

# A theoretical study of stability, electronic, and optical properties of GeC and SnC

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We present the results of a first principles study on the ordered  $\text{Ge}_{0.50}\text{C}_{0.50}$  and  $\text{Sn}_{0.50}\text{C}_{0.50}$  cubic alloys. A linear combination of atomic orbitals approach in the framework of density functional theory is employed for total energy calculations in the zincblende phase. A fitting of the energy surface to the equation of state yields the lattice constant of 4.61 and 5.17 Å and the bulk modulus of 181 and 119 GPa for GeC and SnC, respectively. Analysis of band structure suggests a crossover of the nature of the band gap from indirect to direct in going from SiC to GeC to SnC. Although both alloys predicted to be unstable with respect to their elemental components at zero pressure and temperature, GeC appears to become stable at higher pressure. It appears that both the lattice constant and bulk modulus of the ordered alloys do not follow Végard's linear rule, though the calculated dielectric constant of the cubic alloys is approximately the average of the dielectric constant of their elemental components. © 2000 American Institute of Physics.

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## I. INTRODUCTION

Group IV semiconductor alloys have immense potential for applications in the next generation of Si-based electronic and photonic devices.<sup>1,2</sup> It has been suggested that Ge–C and Sn–C alloys and ordered compounds may have particularly unique optoelectronic properties for applications such as a high band gap semiconductor on Si. Moreover the Ge–C and Sn–C alloy systems on Si appear to provide a wide range of tunable band gap energies, in principle, spanning from the infrared to the near ultraviolet region of the spectrum. Although the constituents of Ge–C alloys are immiscible under equilibrium conditions in the bulk, epitaxial stabilization of these alloys have been explored by various workers. For example, Krishnamurthy *et al.*<sup>3</sup> have studied the epitaxial growth of  $\text{Ge}_{1-x}\text{C}_x$  films with C concentration in the range  $x \approx 0.2$ – $0.8$ . They have observed<sup>4,5</sup> a C-related change near the  $E_1$  critical point in Ge together with the Raman signature of the Ge–C local mode in epitaxially films grown on Ge (100) substrates. The structural and electronic properties of GeC was first reported by Sankey *et al.*,<sup>6</sup> though we are not aware of any theoretical studies on the cubic SnC alloy.

Knowing that a knowledge of stability of an alloy system in conjunction with its electronic and optical properties is critical in promoting alloy thin films for device applications, we have initiated a detailed theoretical study of group IV semiconductor alloys. In an earlier article, we had reported the results of a theoretical study<sup>7</sup> on the ordered

$\text{Ge}_{0.50}\text{Sn}_{0.50}$  alloy. In this work, we will now report the results on the ordered  $\text{Ge}_{0.50}\text{C}_{0.50}$  and  $\text{Sn}_{0.50}\text{C}_{0.50}$  alloy systems. Our aim will be (i) to investigate stability of the ordered SnC alloy with respect to its elemental components and predict its structural, electronic, and optical properties, (ii) to predict optical properties of the ordered GeC alloy together with a comparison of the present study with previously reported study<sup>6</sup> on its structural and electronic properties. Furthermore, we will use the calculated results on SiC to judge the reliability of the computational parameters used here due to availability of extensive theoretical and experimental studies on the cubic SiC.

The rest of the article is organized as follows. In Sec. II, we briefly describe the computational model used in this work. Results and discussion of the structural parameters, band structure, dielectric constant, and stability will be presented in Sec. III, and a summary of the work will be given in Sec. IV.

## II. COMPUTATIONAL METHOD

The computational method is based on a generalized gradient approximation<sup>8,9</sup> (GGA) to the density functional theory (DFT). A linear combination of Gaussian orbitals are used to construct a localized atomic basis from which Bloch functions are constructed by a further linear combination with plane-wave phase factors. The Gaussian basis sets<sup>7,10</sup> used in the present study are three *s*-, two *p*-, and a *d*-type shells for C (i.e., a 621/21/1 set), four *s*-, three *p*-, and two *d*-type shells for Si (i.e., a 8841/841/11 set), five *s*-, four *p*-, and two *d*-type shells for Ge (i.e., a 97631/7631/61 set), and

