First principles calculations of electronic structures and metal mobility of $\text{Na}_x\text{Si}_{46}$ and $\text{Na}_x\text{Si}_{34}$ clathrates

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First principles calculations of electronic structures and metal mobility of $\text{Na}_x\text{Si}_{46}$ and $\text{Na}_x\text{Si}_{34}$ clathrates

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Energetics, geometry, electronic band structures, and charge transfer for $\text{Na}_x\text{Si}_{46}$ and $\text{Na}_x\text{Si}_{34}$ clathrates with different degrees of cavity filling by sodium, and the mobility of the Na atom inside the different cavities are studied using first principles density functional calculations within the generalized gradient approximation. The stabilization of the clathrate lattice and the cell volume variation upon the inclusion of Na (which appears to move easily in the larger cavities of $\text{Na}_x\text{Si}_{34}$, thus justifying the experimental observations) are discussed in connection with the onset of the repulsion between Na and Si for distances shorter than ~ 3.4 Å. For all degrees of filling of the different cavities examined we find that the electron population of the *s* orbitals in the partially ionized Na atoms increases with a decrease in the size of the cavity, and that the Na states contribute significantly to the density of states at the Fermi level and thus influence the properties of these compounds. © 2004 American Institute of Physics. [DOI: 10.1063/1.1650303]

I. INTRODUCTION

Since its discovery nearly four decades ago,^{1,2} the so-called silicon clathrate compounds, made up of tetrahedrally coordinated Si frameworks containing intracrystalline voids in which guest atoms (usually alkaline or alkaline earth elements) can be inserted, have attracted a great deal of attention because of their potential for developing interesting and controllable semiconducting,^{3–5} superconducting,^{6,7} elastic,^{8,9} thermoelectric,^{10,11} or optoelectronic¹² properties. Two types of framework have been found experimentally and characterized for these compounds: The so-called clathrate types I and II, which coincide with two known zeolite topologies (called MEP and MTN,¹³ with 46 and 34 tetrahedral atoms per primitive crystal cell, respectively). These silicon framework structures are semiconductors having indirect and wide band gaps, and constitute promising candidate materials for making optoelectronic devices through the insertion of different metallic guest atoms in their intracrystalline voids. Our interest in these clathrate types arises from the possibility of identifying a new type of intermediate band semiconductor material presenting improved photovoltaic efficiency.^{14,15} According to a recent proposal,¹⁶ similar intracrystalline voids, although with tunnel-like interconnections, might also be present in the so-called *allo*-Si material, a crystalline variety of pure Si formed by the demetalation of the NaLi_3Si_6 compound,¹⁷ the structure of which, however, has not been established to date. It may be added that other clathrate-like structures, composed of the same cages as clathrates I and II, have been proposed as possible polymorphs, and computer simulations of their properties have been

carried out, for example, the so-called Hex-Si40 structure, or, in the case of C frameworks, the related Hex-C61 structure.¹⁸

A few experimental works [using photoemission, nuclear magnetic resonance (NMR) and x-ray absorption spectroscopies]^{19–24} on silicon clathrates of both types I and II, as well as several quantum-theoretical studies,^{3,4,11,12,24–28} have been reported trying to understand their electronic structures. This would allow, among other issues, to clarify the changes which occur in the energy bands of these materials when the internal voids are partially or completely occupied by metallic guest atoms and the degree of charge transfer between these and the Si sublattice. In these theoretical studies, the crystal structures used are those resulting from the most recent crystallographic determinations,^{29,30} all of which describe the solid according to the full symmetry of the cubic framework topology and with the guest atoms located in the center of the voids. However, recent EXAFS measurements²⁰ indicate that, at least for Na inserted into the larger cavities of a Si framework with the type I clathrate structure, a significant displacement (~ 0.9 Å) of the alkali atoms from the center of the cavities may be present (at least at low temperatures), this being explained in terms of a Jahn–Teller or Peierls-type distortion. This fact, incidentally, might help to explain the large, Na concentration-dependent values of the thermal parameters calculated from XRD data for Na (when assumed to be in the center of the cavity) in these structures.²⁹ It must be noted that the possibility of displacing easily the guest atoms away from the cavity centers to achieve low thermal conductivity, besides a large electronic conductivity and Seebeck coefficient (highly dependent on the degree of charge transfer to the Si lattice), constitutes a key factor in achieving good thermoelectric properties in these compounds.¹¹

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In order to address the likelihood and possible implications of such alkali atom off-center deviations, first-principles electronic structure calculations have been carried out in this work for silicon clathrate structures of both types I and II, with different degrees of cavity filling by Na atoms, in which the latter are allowed to move their position away from the cavity centers.

Detailed results of the effect of the Na gradual filling of the different cavities for both types of clathrates structures are also obtained, and presented in terms of formation energy, Mulliken population analysis, massive band structures, density of states (DOS) and the mobility of Na inside the cavities.

