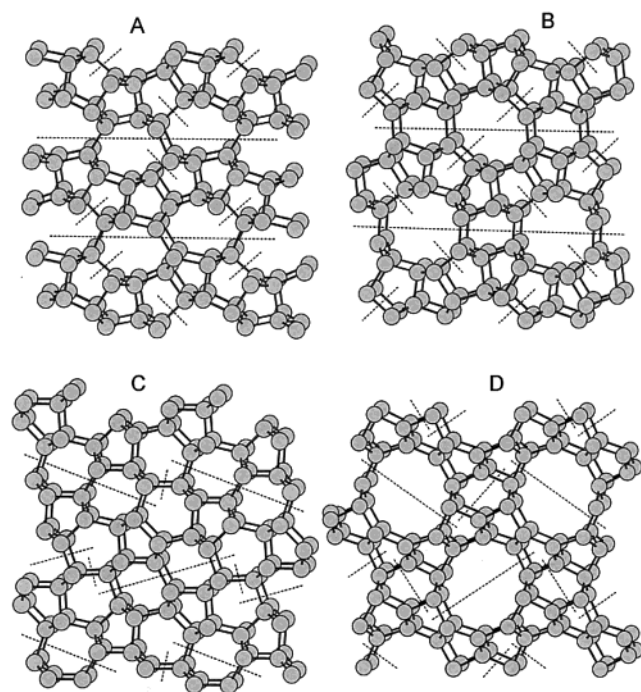


Figure 4. Structures (after geometry relaxation with CASTEP) of some Si frameworks derived from that of NaLi_3Si_6 ; each one of the A–D drawings represent one typical representative for each of the four types SA–SD. Dashed lines are drawn crossing the bonds which are established in each case upon forming the structure from the parent layered compound. Structure D (SD) coincides with zeotype TON.

diffusion of atoms having size similar or higher than that of Na. In the known silicon clathrate polymorphs, temperatures of 650–700 K are needed for the diffusion of Na out of their polyhedral internal cavities,²⁷ the walls of which are formed by five- and six-member rings. For structures such as those derived here, it may become necessary to remain substantially below such temperatures in any eventual experimental handling of them, in view of the fact that *allo*-Si, although improving in lattice ordering at ca. 500 K, recrystallizes easily into the diamond structure below 790 K.¹¹ A similar consideration applies probably also in the case of Ge structures. Thus in the following only rings of seven or more atoms will be considered as significant apertures deserving attention from the point of view of the atomic diffusions of possible interest.

b. Structures Derived from That of NaLi_3Si_6 . Considering first the S-class structures (several representative cases of which are depicted in Figure 5), it is observed that the primary tunnels are characterized by seven-member rings in those of type SC, eight-member rings in those of type SA and 10-member rings of different ellipticity and size in SB- and SD-type ones. Furthermore, all these tunnels have their walls formed by six-member rings, so that within the criterion given above the inter-void connectivity is always strictly one-dimensional. Contrary to the trend observed for zeolite-derived frameworks discussed by Demkov et al.,^{1a} for the structures obtained in this case no significant correlation appears to exist between the energy and the average volume per atom: the only consistent trend related to the framework density is that the latter decreases in the order of types $\text{SC} > \text{SA} > \text{SB} > \text{SD}$, as expected from the dimensions of the tunnels. Taking the CASTEP energy values as more reliable than those given by GULP, the most stable S-class structure appears to be SD, having the lowest density, being very closely followed by structures SC1–SC3, which have rather higher density (actually, close to that of the stable