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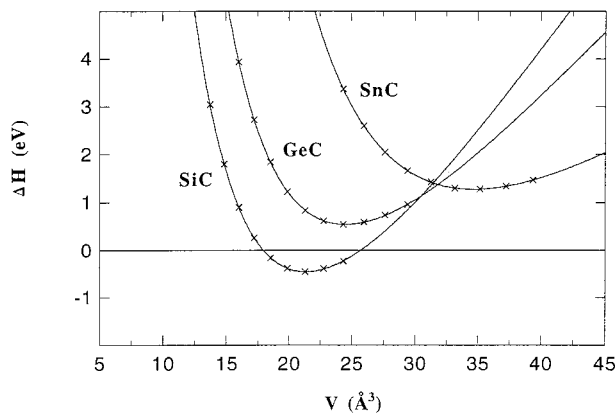


FIG. 1. The energy surface of cubic SiC, GeC, and SnC. Here,  $\Delta H$  is the enthalpy of formation and  $V$  is the unit cell volume. The *negative* value of  $\Delta H$  indicates the stability of the alloy with respect to its elemental components.

seven *s*-, six *p*-, and three *d*-type shells for Sn (i.e., a 9763111/763111/631 set). Such basis sets (which include one function for the core and two *s* and *p* functions for each valence atomic orbital), supplemented by a *d*-type polarization function has been demonstrated to be very good in providing accurate and reliable predictions of structure and energetics of both bulk and surfaces of covalent materials such as Si, C, BN, and GaN.<sup>11–14</sup>

For calculations, we use the program package CRYSTAL<sup>15</sup> in which the tolerance on the total energy convergence in the iterative solution of the Kohn–Sham equations is set to  $10^{-6}$  Hartree and a grid of 29 **k** points is used in the irreducible Brillouin Zone for integration in the reciprocal space. Overall, the residual numerical uncertainty is estimated to be about 0.01 eV per atom.

All electron calculations of the ordered alloys are performed to obtain the potential energy surface (i.e., total energy as a function of volume) in the zincblende phase, considering that structure and local bonding of the ordered alloy is expected to be similar to the constituent elements. We note here that the elemental components of the alloys considered here (i.e., C, Si, Ge, and  $\alpha$ -Sn) can have diamond structure. At ambient pressure, Si and Ge have diamond structure while C crystallizes in the graphite phase. Tin occurs in two phases, namely  $\alpha$ -Sn and  $\beta$ -Sn. The equilibrium structural parameters of the cubic alloys are obtained by fitting the calculated energy surface to Vinet equation of state.<sup>16</sup> At the equilibrium volume, the electronic and optical properties including band structure, dielectric constant, and index of refraction are then obtained.

### III. RESULTS AND DISCUSSION

#### A. Structural properties

Figure 1 shows the energy surface of SiC, GeC, and SnC which is fitted to the equation of state to obtain their equilibrium volume (i.e., lattice constant), bulk modulus, and its pressure derivative in the zincblende phase. The calculated structural parameters are listed in Table I together with those of the elemental components obtained in the cubic phase.

TABLE I. Structural properties [i.e., lattice constant ( $a$ ), equilibrium volume ( $V$ ), bulk modulus ( $B$ ) and its pressure derivative ( $B'$ )] of SnC, GeC, SiC, and the constituent elements.

		$a$ (Å)	$V$ (Å <sup>3</sup> )	$B$ (GPa)	$B'$
SnC	This work (GGA)	5.17	34.61	119	4.3
GeC	This work (GGA)	4.61	24.45	181	4.2
	LDA pseudopotential <sup>a</sup>	4.49	22.63	218	...
SiC	This work (GGA)	4.40	21.30	206	5.3
	Expt.	4.36	20.72	224	...
	LDA pseudopotential <sup>a</sup>	4.28	19.60	245	...
$\alpha$ -Sn	This work (GGA)	6.65	73.38	42	5.1
	Expt.	6.49	68.34	42.6	...
Ge	This work (GGA)	5.74	47.28	71	5.1
	Expt.	5.66	45.33	77	...
	LDA pseudopotential <sup>a</sup>	5.60	43.90	72	...
Si	This work (GGA)	5.45	40.51	96	4.1
	Expt.	5.43	40.03	99	...
	LDA pseudopotential <sup>a</sup>	5.43	40.03	96	...
C	This work (GGA)	3.61	11.76	426	4.1
	Expt.	3.57	11.37	443	...
	LDA pseudopotential <sup>a</sup>	3.56	11.28	488	...

