Electron−Phonon Interaction Contribution to the Total Energy of Group IV Semiconductor Polymorphs: Evaluation and Implications

Arjun Varma Ramasimha Varma, Shilpa Paul, Anup Itale, Pranav Pable, Radhika Tibrewala, Samruddhi Dodal, Harshal Yerunkar, Saurav Bhaumik, Vaishali Shah, Mogadalai Pandurangan Gururajan, and Tiramkudlu R. S. Prasanna*

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: In density functional theory (DFT)-based total energy studies, the van der Waals (vdW) and zero-point vibrational energy (ZPVE) correction terms are included to obtain energy differences between polymorphs. We propose and compute a new correction term to the total energy, due to electron−phonon interactions (EPI). We rely on Allen's general formalism, which goes beyond the quasi-harmonic approximation (QHA), to include the free energy contributions due to quasiparticle interactions. We show that, for semiconductors and insulators, the EPI contributions to the free energies of electrons and phonons are the corresponding zero-point energy contributions. Using an approximate version of Allen's formalism in combination with the Allen−Heine theory for EPI corrections, we calculate the zero-point EPI corrections to the total energy for cubic and hexagonal polytypes of carbon, silicon and silicon carbide. The EPI corrections alter the energy differences between polytypes. In SiC polytypes, the EPI correction term is more sensitive to crystal structure than the vdW and ZPVE terms and is thus essential in determining their energy differences. It clearly establishes that the cubic SiC-3C is metastable and hexagonal SiC-4H is the stable polytype. Our results are consistent with the experimental results of Kleykamp. Our study enables the inclusion of EPI corrections as a separate term in the free energy expression. This opens the way to go beyond the QHA by including the contribution of EPI on all thermodynamic properties.
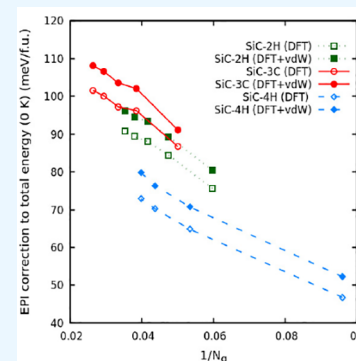
INTRODUCTION

Group IV semiconductors, especially C, Si, and SiC, are of immense scientific and technological importance. Currently, there is enormous interest in predicting new allotropes of C and Si because different crystal structures exhibit differing physical properties and provide a landscape to design materials with specific properties.[1−5] In the case of C, this is evident from the 522 allotropes listed in the Samara carbon allotrope database.[6] In Si, predicting metastable crystal structures with direct band gaps are of particular interest.[7] SiC polytypes are among the most important materials for structural applications.[8] SiC also has promising potential in future high-voltage and low-loss power devices.[9]

Given their importance, several studies have been performed on C, Si and SiC polytypes. The accurate determination of the energy differences is essential in the study of these polytypes. The main SiC polytypes are the cubic zincblende SiC-3C, the hexagonal wurtzite SiC-2H and the hexagonal SiC-4H and SiC-6H. Despite several experimental and computational studies, the stable structure in SiC remains controversial because of the marginal energy differences between the cubic (SiC-3C) and hexagonal SiC polytypes (SiC-4H and SiC-6H). We first summarize the results from experimental studies and later from computational studies.

Greenberg et al.[10] reported thermodynamic data at 298 K for hexagonal α-SiC and cubic β-SiC (SiC-3C) using calorimetric studies. Using the quadrature rule for error propagation, the free energy of transformation can be calculated from their results to be $\Delta_{tr}G_{298}^{0,\alpha\rightarrow\beta} = -1.13 \pm 2.6$ kJ/mol (-11.70 ± 26.94 meV/formula unit, f.u.), and the enthalpy of transformation is $\Delta_{tr}H_{298}^{0,\alpha\rightarrow\beta} = -1.09 \pm 2.6$ (-11.29 ± 26.94 meV/f.u.) using the relation 1 kJ/mol = 10.36 meV/f.u. (henceforth, in all energy data given in units of meV/f.u., f.u. refers to one unit of SiC, i.e., one atom of Si and C). From the JANAF tables,[11,12] the enthalpy of transformation is obtained as $\Delta_{tr}H_{298}^{0,\alpha\rightarrow\beta} = -1.7 \pm 8.9$ kJ/mol (-17.61 ± 92.20 meV/f.u.). (Since Greenberg et al.[10] and the JANAF tables[11] have not specified the polytype (2H, 4H, or 6H) for the hexagonal α-SiC, we cannot be more specific about the particular hexagonal SiC polytype.) From these results, we may conclude that the cubic β-SiC (SiC-3C) has lower enthalpy. However, the large margin of error suggests that the
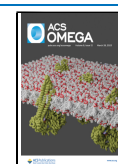
experimental results from calorimetric studies are not conclusive but are indicative.