II. COMPUTATIONAL DETAILS

In this study the electronic structures and total energies were calculated using two different codes, both based on the formalism of the density functional theory (DFT), where the selfconsistent Kohn–Sham equations are solved within the generalized gradient approximation (GGA) for the exchange and correlation potential, but with different types of basis set for valence electrons: The SIESTA³¹ code uses a linear combination of finite range numerical atomic orbitals basis set, while the CASTEP³² code uses a Fourier expansion within a plane wave basis set. CASTEP is preferred for obtaining total energies (for which it is more efficient in obtaining well converged, accurate values) and related properties such as crystal structures, while SIESTA is particularly appropriate for studying in detail electronic band structures and analyzing the atomic composition of wave functions and electron density distributions.

Band diagrams and total and atomic projected density of states calculations were carried out using the SIESTA³¹ code program. The calculations of the nonpolarized Schrödinger equation have been carried out using the GGA corrections of Perdew *et al.*³³ for the exchange correlation potential. This method has been extensively tested for a great variety of semiconductor type systems.^{14,15} Norm conserving pseudopotentials of Troullier and Martins-type³⁴ in the fully separable form of Kleinman and Bylander³⁵ have been used for representing the core electrons of all atoms. These were taken to be the $2p$ and deeper levels for Si and Na atoms. Pseudopotentials were generated from the neutral atoms, and optimization of all orbitals was carried out. A linear combination of finite-range pseudoatomic orbitals of the Sankey and Niklewski-type³⁶ has been used as basis set for the description of valence electrons. Shift energy parameters for the finite range of the pseudoatomic orbitals ΔE_{PAO} were chosen to be less than 0.05 eV to ensure the energy convergence within GGA exchange and correlation potentials used. In the calculations we used a double ζ (DZ: The valence orbitals are split in two components) basis set. Convergence tests including polarization functions were also done in order to ensure the obtaining of the required accuracy. Integration in k -space has been carried out using 18 points in the Brillouin zone, for all calculations in the MTN and MEP unit cells used. Relaxation of the ions to mechanical equilibrium was achieved by the conjugate gradients minimization of the total energy with respect to the ionic positions and cell sizes.

The residual atomic forces were generally less than $0.04 \text{ eV } \text{\AA}^{-1}$ and the stress tolerance less than 0.1 GPa.

Total energy DFT calculations were carried out using the total energy CASTEP code, as implemented in the CERIUS³² suite (version 4.2) of molecular and solid modeling programs. This code uses a plane wave description (i.e., a Fourier expansion) of the periodic single-electron wave functions,³⁷ the atomic cores being represented by pseudopotentials of the ultrasoft Vanderbilt-type.³⁸ To speed up the computation, full use of symmetry was made, allowing the calculations to be carried out including only nonequivalent points in the k -space grid used for sampling the Brillouin zone (BZ). Spin-unpolarized methods and Fermi-level controlled occupancy of the band states (with 25 meV smearing) were used for all the Na-containing structures. The geometry optimizations (with convergence tolerances of $20 \text{ } \mu\text{eV/atom}$, $0.001 \text{ } \text{\AA}$ and $0.05 \text{ eV/\AA}$ for energy changes, rms atomic displacements and forces respectively) were carried out within the generalized gradient approximation (GGA) as specified by Perdew and Wang;³⁹ a moderate precision plane wave cutoff (330 eV: the “medium” cut-off setting in CASTEP for Na, the most demanding element here) was used, together with a Monkhorst–Plank (MP) sampling of the BZ defined by a grid interval of $0.05\text{--}0.06 \text{ } \text{\AA}^{-1}$. For the resulting final structures, more accurate energy values were then computed with the same code, again within GGA, using a more precise cut-off figure (625 eV) and finer MP samplings. The spacing of the latter was (for the clathrates) respectively, $0.03/0.04 \text{ } \text{\AA}^{-1}$ for high–low symmetry structures, leading to 32/14 points in the BZ which, after considering symmetry, are reduced to between 4 and 10 nonequivalent points depending on the specific cases. In both stages of DFT calculations, energy correction for the finite plane wave basis set⁴⁰ was included. Preliminary tests verified that this set of values allowed convergence in the total energy figures to be achieved to within 5 meV/atom, the convergence in energy differences being significantly better. Additional fixed-geometry calculations of total energy with Na atoms displaced from the cavity centers were made, again using GGA and the 625 eV cutoff, within the corresponding (decreased) symmetry.