<sup>a</sup>See Ref. 6.

Table I also includes the results of a theoretical study<sup>6</sup> performed using pseudopotentials in the local density approximation (LDA) which we use to compare the results of the present study. Overall, the calculated structural parameters follow the expected trend; the lattice constant is overestimated by GGA and underestimated by LDA. For example, the GGA value is 1% larger and the LDA value is 2% smaller than the experimental value in SiC. This variation in the lattice constant is also reflected in the calculated values of the bulk modulus of these materials.

For GeC and SnC, the calculated lattice constants are 4.61 and 5.17 Å, respectively while the bulk moduli are 181 and 119 GPa, respectively. It therefore appears that both GeC and SnC alloys do not obey Végard's rule since  $\Delta a$  [e.g.,  $a_{\text{GeC}} - (1/2)(a_{\text{Ge}} + a_{\text{C}})$ ] comes out to be  $-0.065$  Å for GeC and  $+0.04$  Å for SnC. The *negative* deviation for GeC is similar to that observed for SiC and was attributed<sup>17</sup> to the charge transfer from Si to C. In the present study, however, the Mulliken population analysis indicates a charge transfer of about  $0.6e$  from metal cation to C in these materials, though the lattice constant of SnC does not show the *negative* deviation from Végard's linear rule.

The calculated bulk modulus of GeC and SnC are 181 and 119 GPa suggesting that SnC is much softer than GeC, as expected. Interestingly, the variation of the bulk modulus with the lattice constant in SiC, GeC, and SnC follows closely with Cohen's proposition<sup>18</sup> which states that the bulk modulus in group IV elements mainly depends on the covalent character of the bond. The application of the proposed relationship<sup>19</sup> of  $B = 1972d^{-3.5}$  results the values of 207, 175, and 117 GPa for SiC, GeC, and SnC, respectively which are very close to the calculated values of these alloys

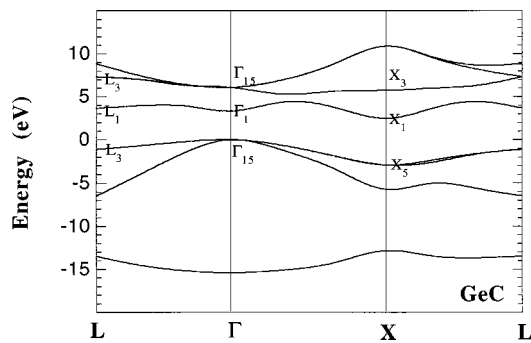


FIG. 2. Band structure of GeC. The zero energy reference is at the top of the valence band.

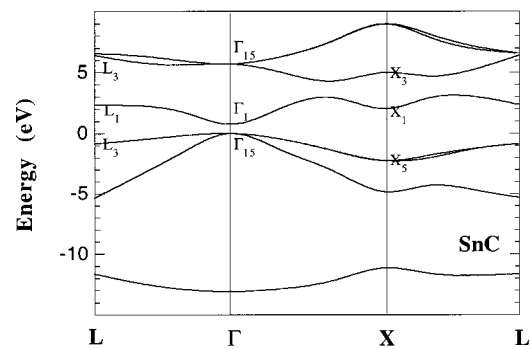


FIG. 3. Band structure of SnC. The zero energy reference is at the top of the valence band.

(Table I). On the other hand, the bulk moduli of the ordered alloys do not fall on the straight-line average of the constituent elements. The difference ( $\Delta B$ ) between the calculated bulk modulus and the average value  $B_{\text{avg}}$  [i.e.,  $(1/2)(B_{\text{Ge(Sn)}} + B_{\text{C}})$ ] is very large for both alloys and the ratio of  $\Delta B/B_{\text{avg}}$  is predicted to be 27% in GeC and 49% in SnC. This is in contrast to the results<sup>7</sup> for the ordered GeSn alloy where the ratio is about 6%. The bond strength in the ordered GeC and SnC therefore appears to be significantly different from the average of that in their elemental components, though the bond character remains the same. We note here that values for the pressure derivative  $B'_0$  are typically between 4 and 5 for most solids. It is seen in Table I that the tabulated  $B'_0$  values fall within this range.