In later studies, Kleykamp[12] reported the results of galvanic cell measurements and found that hexagonal α-SiC is stable. (Kleykamp[12] has reported that the hexagonal α-SiC used in his study was mainly SiC-6H.) In his study, the stable structure was obtained directly from electromotive force (EMF) measurements in galvanic cells. In the temperature range of 1100−1300 K, the cell arrangement with SiC-3C in the negative electrode and SiC-6H in the positive electrode gave a positive EMF of 20 ± 5 mV (indicating a spontaneous process), leading to a Gibbs free energy of transformation $\Delta_{tr}G^{3C \to 6H} = -8 \pm 2$ kJ/mol (82.88 ± 20.72 meV/f.u.). Unlike in most studies, in his study the stability of SiC-6H is outside the margin of error. Kleykamp[12] reported that SiC-6H is also stable at room temperature. For comparison, if the cubic SiC-3C were the stable polytype, there would be no positive EMF in the above cell arrangement. Because of the contrasting nature of the results in electrochemical studies, such experiments give clear indication of the stable polytype. This highlights the importance of Kleykamp's study.[12] A review of various methods to obtain thermodynamic data for ceramic systems considers Kleykamp's study as an elegant method to obtain small free energy differences and states that this was the first time the free energy difference between the two SiC phases was directly measured.[13]

Due to these disagreements in the experimental results, a recent view is that there is no general agreement on the stable SiC polytype.[14] However, based on the above discussion, it is clear that the available experimental data in favor of SiC-6H as the stable polytype is much stronger. If the results of Kleykamp[12] are confirmed by independent electrochemical studies, they will clearly establish the stability of SiC-6H under ambient conditions.

Computational studies using various density functional theory (DFT) codes have consistently shown that the hexagonal SiC-6H and SiC-4H are marginally stable compared to cubic SiC-3C by a few meV/f.u.[15−22] These studies also show that the SiC-4H and SiC-6H polytypes are almost degenerate. (For this reason, the ab initio results for either SiC-4H or SiC-6H have been compared with experimental results in the literature.) Kawanishi et al.[17] and Scalise et al.[18] included the van der Waals (vdW) interaction through the DFT-D2 approximation and found that SiC-3C is the stable polytype. However, Ramakers et al.[22] recently studied the stability using ten different vdW approximations including DFT-D2, DFT-D3, DFT-D3(BJ), and the advanced many-body dispersion (MBD) approximations. They conclude that vdW approximations do not have any significant effect on the relative stabilities obtained from DFT studies. They also conclude that SiC-3C is metastable at all temperatures after vibrational free energy contributions are included, in agreement with the results of Heine et al.[19−21] We note that these results are consistent with the experimental results of Kleykamp[12] discussed above, though the energy differences between polytypes are much smaller in DFT studies.

Recently, for materials where polymorphs differ marginally in energy (SiC, BN, B, Fe_2P, etc.), the stable polymorph has been determined by including the vdW and the zero-point vibrational energy (ZPVE) corrections. Including these corrections frequently alters the polymorph stability order.[17,18,23−26]

However, these studies do not consider the contributions from electron−phonon interactions (EPI). Electron−phonon interactions have been well studied for their role in several electronic and optical properties.[27,28] In semiconductors and insulators, the experimental observation of the temperature dependence of band gaps is explained by EPI which leads to temperature-dependent eigenenergies given by $E_{nk}(T) = \epsilon_{nk} + \Delta\epsilon_{nk}(T)$, where ϵ_{nk} is the static lattice eigenenergy for wave vector $\mathbf{k}$ and band n, and the second term is the EPI correction to the eigenenergy.[27,28] Due to the presence of zero-point vibrations, EPI alters the eigenenergies at 0 K as well. Because all of the eigenenergies are altered, it follows that the total energy will also be altered when EPI contributions are included. Hence, the EPI contributions to the total energy and other thermodynamic properties must be studied.

In this paper, we propose and compute, for the first time, EPI corrections to the total energy and free energy. In order to do so, we briefly describe the quasi-harmonic approximation (QHA). We then discuss Allen's general formalism that goes beyond QHA to include the contributions from quasiparticle interactions (electron−phonon interactions, phonon−phonon interactions, leading to anharmonicity) to the free energy expression.[29−31] We then show that, in semiconductors and insulators, the EPI contributions to the total energy and free energy can be obtained by combining Allen's expression for the free energy with the Allen−Heine theory. We use this approach to calculate the EPI correction to the total energy for C, Si, and SiC polytypes.

Our results show that including the EPI corrections alters the energy differences between polytypes in C, Si, and SiC. For SiC polytypes, the EPI term is more important than the ZPVE and the vdW correction terms in determining relative stability. Inclusion of the EPI contribution clearly establishes the metastability of the cubic SiC-3C polytype in ab initio studies. Our approach enables the inclusion of EPI corrections as a separate term in the free energy expression. This opens the way to go beyond QHA by including the contribution of EPI on all thermodynamic properties.