III. RESULTS AND DISCUSSION

A. Crystal structures

The structures of the clathrates considered, corresponding to the MEP and MTN topologies, are well known.^{1,2,13} Here it may be recalled that both have cubic lattices: MEP has a primitive simple cubic lattice with 46 Si atoms/unit cell arranged according to the symmetry of space group Pm-3n (standard Nr. 223), while MTN has a fcc Bravais lattice, with 34 Si atoms/primitive cell (136 atoms in the nonprimitive standard cubic cell) arranged within the symmetry of space group Fd-3m (standard Nr. 227). Both contain “small” cages made up of 20 Si atoms in a nearly regular pentagonal dodecahedron (2 cages/unit cell in MEP and 4 cages/primitive cell in MTN); in addition to this, the MEP contains larger cavities (6 cages/unit cell) made up of 24 Si atoms arranged in a polyhedra with 12 pentagonal and 2 hexagonal

FIG. 1. (a) Fragment of the MEP lattice, including three Si_{24} cavities (sharing 6-member rings, highlighted in gray) stacked along a line parallel to a horizontal cell axis (and to the drawing plane) as well as one small Si_{20} cavity centered at a cell corner. (b) Fragment of the MTN lattice, including three Si_{28} cavities connected through 6-member rings (highlighted) in an angular way (with the other 6-member rings in the middle cavity highlighted also in lighter gray shades) as well as a small Si_{20} cavity (upper middle part) sharing 5-member rings with the three Si_{28} cavities.

faces, while the MTN has large cavities made up of 28 Si atoms (2 cages/primitive cell) arranged in polyhedra with 12 pentagonal and 4 hexagonal faces.

In the MEP, the Si_{20} cavities lie (isolated from one another) at the corners and center of the unit cell; the Si_{24} cages are interconnected by sharing hexagonal faces in linear stacks running parallel to the cell axes, while their pentagonal faces are shared with Si_{20} and other Si_{24} cells. This arrangement is depicted in Fig. 1(a). In the MTN, the large Si_{28} cavities share hexagonal rings only, in a fourfold-connected topology equal to that of a diamond lattice, while the 5-member rings are shared only with the small Si_{20} cages, which run in mutually intercrossing rows parallel to the $\{110\}$ and equivalent directions. This structure, in which the Si_{28} and Si_{20} cage centers are arranged as the Mg and Al atoms in the MgAl_2O_4 spinel lattice, is less easy to visualize; a fraction of it is represented in Fig. 1(b). For both clathrates, published diffraction-derived data^{29,30} were used as starting configurations in the calculations.

B. Total energy calculations

1. Effects of the gradual filling of the structure cavities by Na

For both the MEP and MTN topologies, structures were built having cavities filled by Na atoms to different extents characterized by a parameter x as defined below. The cases computed here are, besides the Na-free structures:

FIG. 2. Plots, against composition parameter x , of data from total energy calculations for $\text{Na}_{x/2}\text{Si}_{1-x/2}$ clathrate structures. Lower part: Energy of formation (from $\text{Na}_{0.5}\text{Si}_{0.5}$ and diamond Si). Upper part: Volume per Si atom. Full symbols: Structures where the small Si_{20} cavities are never occupied by Na before the larger Si_{24} or Si_{28} cavities are fully occupied. Open symbols: Structures where (some) Si_{20} cavities contain Na while larger cavities are not fully occupied. Each full or dashed line indicates a step in the cavity filling, which is marked (only in the upper figure, for clarity) with an asterisk when it implies adding Na to larger cavities.

- for the MTN topology (with 34 Si in the primitive cell), those having:
 - two Na atoms/primitive cell (formula $\text{Si}_{34}\text{Na}_2$; $x = 0.11111$), filling either the two larger Si_{28} cavities existing in this structure (filled symbol in Fig. 2) or half of the four smaller Si_{20} cavities (open symbol);
 - four Na atoms/p.c. ($\text{Si}_{34}\text{Na}_4$; $x = 0.2106$), filling either the four Si_{20} cavities (open symbol) or the two Si_{28} cavities plus half of the Si_{20} cavities (closed symbol);
 - six Na atoms/p.c. ($\text{Si}_{34}\text{Na}_6$; $x = 0.30$), which fill all cavities.
- for the MEP topology (with 46 Si in the primitive cell), those having:
 - 2 Na/u.c. ($\text{Si}_{46}\text{Na}_2$; $x = 0.08333$), filling the two Si_{20} cavities in this structure;
 - 3 Na/u.c. ($\text{Si}_{46}\text{Na}_3$; $x = 0.1225$), filling one half of the Si_{24} cavities in such a way that no two adjacent such cavities (connected by a 6-member ring) are simultaneously filled by Na;
 - 5 Na/u.c. ($\text{Si}_{46}\text{Na}_5$; $x = 0.1961$), filling the cases (a) and (b) above;
 - 6 Na/u.c. ($\text{Si}_{46}\text{Na}_6$; $x = 0.2308$), filling all the larger Si_{24} cavities of this structure;
 - 8 Na/u.c. ($\text{Si}_{46}\text{Na}_8$; $x = 0.2963$), with all cavities (large and small) occupied.