## B. Electronic properties

The band structure of the cubic GeC and SnC alloys are displayed in Figs. 2 and 3. In the absence of the spin-orbit interaction terms in these calculations, the top of the valence band consists of the triple degenerate  $\Gamma_{15}$  level. The  $p$  states of Ge (Sn) and C forms the upper valence band while the  $s$  states of Ge (Sn) and C form a band at about 13 eV below the top of the valence band. As expected, the  $d$  bands in both alloys are atomic-like with a negligible dispersion appearing at about 25 eV in GeC and at about 23 eV in SnC below the top of the valence band.

The minimum of the conduction band is found to be at  $\Gamma$  in SnC while that in GeC is at  $X$ . Thus, the present GGA

calculations predict SnC to be a direct-gap alloy with the band gap of 0.75 eV. This is in contrast to the Soref's estimation<sup>20</sup> suggesting the gap to be indirect ( $\Gamma-L$ ) with the value of 1.20 eV. For GeC, the calculated results find the minimum energy gap to be indirect with a value of 2.46 eV (Table II). Previously, the LDA-pseudopotential calculations<sup>6</sup> reported GeC to be indirect gap ( $\Gamma-X$ ) alloy. Similarly, calculations<sup>21</sup> using the virtual crystal approximation found the minimum gap to be indirect for  $\text{Ge}_{0.62}\text{C}_{0.38}$ . In Table II, we have also reported our results for SiC for which the calculated results are in agreement with previous calculations and experiment in predicting SiC to be an indirect gap ( $\Gamma-X$ ) material.<sup>6,22,23</sup>

A crossover of the nature of minimum energy gap in going from SiC to SnC can be explained in terms of the conduction level splittings. The lowest two conduction levels at  $\Gamma$  (i.e.,  $\Gamma_1^c$  and  $\Gamma_{15}^c$ ) in these materials represent  $s$ - and  $p$ -like antibonding states. In going from SiC to GeC to SnC, the  $s$ -like antibonding states of heavier cations, being non-zero at the nucleus, are expected to move down relative to the  $p$ -like states at  $\Gamma$ , leading to an increase in the splitting of these levels. This is what we have found in the calculated band structure of SiC, GeC, and SnC where the respective splitting at  $\Gamma$  is 0.92, 2.76, and 4.94 eV. On the other hand, the conduction levels at  $X$  are mixed  $s$ - and  $p$ -like states and their splitting does not therefore show such a variation in going from SiC to GeC to SnC (Table II). Furthermore, a small variation in the splitting at  $X$  suggests<sup>24</sup> that the degree

TABLE II. The minimum-energy direct and indirect band gaps (in eV) and splitting of the conduction levels at  $\Gamma$ , and  $X$  of the cubic SnC, GeC, and SiC.

		Direct gap ( $\Gamma$ )	Indirect gap ( $\Gamma-X$ )	$\Delta E(\Gamma_{15}^c - \Gamma_1^c)$	$\Delta E(X_3^c - X_1^c)$
SnC	This work	0.75	2.0	4.94	2.96
GeC	This work	3.3	2.5	2.76	3.26
	LDA pseudopotential <sup>a</sup>	4.9	1.4		
SiC	This work	6.1	1.6	0.92	3.14
	Experiment	7.4 <sup>b</sup>	2.417 <sup>c</sup>		
	LDA pseudopotential <sup>a</sup>	6.7	1.22		
	LDA-LMTO(ASA) <sup>b</sup>	6.56	1.38	1.15	2.91

<sup>a</sup>See Ref. 6.

<sup>b</sup>See Ref. 22.

<sup>c</sup>See Ref. 23.