■ BRIEF DESCRIPTION OF QHA

In the QHA, the Helmholtz free energy is given by[32,33]

$$F(V, T) = E_{0K}(V) + F_{el}^{QH}(V, T) + F_{vib}(V, T) \quad (1)$$

The $E_{0K}(V)$ term is the total energy at 0 K for a static lattice that is usually calculated from DFT, $F_{el}^{QH}(V, T)$ is the contribution to the free energy due to electronic excitations. The first two terms taken together give the independent particle electronic free energy. The third term, $F_{vib}(V, T)$, is the vibrational free energy contribution from harmonic (non-interacting) phonons. In eq 1, the $F_{el}^{QH}(V, T)$ term is calculated from the relation[32]

$$F_{el}^{QH}(V, T) = E_{el}^{QH}(V, T) - TS_{el}^{QH}(V, T) \quad (2)$$

Both of the right-hand side terms are obtained from the electronic density of states (eDOS) at 0 K as[32]

$$E_{el}^{QH}(V, T) = \int n(\epsilon)f\epsilon d\epsilon - \int_0^{\epsilon_F} n(\epsilon)\epsilon d\epsilon \quad (3)$$

and

$$S_{el}^{QH}(V, T) = -k_B \int n(\epsilon)[f\ln f + (1-f)\ln(1-f)]d\epsilon \quad (4)$$

where f is the Fermi−Dirac distribution.

Allen[29] has shown that the free energy expression in QHA can be derived in two different ways. The starting point is eq 1 of Allen,[29] that is, the general expression for the eigenenergy given by

$$\epsilon_K^{QP}(V, T) = \epsilon_K(V_0) + \Delta\epsilon_K^{QH}(V) + \Delta\epsilon_K^{QP}(V, T) \qquad (5)$$

where K represents $(\mathbf{k}, n)$, the wave vector and band index, respectively. The first term on the right-hand side is the eigenenergy for the equilibrium static lattice parameters. The second term is the change in eigenenergy due to the change in equilibrium volume (or lattice parameters) at finite temperatures. The sum of the first two terms is represented as $\epsilon_K(V) = \epsilon_K(V_0) + \Delta\epsilon_K^{QH}(V)$ and depends implicitly on temperature through the temperature dependence of the equilibrium volume, $V(T)$.[29] Thus, $\epsilon_K(V)$ is the eigenenergy of non-interacting electrons that is used in QHA.

The third term is the contribution from quasiparticle interactions (e.g., EPI, phonon−phonon interactions). This term is ignored in the QHA which is based on the assumption of noninteracting particles.

For noninteracting particles, the free energy can be obtained from two different approaches,[29] (i) from statistical mechanics and (ii) by integrating the expression for the entropy.

In the statistical mechanics approach, the free energy of both electrons and phonons can be obtained[29] for the case of noninteracting particles. We request the reader to refer to Allen,[29] whose eq 11 gives the electronic free energy and eq 12 gives the vibrational free energy. Taken together, they lead to the standard expression used in QHA, eq 1 above.

Alternately, the free energy can also be obtained by integrating the expression for entropy.[29] In this approach, the free energy of electrons and phonons are obtained using the entropy formulas for noninteracting electrons and phonons (eq 23 and eq 24, respectively, of Allen[29]) in the free energy expression, eq 25 of Allen (also given below).

The two approaches to obtain the free energy are equivalent for noninteracting particles.[29]

■ EPI CONTRIBUTIONS TO THE FREE AND TOTAL ENERGY

Allen[29,30] has described a method to go beyond the QHA and incorporate the renormalization of eigenenergies due to quasiparticle interactions (electron−phonon interactions, phonon−phonon interactions, leading to anharmonicity) in the free energy expression.

For interacting quasiparticles, the eigenenergy, $\epsilon_K^{QP}(V, T)$, is obtained by taking all the three terms in eq 5 and is temperature-dependent.

A limitation of the statistical mechanics based approach to obtain free energy is that it is only valid for noninteracting electrons and phonons and not for the case of interacting quasiparticles. However, the alternate approach based on the entropy formula can be applied for the case of interacting particles, provided the quasiparticles have well-defined energies (when the lifetime broadening is not very large).[29,31] The Helmholtz free energy (eq 25 of Allen[29]) is obtained by integrating the expression for the entropy and given as

$$F^{QP}(V, T) = F^{QP}(V, 0) - \int_0^T S_{el}^{QP}(V, T')dT' \qquad (6)$$

where the entropy is given by[29]

$$S_{el}(V, T) = -k_B \sum_K [f_K \ln f_K + (1 - f_K)\ln(1 - f_K)] \qquad (7)$$

and f_K is the Fermi−Dirac distribution. For the case of interacting quasiparticles, the temperature-dependent eigenenergy, eq 5, must be used.[29]

The corrected term $F^{QP}(V, 0)$ in eq 6 is given by[30]

$$F^{QP}(V, 0) = E^{QP}(V, 0) = E_{0K}(V) + \Delta E_{EP}(V, 0) \qquad (8)$$

where $\Delta E_{EP}(V, 0)$ is the zero-point EPI contribution to the total energy given by[30]

$$\Delta E_{EP}(V, 0)$$
$$= \sum_k \left[\langle k|V^{(2)}|k \rangle + \sum_Q \frac{|\langle k|V^{(1)}|k + Q \rangle|^2}{\epsilon_k - \epsilon_{k+Q}}(1 - f_{k+Q}) \right] f_k \qquad (9)$$

The term within the square bracket on the right-hand side of eq 9 is very similar (but not identical) to the original expression for the EPI correction to the eigenenergy $(\Delta\epsilon_{n\mathbf{k}})$[34] and differs in the presence of the factor $(1 - f_{k+Q})$ in the second term.[30]

For semiconductors and insulators, the band gaps are large and the electron occupancies do not change with temperature. Thus, $f_K = 1$ at all temperatures, and hence, the entropy contribution, eq 7, is zero. Thus, for semiconductors and insulators, the free energy of electrons when EPI is included reduces to

$$F_{SC,I}^{QP}(V, T) = E_{0K}(V) + \Delta E_{EP}(V, 0) \qquad (10)$$

For semiconductors and insulators, comparing eq 10 with the electronic free energy for noninteracting particles used in QHA (eq 1), the free energy contribution due to EPI is an additional term, $\Delta E_{EP}(V, 0)$, the zero-point EPI contribution to the total energy. For semiconductors and insulators, the electron occupancies do not vary with temperature and hence, the temperature dependence of eq 10 is only due to the changes in equilibrium volume with temperature, $V(T)$.