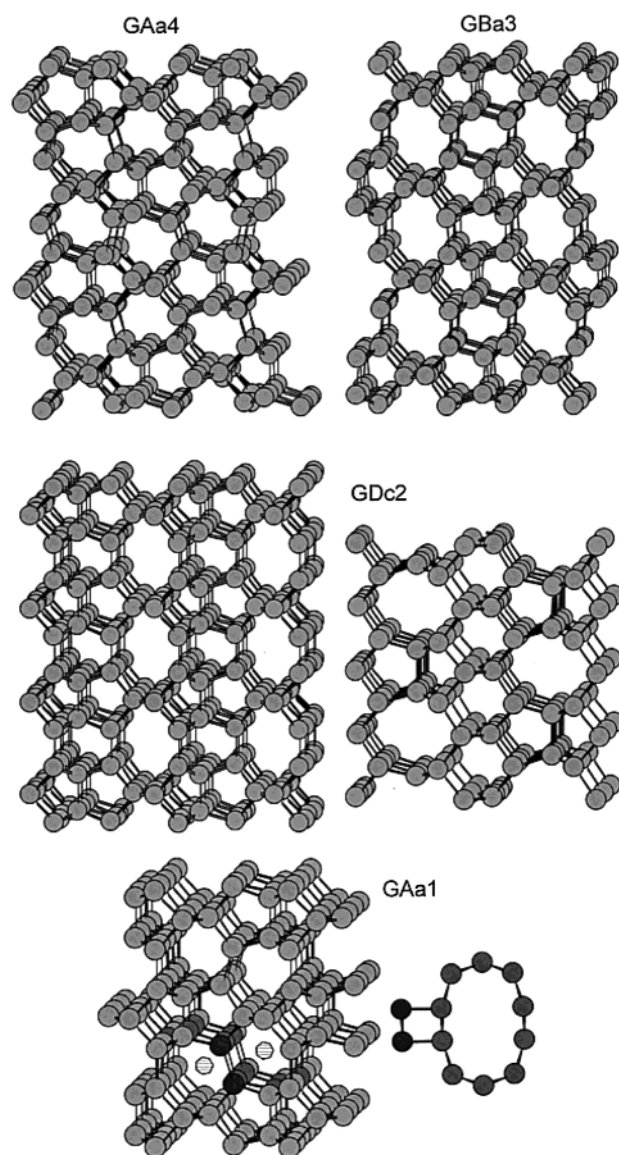


Figure 5. Structures (after geometry relaxation with GULP) of some Ge frameworks derived from that of $\text{Li}_7\text{Ge}_{12}$. For structure GDc2 (middle part of the figure) two views are presented, related by a 90° rotation around a horizontal axis in the plane of the figure; two sets of eight-member ring straight tunnels, which cross mutually in a 2-D connectivity pattern, are appreciated. In the GAa1 case (bottom of the figure) a 10-member ring connecting two parallel seven-member ring tunnels (the centers of which are marked with small polygons) is highlighted, together with one of the accompanying four-member rings; a cross-section view of the 10+4 ring set is also drawn.

diamond lattice DI), and SB1–SB3, with an intermediate density value. Here a higher energy is observed for structures of types SA and SB: this is probably due to the fact that the formation of the latter involves the establishment of intralayer bonds, which implies stronger bond angle distortions. Of all these lattices, the optimal situation for atom diffusion within the voids is given by structure SD. In this framework, the “bottleneck radius” for diffusion (computed as the shortest distance from the easiest diffusion path along the tunnel to the atoms forming its walls) lies between 3.45 and 3.50 Å: this can be compared with the 3.38 Å distance between void center and nearest wall atoms determined for the smaller cavities (formed by 20-atom polyhedra) present in the MEP and MTN structures, and with the 2.86 Å distance from the center of the six-member window of these latter cavities to the nearest atom.

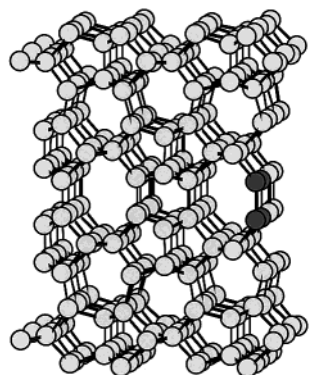


Figure 6. Structure proposed in ref 13 for *allo*-Ge (after relaxation with GULP).