TABLE III. Optical properties of the cubic SnC, GeC, and SiC. [Note: For SiC, the experimental value (Ref. 28) of  $\epsilon$  is reported to be 6.2–6.7]

	Static polarizability $\alpha$ ( $\text{\AA}^3$ )	Dielectric constant $\epsilon(\lambda \rightarrow \infty)$	Index of refraction $n(\lambda \rightarrow \infty)$	Plasmon energy $E_p$ (eV)
SnC	34.57	13.6	3.7	15.0
GeC	12.08	7.2	2.7	18.0
SiC	10.28	7.1	2.7	22.0

of ionicity remains almost the same in SiC, GeC, and SnC, as also indicated by the calculated Mulliken charges.

### C. Optical properties

It is well known that the conduction bands are not well described by density functional theory, though their use in polarizability calculations yield satisfactory values of dielectric response functions in semiconductors.<sup>13,25</sup> In this work, a sum over states (SOS) method is used to calculate the real and imaginary parts of the polarizability from which related functions such as the dielectric constant and energy loss function [i.e.,  $\text{ELF} = -\text{Im}(1/\epsilon(\omega))$ ] can easily be obtained. The SOS method requires calculations of (vertical) transition moments and energies between the valence (occupied) and conduction (unoccupied) states and does not take into account of the coupling between vertical transitions for different wave vectors  $k$ , responsible for the field-induced electron reorganization effects.<sup>26</sup> The gap, which is not well described by density functional theory, can be corrected by a scissor operator. However, we have not applied the scissor operator in this work.

In the SOS calculations, we have used the velocity operator to describe the electric field perturbation in the dipole approximation. The velocity operator,  $\nabla(V)$ , replaces the electron position  $\mathbf{r}$  or length operator ( $L$ ) in the framework of the hypervirial theorem as follows:

$$(E_n - E_0)\langle 0|\mathbf{r}|n\rangle = \langle 0|\nabla|n\rangle, \quad (1)$$

where  $|0\rangle$  and  $|n\rangle$  are eigenvectors of the unperturbed Hamiltonian operator  $H_0$ .

Furthermore, the use of the velocity operator leads to the replacement of the transition moments,  $\langle i|\mathbf{r}|j\rangle_{\mathbf{k}}$  by  $\langle i|\nabla|j\rangle_{\mathbf{k}}/(\epsilon_{j\mathbf{k}} - \epsilon_{i\mathbf{k}})$ . Here,  $|i\rangle_{\mathbf{k}}$  and  $|j\rangle_{\mathbf{k}}$  are occupied and unoccupied crystalline orbitals for  $\mathbf{k}$  point of the reciprocal space (i.e., eigenvectors of the Kohn–Sham equations with the associated eigenvalues  $\epsilon_{i\mathbf{k}}$  and  $\epsilon_{j\mathbf{k}}$ , respectively).

The SOS results<sup>27</sup> of static polarizability, dielectric constant, index of refraction, and plasmon energy are collected in Table III.<sup>28</sup> Accordingly, the optical properties of GeC are predicted to be similar to those of the cubic SiC having the same dielectric constant and index of refraction. However, SnC is predicted to have significantly larger dielectric constant and index of refraction as compared to those of SiC and GeC. We note here that our calculated values are close to the Soref’s empirically estimated values<sup>1</sup> suggesting that the optical constants of the ordered alloys are average of those in the elemental components.

TABLE IV. The enthalpy of formation ( $\Delta H$ ) for the cubic SnC, GeC, and SiC.

		$\Delta H$ (eV)
SnC	This work	1.28
GeC	This work	0.54
	LDA pseudopotential <sup>a</sup>	0.18
SiC	This work	-0.46
	LDA pseudopotential <sup>a</sup>	-0.34

<sup>a</sup>See Ref. 6.

The complex dielectric response function is now used to calculate the plasmon energy corresponding to the maximum of the ELF function. The calculated plasmon energy values are 22, 18, and 15 eV for SiC, GeC, and SnC, respectively. The value for SiC compares very well with the experimental value<sup>29</sup> of 22.1 eV and a previously calculated value<sup>30</sup> of 22.4 eV.