In these structures, filling only half of the small Si_{20} cavities in MTN structures implies a decrease in the symmetry to orthorhombic (space group Imma, Nr. 74). Filling only half of the larger Si_{24} cavities in MEP also implies a decrease in symmetry; here the highest possible remaining symmetry, that of the rhombohedral group R32 (Nr. 155), was chosen from the different possibilities.

These structures were geometry-optimized (relaxing both cell parameters and atom positions) by minimizing the energy evaluated with CASTEP, and the total energies of formation of the thus obtained configurations were computed with the improved planewave cutoff and BZ sampling as previously stated. The results are expressed here as the energy change (per atom) of the hypothetical reaction

Here Si (in the diamond lattice) and the known stable compound NaSi (with monoclinic structure and eight formula units per primitive unit cell⁴¹) are taken as reference states, taking into account that clathrates are frequently synthesized by decomposition of NaSi. In the same way as for the clathrates, these two reference structures were relaxed, and their total energies evaluated at the GGA level. The results are given in Fig. 2, where the energy variation ΔE of this reaction is plotted against the composition parameter x . This way of presenting the results has the advantage that a given composition with $0 < x < 1$ is predicted (within the method used) to be stable against disproportionation in two compositions with higher and lower x values if and only if its representative point lies below a straight line connecting the points which represent the two hypothetical decomposition products.

Figure 2 also presents data on the volumes (per Si atom) of the resulting structures. One may compare the values computed for the Si and SiNa reference solids and for the fully loaded ($\text{Na}_6\text{Si}_{34}$ and $\text{Na}_8\text{Si}_{46}$) and empty Si_{34} clathrates: 19.743, 50.144, 22.623, 22.412, and 22.606 Å³, respectively, with the corresponding values measured experimentally (at ambient temperature): 20.023, 48.796, 23.390 (value³⁰ for $\text{Na}_{5.8}\text{Si}_{34}$), 23.058 and 23.084 Å³ (the latter value²⁹ for $\text{Na}_{0.25}\text{Si}_{34}$); no experimental data seem to be available for the empty Si_{46} (MEP) clathrate. Except for the NaSi compound, where a quite different type of bonding sustains the structure, the predicted values are lower than the experimental ones by $\sim 1.5\% - 3\%$; it is also observed that, for the clathrates, the calculated volumes are higher than those of diamond Si by percentages (15%–17%) only a bit higher than the experimentally measured ones (13.5%–14.5%). A more detailed discussion on the effect of Na filling on the structure volume is given below.

As can be seen in Fig. 2, all ΔE values obtained are positive, indicating that the structures would be unstable in comparison to a mixture of pure Si (diamond phase) and NaSi (represented by the two extremes, at $x=0$ and 1, of the $\Delta E=0$ horizontal line). However, for the completely filled clathrates ($\text{Si}_{46}\text{Na}_8$ and $\text{Si}_{34}\text{Na}_6$) ΔE is very small (this coincidence between both being probably fortuitous), and lies probably within the accuracy limits of the method; one cannot then discard the possibility that van der Waals dispersion

(London) interactions (i.e., those leading typically to attractive terms of the C/r^6 kind), which are not accounted for by these standard DFT methods, produce an energetic effect which in the case of the clathrates is different to that occurring in the case of pure Si and the SiNa compound, so as to lead to a specific stabilization effecting the former.

These results are, therefore, compatible with the experimentally observed stability of the completely filled clathrates in comparison with a Si+NaSi mixture. In the case of partially filled clathrates, the larger ΔE values predict that they are unstable against decomposition. This does not contradict the experimental results showing that they can be prepared by eliminating thermally Na from the wholly filled structures; the lower temperatures used in this last synthesis step are probably high enough to achieve high mobility of Na atoms within the structure and their equilibration among the different cavities, but insufficient to break the Si–Si covalent bonds and provoke the alteration of the clathrate framework. Thus it is admissible to discuss in connection with the experimental observations the relative stabilities computed for the different locations of Na within one same structure even when the latter is clearly metastable against decomposition in Si(diamond) and NaSi.