We next discuss the EPI contribution to the phonon energies. The EPI corrections to the phonon frequencies and energies consists of two parts, adiabatic and nonadiabatic components.[27,31,35] Of these, the adiabatic component is already included in a density functional perturbation theory (DFPT) calculation.[27,29,31,35] The nonadiabatic component can be obtained by using time-dependent DFT.[35−37] However, the nonadiabatic correction is important only in metals and narrow band gap semiconductors.[27,37] It is negligible in insulators and large band gap semiconductors where the band gap is much larger than the phonon energy.[27,37] Thus, for large band gap semiconductors and insulators, only the adiabatic component of the EPI contribution to phonon energies must be considered and it is already included in a DFPT calculation.[27,29,31,35]

The phonon spectra and the vibrational free energy obtained from DFPT and other methods, e.g., bond-charge model (BCM) and finite difference (FD), are reported to be similar in literature.[38,39] Any method to calculate the phonon spectra and phonon free energies that gives identical values to the DFPT method implicitly includes the adiabatic phonon contribution.[31] It follows that the vibrational free energy can be calculated from any of the above methods when EPI is included.

Allen and Hui[40] have shown that the EPI contribution to the electronic and vibrational specific heats are equal to order $\langle u^2 \rangle$ i.e., $\Delta C_{el}^{EP} = \Delta C_{ph}^{EP}$. For semiconductors and insulators, ΔC_{el}^{EP} is zero due to the $f(\epsilon)[1 - f(\epsilon)]$ factor,[40] and hence, ΔC_{ph}^{EP} is also zero. Thus, the EPI contribution to the phonon free energy will be a zero-point correction, which is included in a DFPT calculation.

In summary, for semiconductors and insulators, because $\Delta C_{el}^{EP} = \Delta C_{ph}^{EP} = 0$, the EPI contributions to the free energies of electrons and phonons are the corresponding zero-point energy contributions. The temperature dependence of the EPI contributions will only come from the changes in the volume, $V(T)$.[31]

An important consequence for semiconductors and insulators is that any experimentally observed anomalous temperature dependence of the phonon spectra is most likely due to other quasiparticle interactions, e.g., phonon−phonon interactions leading to anharmonicity.

Another important implication follows for QHA studies where the free energy is given by eq 1, though sometimes the vdW contributions are also included in the DFT total energy. The EPI contribution to the electronic free energy must be neglected in QHA. However, the vibrational free energy calculated using DFPT and other (FD, BCM, etc.) methods include, explicitly and implicitly, respectively, the adiabatic EPI contribution.[31] To be consistent with the neglect of EPI contribution to the electronic free energy, the adiabatic EPI contribution to the phonon spectra and vibrational free energy must be subtracted in QHA studies.

EPI CORRECTIONS TO THE TOTAL ENERGY FROM THE ALLEN−HEINE THEORY

The Allen−Heine theory[34,40−43] is widely used to obtain the EPI corrections to the eigenenergies in semiconductors and insulators. In this theory, electron−phonon interactions lead to contributions from the Fan−Migdal (FM)[44,45] and the Debye−Waller (DW)[46] terms to the eigenenergies. The temperature-dependent eigenenergies are given by $E_{n\mathbf{k}}(T) = \epsilon_{n\mathbf{k}} + \Delta\epsilon_{n\mathbf{k}}(T)$, where $\epsilon_{n\mathbf{k}}$ is the static lattice eigenenergy for wave vector $\mathbf{k}$ and band n and the EPI correction is given by $\Delta\epsilon_{n\mathbf{k}}(T) = \Delta^{FM}\epsilon_{n\mathbf{k}}(T) + \Delta^{DW}\epsilon_{n\mathbf{k}}(T)$. Due to the presence of zero-point vibrations, the zero-point renormalization (ZPR) of electron eigenenergies, $\Delta\epsilon_{n\mathbf{k}}(0)$, has finite values.

The Allen−Heine theory allows the calculation of EPI correction to any arbitrary eigenstate, $\Delta\epsilon_{n\mathbf{k}}(T)$, including for the valence band maxima (VBM) and the conduction band minima (CBM). For this reason, it is the most widely used ab initio method in EPI studies of band gaps and band structures.[47−58] We note that there are other recent methods to obtain the EPI contributions to band gaps and band structures.[59,60]

The zero-point EPI contribution to the total energy, $\Delta E_{EP}(V, 0)$ is given by eq 9, where the second term has a $1 - f_{k+Q}$ factor that is not present in the original expression for $\Delta\epsilon_{n\mathbf{k}}(T)$.[30] This implies that the present methods used to calculate $\Delta\epsilon_{n\mathbf{k}}(T)$ cannot be used to obtain the zero-point EPI contribution to the total energy, $\Delta E_{EP}(V, 0)$. The correct evaluation of $\Delta E_{EP}(V, 0)$ will be possible for the wider computational community only after the computation of eq 9 is included in software packages.