A second interesting observation is that none of these lattices is isostructural with any of the proposed known zeolite structures, except in one case: the SD structure, which coincides with the TON zeolite.⁵ The observation that this lattice, presenting a straight 10-member ring tunnel (the widest one), is one of the most stable ones among all those potentially obtainable by topotactical demetalation of NaLi_3Si_6 , is an interesting result, as it implies that there might be a route here for obtaining at least one zeolite-like structure which, because of the size of its openings, could allow to introduce easily atoms such as Na, K, etc. Certainly, the *allo*-Si phase reported in ref 11 does not coincide with any of the S-class structures generated here: the polycrystalline X-ray diffraction patterns computed for these latter (data not shown) seem rather different from those reported to appear during the transformation of NaLi_3Si_6 into *allo*-Si.¹¹

c. Structures Derived from That of $\text{Li}_7\text{Ge}_{12}$. In the case of the G-class frameworks, which can potentially appear starting from the $\text{Li}_7\text{Ge}_{12}$ type structure, Figure 2 shows that the correlation between energy and volume per atom is followed to some extent. Close examination of the structures obtained reveals that the two main factors affecting the energy values are whether **d**–**e** atom bonds are formed (GB and GD types) or not (GA and GC) and the appearance of four-member rings in some of them (only within the A and D types); the latter feature implies bond angles of 90° or lower, and thus introduces a significant level of destabilizing strain which leads to a separation of these structures in groups (according to the relative number of such four-member rings), discernible in Figure 3. One might think that this structural feature will hardly appear in real situations; however, four-member rings do appear in the reported *allo*-Ge structure,¹³ which is depicted in Figure 6 after relaxation. It is noted that the most stable structures are those of GA type, with seven-member ring tunnels, which do not contain four-member rings, and that the stability of the reported *allo*-Ge structure lies, as could be expected, close to the group of GA-type structures which have an intermediate density of four-member rings, similar to that present in *allo*-Ge.

Concerning the structural details, the first observation is that here the primary tunnels have cross sections characterized by seven-member rings (for the GA and GC types) or elongated eight-member rings (for the GB and GD types); some examples are displayed in Figure 6. A second relevant feature is that, at difference with the S-class frameworks, in those of G-class some of the atom rings forming the primary tunnel walls have more than six-members; in particular, more or less puckered seven-, eight-, and 10-member openings can be observed. It is noted that 10-member openings always appear accompanying four-member rings, and thus are not present in the more stable

structures; Figure 6 highlights at its bottom one such case of combination between four-member and 10-member rings. Those openings, of larger sizes than found in S-class frameworks, lead to void connectivities between primary tunnels which may make atom diffusion easier. It is worth noting here that none of the G-class structures corresponds to any of the 135 known zeotypes,⁵ and also that none of these zeotypes has the characteristic, present in the GA and GC structures (and also in those of SC type mentioned above), of having the main diffusion paths defined by seven-member ring tunnels. Indeed, seven-member ring straight tunnels are known only for two of those 135 zeotypes: the MEI and STT frameworks, in which they coexist with respectively 12-member and nine-member ring tunnels.

Close examination of these G-class structures reveals a variety of topologies for these connectivities between tunnels. One extreme is presented by structures such as GAa4 (having the lowest energy of all; it is represented in Figure 6). In these, seven-member primary tunnels are connected only in pairs by seven-member lateral openings; this leaves practically a one-dimensional connectivity, although in a ladder-like fashion so that at least some atom counterdiffusion would be allowed. Strict one-dimensionality is presented also by structures such as GBa3 (also displayed in Figure 6) or GDa1, where the primary tunnels, defined by eight-member ring apertures, have no side connectivity with other tunnels; here not even a pairwise tunnel connection exists such as that mentioned for the GAa4 case, which could ease counterdiffusion. In the other extreme one may note structures where the primary tunnels are intersected by other tunnels of seven- or eight-member ring cross sections, straight or zigzag-shaped, running along a different crystal axis, so that two-dimensional tunnel networks appear; see in Figure 6 an example (structure Gdc2) of such an intersecting eight-member secondary tunnel. Another structural feature to be noted in a number of these frameworks is the presence of 10-member ring lateral apertures in the tunnels (always accompanied by four-member rings which introduce strain and instability). These 10-member apertures correspond in some cases to communications between tunnels, either parallel as it occurs for structure Gaa1, or intersecting as in the Gdc2 case (both depicted in Figure 6), but in others (e.g., structure GDb1, not shown) they form just lateral pouches which leave a strict 1-D connectivity but could at least ease counterdiffusion. Finally, one notes a couple of cases (structures Gca1 and Gcc2, not shown) in which three-dimensional communication exists, as the seven-member ring primary tunnels are mutually connected in the other two crystal directions through eight-member ring apertures with neighboring tunnels.