### D. Phase stability

Finally, we address the question of the phase stability of the ordered GeC and SnC alloys with respect to their elemental components by calculating the enthalpy of formation ( $\Delta H$ ) of the cubic alloys.<sup>17</sup> For GeC and SnC,  $\Delta H$  is found to be 0.27 and 0.64 eV/atom, respectively. The results therefore predict the instability of GeC and SnC at zero pressure and temperature. On the other hand, the expected stability of cubic SiC is reproduced by our calculations (see, Table IV). Note that the LDA-pseudopotential calculations<sup>6</sup> also reported the instability of GeC at zero pressure with  $\Delta H$  of 0.18 eV/atom.

We now explore the possibility of high-pressure synthesis or epitaxial stabilization of GeC and SnC and investigate the effect of pressure on the stability of these alloys. Employing the equation of state obtained earlier in Sec. III A, a variation of the Gibbs free energy with the pressure can easily be determined for both alloys neglecting the temperature dependent term. In Fig. 4, we plot the Gibbs free energy of the alloy with respect to that of the elemental components ( $\Delta G$ ) in which the negative value of  $\Delta G$  indicates the sta-

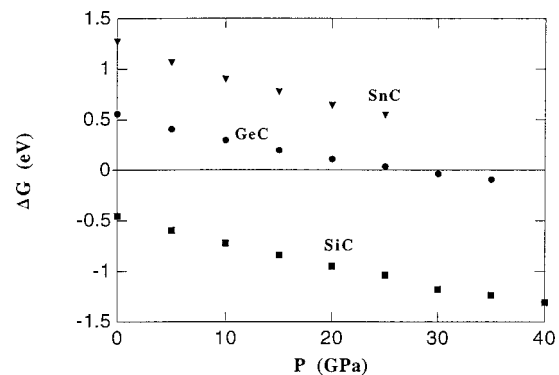


FIG. 4. A variation of Gibbs free energy with pressure for SiC, GeC, and SnC. The negative value of  $\Delta G$  indicates the stability of the alloy with respect to its elemental components.

bility of an alloy. Accordingly, the cubic GeC appears to be stabilized at higher pressures with respect to its elemental components. This prediction of the high-pressure stability, however, should be treated with caution since we have ignored the possibility of a high-pressure phase transition for one of the elemental components, Ge<sup>31</sup> in this analysis. We note here that self-consistent pseudopotential calculations<sup>32</sup> have reported the Ge (diamond to  $\beta$ -tin) phase transition to occur at about 9 GPa with a gain of energy of 0.25 eV. A similar suggestion on the high-pressure stability of GeC was made by the LDA-pseudopotential study.<sup>6</sup>

#### IV. SUMMARY

In summary, we have calculated structural parameters, optical constants, and enthalpy of formation for cubic GeC and SnC alloys. It appears that the calculated lattice constant and bulk modulus of the ordered alloys do not follow Végard's linear rule, though the calculated dielectric constant of the cubic alloys is approximately the average of the dielectric constant of their elemental components. A crossover of the nature of the band gap is also predicted in going from SiC to GeC to SnC. Although the calculated enthalpy of formation indicates the instability of both alloys at zero pressure and temperature, a possibility of the high-pressure stabilization of GeC appears to exist.

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<sup>1</sup>R. A. Soref, *J. Vac. Sci. Technol. A* **14**, 913 (1996).

<sup>2</sup>R. A. Soref, *J. Appl. Phys.* **70**, 2470 (1991).

<sup>3</sup>M. Krishnamurthy, J. S. Drucker, and A. Challa, *J. Appl. Phys.* **78**, 7070 (1995).

<sup>4</sup>M. Krishnamurthy, B.-K. Yang, and W. H. Weber, *Appl. Phys. Lett.* **69**, 2572 (1996).

<sup>5</sup>W. H. Weber, B.-K. Yang, and M. Krishnamurthy, *Appl. Phys. Lett.* **73**, 626 (1998).

<sup>6</sup>O. F. Sankey, A. A. Demov, W. T. Petuskey, and P. F. McMillan, *Modell. Simul. Mater. Sci. Eng.* **1**, 741 (1993).

<sup>7</sup>R. Pandey, M. Rérat, and M. Causà, *Appl. Phys. Lett.* **75**, 4127 (1999).