Therefore, in the present paper, we calculate an approximation to $\Delta E_{EP}(V, 0)$ by summing over the eigenenergies, $\Delta\epsilon_{n\mathbf{k}}(T)$. In this case, $\Delta E_{EP}(V, 0)$ is given by

$$\Delta E_{EP}(V, 0) \approx \Delta E_{av}^{ep}(V, 0) = \sum_{K}^{occ} \Delta\epsilon_{n\mathbf{k}}(V, 0)$$

$$= 2 \sum_{n,\mathbf{k}}^{occ,IBZ} w_{\mathbf{k}} \Delta\epsilon_{n\mathbf{k}}(V, 0) \tag{11}$$

where $\Delta E_{EP}(V, 0)$ is approximated by the zero-point EPI correction to the band-structure energy, $\Delta E_{av}^{ep}(V, 0)$, $w_{\mathbf{k}}$ is the weight of the $\mathbf{k}$-point in the irreducible Brillouin zone (IBZ) and $\Delta\epsilon_{n\mathbf{k}}(V, 0)$ is the zero-point EPI correction to the static lattice eigenenergy $\epsilon_{n\mathbf{k}}(V)$.

The approximation, eq 11, is likely to introduce some errors compared to eq 9 due to the neglect of the $1 - f_{k+Q}$ factor. However, the main interest in relative stability studies is in the EPI contribution to the total energy differences between polytypes. In this case, the errors are expected to be much less due to the neglect of the $1 - f_{k+Q}$ factor in all polytypes. Comparing eq 9 and eq 11, the contribution from the Debye−Waller term remains unchanged. The approximate expression, eq 11, introduces errors only in the Fan−Migdal term because some of the contributions that must be neglected are included. Thus, the error in using eq 11 is due to only a part of the Fan−Migdal term. Since this error is present in all polymorphs, the cancellation of errors for energy differences between polymorphs implies that the trends observed from using eq 11 are likely to remain valid even when eq 9 is used. This is corroborated by the better match with experimental results when EPI corrections are included using eq 11 compared to earlier DFT based studies,[15−22] as seen below. Further justifications for specific systems are given later.

A perusal of the ZPR shifts, $\Delta\epsilon_{n\mathbf{k}}(V, 0)$, of all occupied states in the IBZ for C, Si, and SiC polytypes (in this study) does not reveal any discernible trend. For each $\mathbf{k}$-point, $\Delta\epsilon_{n\mathbf{k}}(V, 0)$ has positive and negative values for some occupied n-band. There is no $\mathbf{k}$-point where $\Delta\epsilon_{n\mathbf{k}}(V, 0)$ for the occupied n-bands are all positive or all negative. The zero-point EPI correction to the band-structure energy, $\Delta E_{av}^{ep}(V, 0)$ is a weighted sum over several positive and negative values of $\Delta\epsilon_{n\mathbf{k}}(V, 0)$. Thus, presently, no general conclusions can be drawn about the effect of the $1 - f_{k+Q}$ factor.

It is also seen that $\Delta E_{av}^{ep}(V, 0)$ for different polytypes are similar but not equal. Further, the convergence behavior of $\Delta E_{av}^{ep}(V, 0)$ is similar for different polytypes. In this case, it is justified to assume that the Debye−Waller contributions and also the Fan−Migdal contributions are also similar for different polytypes. That is, the Fan−Migdal contributions to the total energy from terms affected and unaffected by the $1 - f_{k+Q}$ factor are also likely to be similar for different polytypes. Hence, as a first approximation, we can assume that the neglect of the $1 - f_{k+Q}$ factor in eq 11 is unlikely to significantly alter the energy differences between polytypes due to cancellation of errors.

Otherwise, it would imply that the terms affected by the $1 - f_{k+Q}$ factor in eq 9 are the dominant terms in the EPI contribution to the energy differences between polymorphs even when $\Delta E_{av}^{ep}(V, 0)$ values are similar. At present, there is no basis for such a conclusion.

Therefore, in this study, we have calculated the EPI corrections to the total energy for the cubic and hexagonal polytypes of C, Si, and SiC using eq 11.