Concluding Remarks

In summary, a rich variety of clathrate-like frameworks appear as potentially derivable from the experimentally known compounds NaLi_3Si_6 and $\text{Li}_7\text{Ge}_{12}$; they may be considered as models of the experimentally prepared but structurally not yet well characterized *allo*-Si and *allo*-Ge materials. Of course, during the demetalation of those compounds more complicated structures may appear, corresponding to intergrowths or those built here and thus having larger unit cell volumes; indeed, the *allo*-Ge structure reported to be experimentally prepared¹³ can be considered as a hybrid of several of the simpler G-class structures handled here. In principle, one would think that among all of them only those with lowest energies have possibilities of being actually obtained; in this sense it is interesting that in the case of the Si compound the seemingly most favorable case

(SD) corresponds to a structure (the TON zeolitic framework) with wide tunnels and relatively high symmetry: it has just 12 atoms per primitive cell in its face-centered orthorhombic lattice. However, one notes that, as shown in Figure 3, the *allo*-Ge structure reported to be experimentally prepared¹³ is not among the more stable ones which are potentially obtainable from the same precursor. It seems thus that the obtained framework may be determined not thermodynamically, but by kinetic factors which control the diffusion paths for Li atom elimination and thus the ways and order in which dangling bonds successively appear and are healed by the formation of new Ge–Ge bonds in the process. This highlights the importance of preparation details in determining the topology of the structures which may result from the demetalation of these alkali silicides or germanides.

The data presented here indicate that it might be possible to obtain Si or Ge 4-fold connected frameworks with intracrystalline void spaces which are mutually connected with different dimensionality and topology. The inclusion of chosen atoms in them (which may be easier to achieve thanks to these connections) in a manner similar to that occurring in the known Si and Ge clathrates might produce materials with particular physical characteristics (e.g., low-dimensional metal structures hosted inside a semiconducting framework), leading to unique and interesting electronic, optic, magnetic, or even chemical or electrochemical properties.

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Supporting Information Available: Supporting Information provided, giving (a) the complete set of data of relative atomic volumes and excess cohesive energies per atom (in respect to the diamond structure) for all Si and Ge frameworks discussed here and (b) the optimized crystal structures of these lattices. This information is available free of charge via the Internet at <http://pubs.acs.org>.

Appendix

Model Building for *allo*-Ge Structures. Models for *allo*-Ge can be built based on the characteristics of the above-mentioned $\text{Li}_{4+2/n}\text{Ge}_8$ series of structures. As described previously,¹³ in the first member of the series, Li_3Ge_4 ($n = 1$), all **d**-type atoms are 2-fold bonded to others of types **c** and **a**; in members further away ($n > 1$), in which the Li/Ge ratio decreases, the resulting dangling bonds are "healed" by the formation of additional intralayer Ge–Ge bonds (parallel to the direction of axis *a*) between neighboring **d**-type atoms, which thus become 3-fold bonded, while a fraction $1/n$ of the **d** atoms remains 2-fold bonded; in the end member ($1/n = 0$), with atomic ratio $\text{Li/Ge} = 1/2$, all **d**-type atoms have become 3-fold coordinated. The experimentally prepared $\text{Li}_7\text{Ge}_{12}$ compound (shown in Figure 1) is the series member with $n = 3$; one-third of the **d** atoms in it are still 2-fold bonded to other Ge atoms, and the other two-thirds are 3-fold bonded. It is worth noting that in this compound alternate layers arrange the 8-atom basic motifs with opposite orientation in respect to the *b* direction: this is highlighted with the alternately oriented arrows drawn in the right side of Figure 1. This implies that in the crystalline structure the periodicity along the *c* axis is (at least) double of the interlayer distance.