<sup>8</sup>A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).

<sup>9</sup>J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13 244 (1992).

<sup>10</sup>We use a contracted Gaussian basis set for each atom in which each shell can be described by a linear combination of Gaussians with different ranges. For example, a (621/ 21/ 1) basis set represents three *s*-, two *p*-, and a *d*-type shells for C. The first and second *s* shells are given by a linear combination of 6 and 2 Gaussians, respectively while the third *s* shell consists of single Gaussian. Similarly, the first *p* shell is given by a linear combination of 2 Gaussians whereas the second *p* and *d* shells consist of a Gaussian. The basis sets used in this work can be obtained from the authors (pandey@mtu.edu).

<sup>11</sup>M. Causà, R. Dovesi, and C. Roetti, *Phys. Rev. B* **43**, 11 937 (1991).

<sup>12</sup>R. Pandey, M. Causà, N. M. Harrison, and M. Seel, *J. Phys.: Condens. Matter* **8**, 3993 (1996).

<sup>13</sup>D. Ayma, M. Rérat, and A. Lichanot, *J. Phys.: Condens. Matter* **10**, 557 (1998).

<sup>14</sup>R. Pandey, P. Zapol, and M. Causà, *Phys. Rev. B* **55**, 1 (1997).

<sup>15</sup>R. Dovesi, V. R. Saunders, C. Roetti, M. Causà, N. M. Harrison, R. Orlando, and E. Aprà, *CRYSTAL95 User's Manual*, Università di Torino, 1996.

<sup>16</sup>P. Vinet, J. Ferrante, J. H. Rose, and J. R. Smith, *J. Geophys. Res.* **92**, 9319 (1987).

<sup>17</sup>J. L. Martins and A. Zunger, *Phys. Rev. Lett.* **56**, 1400 (1986).

<sup>18</sup>M. L. Cohen, *Phys. Rev. B* **32**, 7988 (1985).

<sup>19</sup>*B* is the bulk modulus in GPa and *d* is the near-neighbor distance in Å. The values of *d* are 1.905, 1.996, and 2.239 Å in SiC, GeC, and SnC, respectively.

<sup>20</sup>R. A. Soref, *J. Appl. Phys.* **72**, 626 (1992).

<sup>21</sup>B. A. Orner and J. Kolodzey, *J. Appl. Phys.* **81**, 6773 (1997).

<sup>22</sup>For example, W. R. L. Lambrecht, B. Segall, M. Yoganathan, W. Suttrop, R. P. Devaty, W. J. Choyke, J. A. Edmond, J. A. Powell, and M. Alouani, *Phys. Rev. B* **50**, 10 722 (1994).

<sup>23</sup>R. G. Humphreys, D. Bimberg, and W. J. Choyke, *Solid State Commun.* **39**, 163 (1981).

<sup>24</sup>The splitting at *X* (i.e.,  $X_3^c-X_1^c$ ) can be taken as a measure of ionicity in a nearly free electron model.

<sup>25</sup>C. S. Wang and B. M. Klein, *Phys. Rev. B* **24**, 3417 (1981).

<sup>26</sup>B. Champagne, J. G. Fripiat, and J. M. André, *J. Chem. Phys.* **96**, 8330 (1992).

<sup>27</sup>We do not take account of the local field effects in polarizability calculations which are expected to reduce the value of  $\epsilon$  by about 10%.

<sup>28</sup>D. Ayma, A. Lichanot, and M. Rérat, *J. Phys. Chem. B* **103**, 5441 (1999).

<sup>29</sup>H. Raether, in *Excitations of Plasmons and Interband Transitions by Electrons*, Springer Tracts in Modern Physics Vol. 88 (Springer, Berlin 1980).

<sup>30</sup>W. H. Backes, P. Robbert, and W. van Haeringen, *Phys. Rev. B* **51**, 4950 (1995).

<sup>31</sup>M. Baublitz and A. L. Ruoff, *J. Appl. Phys.* **53**, 5669 (1982).

<sup>32</sup>M. T. Yin and M. L. Cohen, *Solid State Commun.* **38**, 625 (1981).