Considering first the extreme situations, one observes that both Na-free clathratelike structures ($x=0$) appear, as expected, as more energetic than Si (diamond), the empty MTN lattice being slightly more stable (by ~ 8.5 meV/atom) than the MEP-type one. This coincides with previous DFT evaluations using a local orbital method,³ although the differences obtained here are a bit smaller. On the other hand, the Na-filled structures are clearly more stable than a mixture of NaSi and the corresponding empty clathrate, indicating that the Na–Si interaction in them is more favorable than that which makes up the NaSi compound. This can be explained by considering that, in this latter, the structure is made up of Si_4 tetrahedra in which each Si has only threefold Si–Si connectivity (with very strained Si–Si–Si angles of 60°) and can be considered to have one lone electron pair (thanks to the transfer of an electron from Na); i.e., the material can be described as constituted by $[\text{Si}_4]^{4-}$ tetrahedral units the charge of which is compensated by Na^+ ions. This situation is understandably less favorable than achieving a fourfold Si–Si connectivity of the type present in these clathrates. A similar trend is observed for the MEP and MTN data leading to the suggestion that, if there were some other clathratelike Si lattice having full fourfold connectivity and an intrinsic formation energy similar to that of the MEP and MTN, and which allowed the inclusion of higher proportions of Na in cavities such as those found here, it would probably be formed preferentially. The fact that this has not been observed suggests that there is no such structure.

One can also see that the variation in ΔE with x is, especially when the larger cavities are filled first, close to linear, i.e., the (negative) sodium inclusion energy per atom is to first approximation constant in each lattice. Furthermore, this inclusion energy seems to be of a somewhat higher magnitude in the complete or near complete filling of the MEP lattice than in the filling of the smaller cavities of the MTN lattice in view of the appreciably higher overall

slope of the graph in the first case. The latter effect would have as consequence that, in any mixture of both clathrates in which the total amount of sodium available is not enough to fill all cavities but can reach equilibrium distribution among them, it would be more favorable (so long as the proportion between the amounts of both lattices is kept fixed) to fill the cavities of the MEP lattice completely and minimize the occupation of the small ones (the majority) in the MTN component. This agrees with experimental observations made in cases in which both compounds appear simultaneously during the synthesis.^{29,30}

Going into finer details, one particular effect is observed for structures with only partial filling of the cavities. If one compares the situations in which the larger cavities are filled first (full symbols) with those in which the smaller cavities are filled first (empty symbols), the latter always appears higher in energy. This can be explained assuming that, when the Si₂₀ cages are occupied, the some of the Na–Si distances which appear (3.15 and 3.34 Å for MTN, 3.22 and 3.33 Å for MEP) are rather short and lead to some Na–Si repulsion which makes the situation less stable than that in which Na occupies only larger cavities. However, this might not be the main (or only) factor determining the energy difference, since this latter seems to be somewhat larger for the MEP structure in spite of the fact that the Na–Si distances in the small cages are somewhat larger than in MTN as said before. For MTN, the energy difference is computed to be 0.091 eV/Na; this is $\sim 50\%$ of the value deduced in the literature from an analysis of partial occupancy values determined from experimental x-ray diffraction data.³⁰ These differences in cavity filling energies lead to small nonlinearities in the plots of Fig. 2 which imply that structures with the large and small cavities respectively full and empty are the most stable ones against disproportionation; but the differences are small, and might be overridden by thermal effects at the temperatures typically used to prepare the partially Na-loaded materials from the fully loaded ones^{29,30} (between ~ 620 and 720 K). Indeed, it must be recognized that dispersion interactions (that as mentioned above cannot be calculated with these methods) and thermal or entropy effects may introduce energy differences in addition to those computed here; therefore, only the main trends found should be considered reliable.

It is also of interest to examine the variations in cell volume appearing upon the occupation of the cavities by Na. From Fig. 2, which also summarizes these results, it is clear that for both the MEP and MTN structures an initial filling of the larger cavities with Na leads to a decrease in overall cell volume. This qualitatively agrees with some experimental observations²⁹ made for MTN (although this was not observed in other cases³⁰), and may be explained as due to electrostatic attraction between the opposite charges of Na and Si atoms resulting from charge transfer (explained below). Indeed, the shortest distances between Si atoms and the centers of these large cavities are seen to become shorter by ~ 0.02 Å upon the location of Na in them. Occupation of only the smaller cavities produces a much smaller overall contraction, and indeed it is observed that the Si-cavity center distances do not decrease, in spite of the fact that the

extent of charge transfer is larger than for larger cavities (see below). These results agree with the above hinted at idea that the free room in the smaller ones is a bit too narrow for occupation by Na, so that the Na–Si repulsion resulting from this steric hindrance counteracts the electrostatic attraction. However, the reasons might be not so simple, since Fig. 2 shows that, in general, any cavity filling step leads to lower contraction or higher expansion if it is produced at higher values of x . This indicates that other factors may be at play; one may be, for example, the decreased degree of bonding between Si atoms which will occur when the excess electron density transferred to them populates, to significant extent, the conduction band, the orbitals of which will have mostly antibonding character, so that the Si–Si bonds will become progressively weaker and longer.