Table 1. Lattice Parameters, Band Gaps, and Energy Differences of the Hexagonal Polytypes with Respect to the Corresponding Diamond Polytypes for Carbon and Silicon

| material | a,c (Bohr) | band gaps | | ΔE (DFT) (meV/atom) | ΔE (DFT+EPI) (meV/atom) |
		indirect (eV)	direct (eV)		
C-dia	6.75	4.18	5.61	0	0
C-hex	4.75, 7.90	3.40	5.01	24.3	67.9
Si-dia	10.34	0.61	2.55	0	0
Si-hex	7.28, 12.03	0.45	0.98	9.7	17.3

COMPUTATIONAL DETAILS

All calculations were performed using the ABINIT software package[61−63] that has been used in several ZPR band gap studies.[50,53−57]

For SiC polytypes, the vdW approximations, DFT-D2 and DFT-D3(BJ),[64,65] were also applied to calculate the total energies and lattice parameters. DFT-Dn methods were chosen because of the advantage that the vdW and EPI corrections are both incorporated by calculating the EPI corrections at the altered lattice parameters.[55,66]

We present results obtained using the ONCV pseudopotentials[67] with PBE exchange-correlation functional.[68] Similar results were obtained for other pseudopotentials (see Supporting Information). The energy cutoffs used were 30 Ha (Si) and 50 Ha (C and SiC). For hexagonal structures, the Broyden−Fletcher−Goldfarb−Shanno (BFGS) algorithm was used for structural optimization.[61,62] An unshifted $8 \times 8 \times 8$ **k**-point grid was used for cubic structures. For all hexagonal structures (except for SiC-4H for which $9 \times 9 \times 3$ **k**-point grid was used), an unshifted $9 \times 9 \times 5$ **k**-point grid was used.

The ABINIT module on temperature dependence of the electronic structure that calculates EPI corrections using Allen−Heine theory was used.[63] We provided the list of **k**-points in the IBZ and additional **k**-points corresponding to CBM. The **q**-point grids were increased by 200−300 **q**-points in IBZ. To accelerate convergence, an imaginary smearing parameter, $i\delta$, of 100 and 50 meV was used.[51,55,63] The optimized number of bands used was 30 for SiC-4H and 22 for all other C, Si, and SiC polytypes. EPI corrections for SiC-6H could not be calculated due to computational constraints.

The adiabatic and nonadiabatic approximation must be used to obtain the $\Delta\epsilon_{n\mathbf{k}}(T)$ for IR-inactive and IR-active materials, respectively.[51] The adiabatic and nonadiabatic formulas to calculate $\Delta\epsilon_{n\mathbf{k}}(T)$ in ABINIT are given by eqs 15−17 of Poncé et al.[51]

For IR-active materials, the ZPR shift, $\Delta\epsilon_{n\mathbf{k}}(T)$, varies linearly with $1/N_q$, where N_q^3 is the total number of **q**-points in the BZ.[51,56] It follows from the linearity property of eq 11 that $\Delta E_{av}^{eq}(T)$ will also vary linearly with $1/N_q$ (proof in Supporting Information).

RESULTS AND DISCUSSION

EPI Contributions in Carbon and Silicon Polytypes.

Table 1 gives the lattice parameters, band gaps, and the relative energy stability with and without EPI corrections at 0 K for the C and Si polytypes. Our DFT lattice parameters and relative energies are similar to those in literature.[2,69,70]

For C-dia, the ZPR of VBM, CBM, and the lowest CB at Γ-point are 142, −151.4, and −272.5, respectively. For Si-dia, they are 34.27, −21.24, and −8 meV, respectively. These values are similar to the reported values.[63] Because, the ZPR

for other eigenstates in the IBZ were obtained in the same calculation, it follows that they are reliable.

Figure 1 shows the convergence behavior of the EPI correction to the total energy, $\Delta E_{av}^{ep}(0)$, with $1/N_q$ for $i\delta = 100$
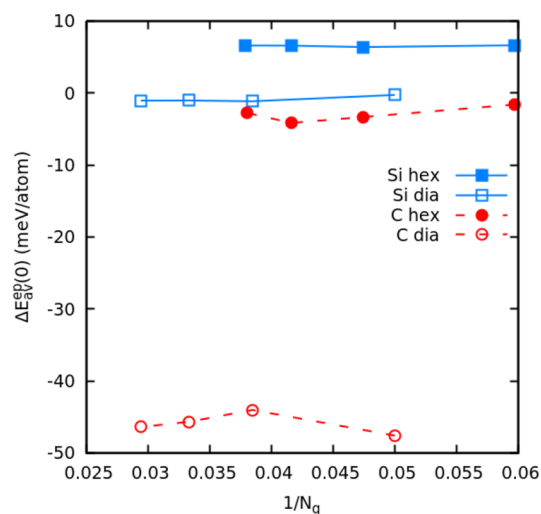

Figure 1. Convergence of EPI correction to total energy at 0 K with **q**-point grid density (adiabatic approximation) for a smearing parameter of 100 meV for carbon and silicon polytypes.

meV. A strong EPI correction is seen for carbon polytypes, whereas a weak EPI correction is seen for silicon polytypes. This is consistent with the weaker electron−phonon interaction in silicon compared to carbon.[48−55,59,60] Figure 1 also shows a significant crystal structure dependence of the EPI correction to the total energy, especially in carbon polytypes where the electron−phonon interaction is strong.

The negative value of $\Delta E_{av}^{ep}(0)$ for C-dia implies that, averaged over the BZ, the FM term is greater than the DW term. In contrast to C-dia, a small value of $\Delta E_{av}^{ep}(0)$ is obtained for C-hex. The ZPR of VBM, CBM, and the lowest CB at Γ-point for C-hex are 117, −172.6, and −313.9 meV, respectively. They are comparable to those for C-dia indicating a strong electron−phonon interaction in C-hex. Thus, the small value of $\Delta E_{av}^{ep}(0)$ in C-hex indicates a near balance between the FM and DW terms when averaged over the BZ.