If the Li/Ge ratio is lowered beyond the mentioned $1/2$ value, as will happen upon deeper delithiation, the new dangling bonds formed in Ge atoms of type **d** and/or **e** are repaired by establishing bonds between layers, until ultimately all Ge atoms become 4-fold coordinated simultaneously to the full elimination of the Li atoms. In principle, there are many possible ways of organizing in the final product the relative positions of the intra- and interlayer bonds which are formed according to the above-described scheme. Highly ordered distributions will produce smaller crystal unit cell sizes, complex distribution patterns may result in large cells. If the mentioned alternating character of the layers present in the $\text{Li}_7\text{Ge}_{12}$ is kept, the topotactically derived demetalated structures will have a similar doubled periodicity (or a multiple thereof) in the direction perpendicular to the layers. Also, the formation of bonds between **d**-type atoms pairs parallel to the *a* axis implies for the resulting structures a periodicity along this direction of at least twice the separation between adjacent 8-atom motifs. Thus the minimum cell that can result in the final Li-free structures would contain 32 atoms. It may be noted, however, that the structure derived for *allo*-Ge in ref 13, with 128 atoms/unit cell, has not the mentioned alternating layer character; on the contrary, all layers are oriented equally (this implies that when the Li atoms depart bond rearrangements within the layers would occur). In one accepts also structures of this latter type, it would be possible to have a single-layer periodicity along the *c* axis and therefore structures with 16 atoms/cell.

In this work, where relatively simple models are sought for the study, structures have been constructed with the two topologically distinct ways of connecting adjacent layers, i.e., either forming only **d**–**d** and **e**–**e** bonds, or only **d**–**e** bonds. This leads to the formation of straight tunnels with cross sections defined by seven-member rings or by eight- and six-member rings; the structures with these two types of tunnels are named here respectively as type A and B when formed with the alternating layer orientation character, and C and D when formed with equal layer orientations such it has been proposed to be the case, as said above, in the experimentally obtained *allo*-Ge structure.¹³ In each case all the topologically distinct ways of forming the intralayer **d**–**d** bonds were examined which result in primitive unit cells of the minimum possible volumes (with a total content of 32 atoms in cases A and B and 16 in C and D). They are differentiated here using additional label elements: an appended lowercase letter distinguishes various ways of forming crystallographically primitive or centered lattices from the initial eight-atom motif, and a number further distinguishes different relative dispositions of the intralayer **d**–**d** bonds. The several individual topologies generated for the *allo*-Ge models (18, 12, 4, and 8 for types A, B, C, and D respectively) are thus designated as GAa1, GAa2, ...; GAb1, GAb2, ...; GBa1, GBa2, ...; etc.

Model Building for *allo*-Si Structures. In contrast with the situation prevailing for *allo*-Ge structures, the orientations of the dangling bonds which may appear at the Si atoms when the alkali elements in NaLi_3Si_6 are extracted do not favor the easy establishment of intralayer bonds. The only acceptable way to achieve intralayer bonding seems to be by connecting 2-fold and 3-fold coordinated atoms, labeled **f** and **d**, respectively, in Figure 1 (arrows are drawn in the latter to mark such connections); it is noted that this requires significant bond angle distortions within the layers. If such intralayer bonding occurs, interlayer bonds involving atoms of types **e** and **f** (of Figure 1) could be formed in the resulting framework, to heal the remaining dangling bonds and achieve a purely 4-fold connected

silicon polymorph; these structures are designated here as of type A (if having **e–e** and **f–f** interlayer bonds) or B (if having only **e–f** type bonds). Alternatively, if intralayer bonding is not established all new bonds occur between adjacent layers, and involve now atoms of types **d**, **e**, and **f** (of Figure 1); the two sets of connections possible are {**f–d**, **f–f**, **e–e**} and {**f–d**, **f–e**}, and are here labeled as types C and D, respectively. All these hypothetical connectivities (within the requirement of minimum primitive cell) were examined. It is noted that only for type D can these connections be established while keeping all Si atoms in the symmetry planes of the parent structure (which has the symmetry group *Pnma*); the resulting unique structure is called SD. In the other cases symmetry reductions are required; here all immediate subgroups of the parent one (*Pnma*) have been considered, and the structure topologies thus resulting for these *allo*-Si models (4 for each type A–C) are here labeled SA1, SA2, ..., SB1, SB2, ..., etc.