C. Electronic structures

1. Band structures and density of states calculations

Using the atomic geometries given by the afore mentioned optimized crystal structures, we have calculated the atomic band structures and its density of states for both the MEP and MTN structures with their cavities filled by Na atoms at different proportions using the SIESTA code. Calculations were made with DZ-GGA corrections in the zero temperature structures. In all structures atomic position parameters were allowed to relax. Band structures near the band-gap region (for the minimum energy configuration) for different schemes of cavity filling (only small ones, only large ones of complete filling, besides the Na-free case) are plotted in Fig. 3 for the MTN structures and in Fig. 4 for the corresponding MEP structures, showing the semiconductor-metal transformation occurring upon Na inclusion for both of them. In these figures, the zero of energy is taken at the Fermi level. Due to the large number of atoms in the unit cells, the two series display a large number of bands and complex electronic band structures. Semiconductor band structures with wide indirect energy band gaps have been calculated for the MEP Si₄₆ and MTN Si₃₄ structures by several groups,^{3,4,11,12,24–28} most of them using local density approximation (LDA) approximation, showing band gap values ~ 0.7 eV larger than those computed for crystalline silicon (i.e., predicting gap values of ~ 1.9 eV). It is well known that the LDA generally underestimates semiconductor band gaps. In our GGA studies we find band gaps of 2.30 eV for both the MEP Si₄₆ and the MTN Si₃₄ frameworks. In the case of Si₃₄, a minimum indirect gap clearly occurs between the W points at the top of the valence band and the Γ point at the bottom of the conduction band. However, in the case of Si₄₆ the maximum in the valence band appears in the Γ –X line, although it is difficult to precise it due to the flatness of this band, which has nearly the same energy at the Γ and X points. The conduction band minimum is at the same line although closer to the Γ point, giving a nearly direct band for this material.

The comparisons of band gap behavior within the two series with structures differing only in the degree of cage filling by Na, using accurate DZ-GGA calculations are shown in Figs. 3 and 4. Valence bands of Na_{*x*}Si₄₆ and

FIG. 3. Electronic band structure for MTN Si clathrate structures with different degrees of Na atom cavity filling, using DFT DZ-GGA calculations. The $\text{Na}_2\text{Si}_{34}$ case corresponds to the structure with two Na atoms filling the two larger Si_{28} cavities and $\text{Na}_4\text{Si}_{34}$ to that with four Na atoms in the four Si_{20} cavities. The diagram displays the band positions along several main directions of the first Brillouin zone corresponding to the fcc lattice. Energies are measured in eV and Fermi levels, which are denoted by a horizontal line, have been set as zero of energy.

$\text{Na}_x\text{Si}_{34}$ have features very close to those of the parent Si_{46} and Si_{34} , while conduction band structures become modified (and partially occupied by electrons) upon the inclusion of different numbers of guest alkali atoms. The minimum gap for each different compound is also shown in this calculation to be indirect in all cases except in the $\text{Na}_2\text{Si}_{34}$ and $\text{Na}_2\text{Si}_{46}$ structures, where only two Na atoms completely fill one type of cavity. In all these clathrate compounds the extra electrons (majority carriers) coming from the guest (donor) Na atoms populate the conduction states resulting in metallic behavior as inferred from the crossing of several bands by the Fermi level (determined by the number of metallic atoms inserted in the different cages). Ionic behavior, which would result from complete electron transfer from Na to the conduction band (originally of Si–Si antibonding character) is not produced probably due to the strength of the Si–Si bond. These behaviors are in agreement with the available experimental results about transport properties.^{20,21}

FIG. 4. Electronic band structure for the MEP Si clathrate structures with different degrees of Na atom cavity filling, using DFT DZ-GGA calculations. The $\text{Na}_2\text{Si}_{46}$ case corresponds to the structure with two Na atoms filling the two smaller Si_{20} cavities and $\text{Na}_6\text{Si}_{46}$ to that with six Na atoms in the six Si_{24} cages. The diagram shows the band positions along several main directions of the first Brillouin zone of the primitive cubic lattice. Energies are measured in eV and Fermi levels, which are denoted by a horizontal line, have been set as zero of energy.

Figures 5 and 6 show density of states (DOS) curves, total and projected on the Na atoms (*the latter multiplied by a factor of three for a best visualization*), for the two series of clathrates. To compute the DOS a peak width for broadening the eigenvalues of 0.05 eV has been used in all cases. An analysis of the difference in the electronic properties of the Na filling variations for the two systems can be reached by comparing their electronic density of states. The position of the Fermi levels above the bottom of the conduction band rises with Na content, the distance reaching 0.60 eV in the case of $\text{Na}_8\text{Si}_{46}$ and 0.72 eV in the case of $\text{Na}_6\text{Si}_{34}$. The gap between the valence band top and the conduction band bottom is, in the case of $\text{Na}_8\text{Si}_{46}$, 0.79 eV narrower than in the Na-free Si_{46} host, and, in the case of $\text{Na}_6\text{Si}_{34}$, 0.77 eV narrower than in Si_{34} . The distributions of partial and total DOS at the first levels of the conduction bands show a charge