Figure 1 shows that the $\Delta E_{av}^{ep}(0)$ values for the silicon polytypes are similar. Hence, their difference is unlikely to be significantly affected when the correct expression, eq 9, that includes the $1 - f_{k+Q}$ factor is used. However, Figure 1 shows that the $\Delta E_{av}^{ep}(0)$ values for the carbon polytypes are not similar. It is a small negative value for C-hex and relatively large negative for C-diameter One possibility is that the large difference is due to the stronger EPI interaction in carbon. However, another possibility is that using the correct expression, eq 9, that includes the $1 - f_{k+Q}$ factor, could lead

to significant changes in the energy differences. Hence, the results for carbon polytypes should be considered to be less reliable than the results for silicon polytypes.

Table 1 shows that after including EPI corrections the C-dia structure is more stable than the C-hex structure by ≈ 68 meV/atom compared to ≈ 24 meV/atom from DFT studies.[2,69,70] The Si-dia stability also increases from ≈ 10 to ≈ 17 meV/atom. It clearly follows that including EPI corrections in ab initio studies of relative stability of polymorphs is essential.

EPI Contributions in SiC Polytypes. Table 2 shows the lattice parameters, ZPR of the VBM/CBM and the energy

Table 2. Lattice Parameters, ZPR, and Energy Stability of SiC Polytypes Relative to SiC-3C for DFT, DFT-D2, and DFT-D3(BJ) Calculations

polytype	a, c (Bohr)	ZPR VBM/CBM (meV)	ΔE (meV/f.u.)
3C-SiC			
DFT	8.28	93.6/−56.3	0
DFT-D2	8.23		0
DFT-3(BJ)	8.21	95.4/−55.6	0
4H-SiC			
DFT	5.85, 19.14	84.7/−61.3	−2.15
DFT-D2	5.81, 19.06		2.31
DFT-D3(BJ)	5.80, 18.99	86.3/−60.8	−1.81
2H-SiC			
DFT	5.84, 9.59	78.6/−88.9	5.07
DFT-D2	5.81, 9.56		14.2
DFT-D3(BJ)	5.80, 9.52	80.0/−86.5	6.32

stabilities relative to the SiC-3C polytype. The indirect/direct band gaps (at the Γ-point) are 1.41 eV/6.13 eV (SiC-3C), 2.32 eV/4.72 eV (SiC-2H), 2.26 eV/5.01 eV (SiC-4H), and 2.07 eV/5.10 eV (SiC-6H). These results are very similar to literature values.[15−18]

In our DFT results, SiC-4H is more stable than SiC-3C, similar to previous studies.[15−18] Including the DFT-D2 approximation makes SiC-3C to be the stable polytype, similar to recent studies.[17,18] However, including the DFT-D3(BJ) approximation retains the DFT stability order where SiC-3C is metastable, consistent with the results of Ramakers et al.[22] As discussed earlier, Ramakers et al.[22] have considered ten

different vdW approximations and concluded that the DFT stability order should be retained.

In Table 2, the ZPR of VBM/CBM for SiC-3C (obtained using parameters similar to those used in other studies[55]) is comparable to reported values.[57,58]

Figure 2 shows the convergence behavior of the EPI correction to the total energy, $\Delta E_{av}^{ep}(0)$. The $\Delta E_{av}^{ep}(0)$ for SiC-4H (50% hexagonality)[17,18] does not lie between the values for SiC-3C (0% hexagonality) and SiC-2H (100% hexagonality). A similar trend is also seen for DFT total energies (Table 2 and refs 15−18).

Figure 2 shows that $\Delta E_{av}^{ep}(0)$ varies substantially among SiC polytypes compared to the marginal DFT energy differences. For example, the EPI contribution to the total energy for SiC-3C and SiC-4H differ by >20 meV/f.u. This difference is much higher than the marginal (1−2 meV/f.u.) difference in the DFT total energy.

Figure 2 shows that $\Delta E_{av}^{ep}(0)$ has similar convergence behavior for the SiC polytypes. This suggests that the DW and FM terms have similar values in SiC-polytypes. In this regard, in their supplementary Table 2, Miglio et al.[57] compared the calculated ZPR of the SiC-3C band gap with the experimental data for the SiC-15R (40% hexagonality) with the justification that the two SiC polytypes have sp³-bonding and differ only in the stacking sequence of the tetrahedra.[17,22] Underlying the above comparison is the implicit assumption that the ZPR (DW and FM terms) behave similarly in SiC polytypes. The assumption of Miglio et al.[57] that the structural similarity of SiC polytypes lead to similar EPI behavior is also seen in Figure 2. It follows that the FM terms affected and unaffected by the $1 - f_{k+Q}$ factor also behave similarly in the SiC polytypes; which is our assumption. In structurally similar polytypes, the errors due to the neglect of the $1 - f_{k+Q}$ factor are likely to be similar, leading to small energy differences among them due to cancellation of errors. This provides additional justification for our assumption that neglect of the $1 - f_{k+Q}$ factor will not have a dominant effect on energy differences. Thus, these are strong reasons to assume that using the correct eq 9 is likely to lead to similar trends for energy differences as obtained from the approximate eq 11.