References and Notes

- (1) (a) Demkov, A. A.; Windl, W.; Sankey, O. F. *Phys. Rev. B* **1996**, 53, 11288. (b) Galvani, E.; Onida, G.; Serra, S.; Benedek, G. *Phys. Rev. Lett.* **1996**, 77, 3573.
- (2) Demkov, A. A.; Sankey, O. F.; Gryko, J.; McMillan, P. F. *Phys. Rev. B* **1997**, 55, 6904.
- (3) Kawaji, H.; Horie, H.; Yamanaka, H.; Ishikawa, M. *Phys. Rev. Lett.* **1995**, 74, 1427.
- (4) Nolas, G. S.; Cohn, J. L.; Slack, G. A.; Schujman, S. B. *Appl. Phys. Lett.* **1998**, 73, 178.
- (5) See Meier, W. M.; Olson, D. H.; Baerlocher, Ch. *Atlas of Zeolite Structure Types*, 4th revised ed.; Elsevier: London, 1996, containing 98 structures; and another 37 types approved by the International Zeolite Association as of July, 2001 (see Internet URL <http://www.iza-structure.org/databases/>).
- (6) (a) Benedek, G.; Galvani, E.; Sanguinetti, S.; Serra, S. *Chem. Phys. Lett.* **1995**, 244, 339. (b) O'Keeffe, M.; Adams, G. B.; Sankey, O. F. *Philos. Mag. Lett.* **1998**, 78, 21.
- (7) Smelik, E. A.; King, Jr., H. E.; Z. *Kristallogr.* **1996**, 211, 84.
- (8) Nesper, R.; Vogel, K.; Blöchl, P. E. *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 701.
- (9) Blase, W.; Cordier, G. Z. *Naturforsch. B* **1988**, 43, 981.
- (10) Bryan, J. D.; Stucky, G. D.; *Chem. Mater.* **2001**, 13, 253.
- (11) von Schnering, H.-G.; Schwarz, M.; Nesper, R. *J. Less-Common Met.* **1988**, 137, 297.
- (12) Grüttner, A.; Nesper, R.; von Schnering, H.-G. *Angew. Chem., Int. Ed. Engl.* **1982**, 21, 912.
- (13) Grüttner, A. Dissertation, University of Stuttgart, Stuttgart, 1982.
- (14) Gale, J. D. *J. Chem. Soc., Faraday Trans.* **1997**, 93, 629.
- (15) Stillinger, F. H.; Weber, T. A. *Phys. Rev. B* **1985**, 31, 5262.
- (16) Ding, K.; Andersen, H. C. *Phys. Rev. B* **1986**, 34, 6987.
- (17) Laradji, M.; Landau, D. P.; Dünweg, B. *Phys. Rev. B* **1995**, 51, 4894.
- (18) Cerius2 Quantum Mechanics User Guide; MSI: San Diego, 1998.
- (19) Payne, M. C.; Teter, M. P.; Allan, D. C.; Arias, T. A.; Joannopoulos, J. D. *Rev. Mod. Phys.* **1992**, 64, 1945.
- (20) Vanderbilt, D. *Phys. Rev. B* **1990**, 41, 7892.
- (21) Perdew, J. P.; Zunger, A. *Phys. Rev. B* **1981**, 23, 5048.
- (22) (a) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, 46, 6671. (b) White, J. A.; Bird, D. M. *Phys. Rev. B* **1994**, 50, 4954.
- (23) Francis, G. P.; Payne, M. C. *J. Phys.: Condens. Matter* **1990**, 2, 4395.
- (24) MS-DOS Program kplote.exe by Rudolf Hundt, 2000.
- (25) Kraus, W.; Nolze, G. *Powder Cell for Windows* v. 2.3; program described and available at Internet URL <http://www.bam.de/service/download/download.html>.
- (26) Gryko, J.; McMillan, P. F.; Marzke, R. F.; Ramachandran, G. K.; Patton, D.; Deb, S. K.; Sankey, O. F. *Phys. Rev. B* **2000**, 62, R7707.
- (27) Ramachandran, G. K.; Dong, J.; Diefenbacher, J.; Gryko, J.; Marzke, R. F.; Sankey, O. F.; McMillan, P. F.; *J. Solid St. Chem.* **1999**, 145, 716.