FIG. 5. Total density of states and projected density over all Na atoms (the latter displayed as a thick line and multiplied by a factor of three) for the different MTN structures, using DZ-GGA calculations. Fermi level is displayed by a broken line. Energies are in eV.

transfer from Na atoms to the Si skeleton, with both components contributing to the filled bands as results of some overlapping between their low lying orbitals. Comparison of the DOS at the Fermi levels shows moderate metallic peaks for both series of clathrates, the number of carriers being a bit lower in the case of $\text{Na}_x\text{Si}_{46}$. A peak of DOS at the Fermi level could be observed mainly in $\text{Na}_x\text{Si}_{34}$, in the two cases where Na atoms completely fill the small Si_{20} cavities independently on the degree of filling of the larger cavities.

2. Mulliken population analysis

The degree of charge transfer occurring between Si and Na upon the inclusion of the latter atom(s) in the clathrate structures can be examined through a Mulliken population analysis, which provides values for the degree of occupation of the different atomic orbitals. Of course, Mulliken charges cannot be taken as absolute values, and other electron partitioning schemes (e.g., Hirschfeld or Voronoi charges, Bader analysis charges, etc.) may be argued as preferable; but the former are the easiest to obtain, and serve at least for com-

FIG. 6. Total density of states and projected density over all Na atoms (the latter displayed as thick line and multiplied by a factor of three) for the different MEP structures, using DZ-GGA calculations. Fermi level is displayed by a broken line. Energies are in eV.

parative purposes. In particular, it is instructive to examine the electronic population of the Na *s* orbitals in this way; since in the isolated Na atoms these orbitals contain exactly one electron each, the lower their occupation number the higher the extent of electron transfer from them to the framework.

The results show one clear and simple trend: Whatever the order of filling of the different cavities may be, within each clathrate type the electron population of the Na *s* orbitals increases with the decrease in the size of the cavity in which they reside. This fact is also reflected in the Na-projected DOS data obtained for both structures with only one type of cavity filled (Figs. 5 and 6). In particular, in the case of the MTN structure the average Na *s* orbital populations lie around $0.51 (\pm 0.015)$ for atoms in the Si_{28} cavities and around $0.63 (\pm 0.02)$ for those in the Si_{20} cavities, while in the MEP case they lie around $0.57 (\pm 0.005)$ for those in the Si_{24} cavities and around $0.62 (\pm 0.02)$ for those in the Si_{20} cavities. Thus, according to this analysis it appears that in each structure the transfer of charge from an occluded Na

atom to the Si framework is somewhat lower if the number of Si neighbors is lower.

Test calculations for both MTN and MEP structures with 2 Na atoms that completely fill one type of cavity, have been done using also polarization function on all the atoms. Results with these DZP basis, show that in both cases Na atoms are actually less ionic. Also, test calculations with DZP basis show that Na ionicity do not change significantly with the Na mobility inside of the cavity.

D. Mobility of sodium inside the structure cavities

The geometry optimizations performed in order to obtain the relaxed structures used in the above analyses were carried out initially keeping the maximal symmetry allowed by the topology of the structure, with any Na atoms present located at the centers of the cavities following the results of the diffraction studies published in the literature.^{29,30} Tests with decreased (or completely destroyed) symmetry were also made in which the Na atoms were initially more or less displaced from the centers of the cavities, particularly for the larger ones. The energies found with the atoms located at the cavity centers were always the lowest; however, in some cases it was found that only very small energy changes were obtained by subjecting the Na atoms to quite significant displacements. This was most remarkable in the case of the MTN structure, when displacing Na from the center of its larger cavities; as an example, Fig. 7 shows the energy changes obtained for this structure, with both large cavities in the primitive cell occupied, when moving the two Na atoms along one (common) ternary axis of the respective cavities, while keeping a trigonal symmetry (rhombohedral space group $R\bar{3}m$, Nr. 166), so that these atoms approach symmetrically the six-member ring connecting both cavities [the situation depicted in Fig. 8(a)]. A very similar behavior is found when the movement does not imply an approach between neighboring Na atoms [as in the situation given in Fig. 8(b)]. Significant movements of Na away from the cavity center would therefore be allowed; for example, a 0.65 Å displacement, reducing the shortest Na–Si distances to values around 3.35 Å, would be possible within an energy increase per Na atom lower than the ambient thermal energies ($kT=0.026$ eV at $T=300$ K). It thus seems that the Na atoms can move rather freely within a large space in these large cavities, which act as an oversized container.

It must be noted that the results do not reveal any specific Na atom-pairing interaction, which if present would probably lead to a net difference in energy between the configurations in Figs. 8(a) and 8(b). The flatness of the potential well in Fig. 7 indicates rather that the off-center Na atom displacement is not driven by DFT-addressable electronic effects. The Jahn–Teller or Peierls interaction mechanisms suggested in Ref. 20 are therefore not supported by the present calculations. Concerning the energy rise occurring upon Na–Si approach (displayed in Fig. 7), with the present calculation results it is not possible to say whether it reflects interactions additional to the expected Pauli repulsion. The shortest Na–Si distance seemingly achievable ($\sim 3.3\text{--}3.4$ Å) is larger than that between Na^+ and the

FIG. 7. Plot of the increase in total energy computed for a $\text{Na}_2\text{Si}_{34}$ MTN-type clathrate, with all large Si_{28} cavities occupied by Na, against a symmetric displacement of Na [in the mode shown by Fig. 8(a)] away from the cavity center, with the Si_{34} lattice remaining fixed (the not displaced situation being taken as energy reference).

$(\text{Si})_4^{4-}$ clusters in the rather ionic NaSi compound (2.9–3.0 Å), indicating a significantly lower Coulomb attraction in agreement with an only partial ionic character of the Na–Si interaction in the clathrates.

One can thus explain the EXAFS results given in the literature²⁰ which indicate the presence in these situations of short Na–Si distances, which would correspond to displacements away from the large cavity center as large as 0.9 Å. Here it should be recalled again that these DFT methods are not able to reproduce dispersion interactions; inclusion of these might well lead to the appearance of a distinct minimum in the graph in Fig. 7 for displacements of ~ 0.7 Å or higher, in agreement with the EXAFS results. In any case, the results of the calculations made here justify the large thermal parameters determined for the Na atoms from the diffraction data of these compounds,²⁹ and agree with the usual assumption that these atoms, being able to rattle largely inside the cavities, lead to large phonon scattering effects which make it possible to achieve a low thermal conductance and consequently important thermoelectric properties.¹¹

The study of similarly displaced locations of the Na atoms inside the Si_{24} cavities of the MEP structure indicated a much narrower range for movement; significant Na–Si repulsive interactions [at the same level as those corresponding to the situation of Fig. 8(a)] already began to appear for

FIG. 8. Schematic pictures of pairs of large cavities in the $\text{Na}_2\text{Si}_{34}$ (MTN-type) and $\text{Na}_6\text{Si}_{46}$ (MEP-type) clathrates, with the Na atoms displaced from the cavity centers to positions where Na–Si interaction begins to raise the energy by ~ 15 meV (picture a corresponds to the point with displacement $= 0.63$ Å in Fig. 7). (a) and (b): MTN structures with viz. symmetric and nonsymmetric Na displacements; (c): MEP structure (with symmetric displacement). Some significant Na–Si distance values are highlighted.

displacements towards the six-member windows of ~ 0.1 Å [situation depicted in Fig. 8(c)]. Note that this occurs for Na–Si distances similar to those appearing in Fig. 8(a) (around 3.35 Å). It seems unlikely that such small displacements may be experimentally detectable with either EXAFS or x-ray diffraction. On the other hand, for the smaller Si_{20} cavities present in both the MEP and MTN structures such off-center deviations appear as clearly unfavorable; indeed, the calculations summarized in Fig. 7 show repulsions between Na and Si when the distance between them in these structures decreases below 3.30 Å. This repulsion most likely determines the previously discussed fact that filling these cavities before the larger ones is unfavorable.

IV. CONCLUSIONS

Filled cage systems like the known MTN and MEP clathrate compounds are interesting for future materials research. A comparative study is reported here on clathrates derived from both structures in which the guest sites located at the different cages are partially or fully occupied by Na metal atoms. Using first principles calculations within the

framework of density functional theory, band diagrams, DOS, Mulliken population, relaxed structures and total energies for these compounds are studied to elucidate the effects of the inclusion of Na atoms. We find that the electron population of Na s orbitals increases (i.e., the degree of electron density transfer to the surrounding Si lattice decreases) with a decrease in the size of the cavity and also that Na orbitals strongly contribute to the density of states at the Fermi level, especially in the case of the Si_{34} clathrate, and can influence the properties of the compounds. The experimental crystal cell sizes of the structures, where known, are rather well reproduced, and the completely filled clathrates are predicted to be nearly as stable as a mixture of pure Si(diamond) and NaSi phases; their real stability, deduced from the experimentally proven feasibility of their preparation, might be the result of dispersion interactions and/or vibrational contributions at finite temperatures. On the other hand, the study on the mobility of sodium inside the structures cavities clearly shows that preferential filling of larger cavities (where large free movement of the Na atom is allowed in the MTN case, explaining experimental EXAFS observations) is favored due to Na–Si repulsive interactions appearing for Si–Na distances below ~ 3.30 Å.

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