Table 3 shows the stability of SiC-polytypes obtained by combining the EPI corrections to total energy in Figure 2 with
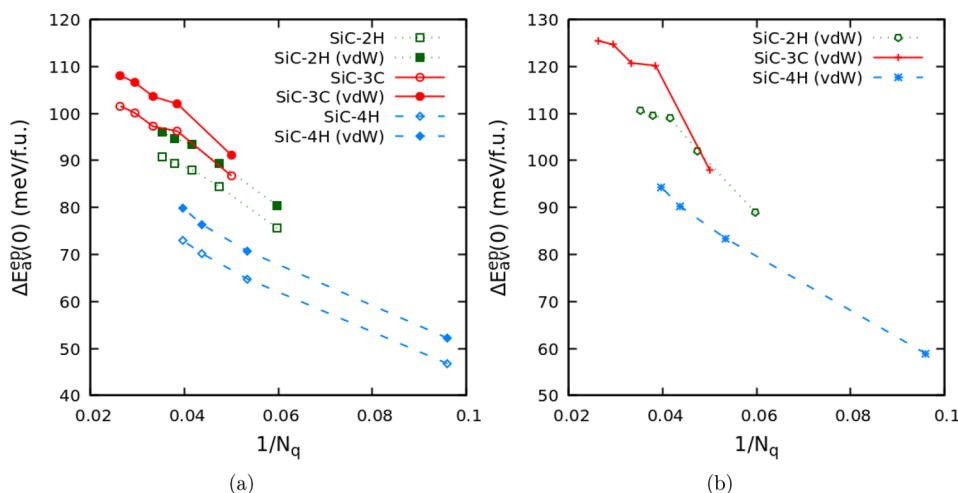

Figure 2. Convergence of EPI correction to total energy at 0 K with **q**-point grid density (nonadiabatic approximation) for smearing parameters: (a) 100 meV and (b) 50 meV for SiC polytypes for DFT and DFT-D3(BJ) lattice parameters.

Table 3. Relative Stability (meV/f.u.) of SiC Polytypes for Smearing Parameters of 100 and 50 meV Calculated for the Smallest $1/N_q$ Used[a]

polytype→ stability ↓	SiC-3C	SiC-4H	SiC-2H
DFT + EPI (100 meV)	0	−30.8/−25.5	−5.7
DFT-D2 + EPI (100 meV)	0	−25.6/−19.9	+2.8
DFT-D3(BJ) + EPI (100 meV)	0	−30.0/−24.0	−5.6
DFT-D3(BJ) + EPI (50 meV)	0	−32.9/−27.6	−8.5

[a]The second value in column 3 corresponds to the relative stability at $1/N_q \approx 0.039$ for both SiC polytypes. The D2 values are estimated from DFT and D3(BJ) values as its lattice parameters are between their lattice parameters.

the relative stability data in Table 2. For SiC-3C and SiC-2H, we consider $\Delta E_{av}^{ep}(0)$ for the smallest value of $1/N_q$. However, for SiC-4H, the $\Delta E_{av}^{ep}(0)$ varies by ≲3 meV/f.u. for the smallest two $1/N_q$ values. Therefore, we report two values for SiC-4H in Table 3: the difference in $\Delta E_{av}^{ep}(0)$ (a) between the smallest values of $1/N_q$ for SiC-3C and SiC-4H and (b) at approximately the same $1/N_q \approx 0.039$. The actual stability value for SiC-4H is likely to be between these values.

Table 3 shows the importance of EPI corrections. SiC-4H is the stable polytype with much greater relative stability (≥20 meV/f.u.), irrespective of the DFT-D approximation, compared to the marginal stability (≈ 2 meV/f.u.) under DFT and DFT+vdW conditions. For SiC-2H, the relative stability depends on the DFT-D approximation used, though it is more stable in the widely used D3(BJ) approximation.[23,71] However, the stability is <10 meV/f.u., indicating that it is within the range of dispersion approximation errors.[23]

The similar trends for $i\delta$ = 50 meV suggests that SiC-4H will likely be the stable polytype when $i\delta$ is decreased further for full convergence.[51]

We now discuss the EPI correction to the phonon frequencies and energies. As discussed earlier, the correction has two components, adiabatic and nonadiabatic. For insulators and large band gap semiconductors, the non-adiabatic component is negligible and it is justified to consider only the correction from the adiabatic component.[27,37]

The adiabatic component is already included in DFPT calculations.[27,29,31,35] In the case of SiC-3C, Zywietz et al.[38] calculated the vibrational Helmholtz free energy, $F_{vib}(T)$, by two different methods, (i) generalized bond-charge model (BCM) and (ii) DFPT. They showed that the difference in $F_{vib}(T)$ between the two methods is small for SiC-3C. Indeed, Zywietz et al.[38] used this small difference in $F_{vib}(T)$ for SiC-3C as the justification to obtain the $F_{vib}(T)$ for SiC-2H, SiC-4H, and SiC-6H using only BCM. The underlying assumption being that the Helmholtz free energy obtained using BCM are likely to be similar to those obtained using DFPT. The difference in $F_{vib}(T)$ between SiC-4H and SiC-3C, obtained from the BCM method, is reported to be[38] $\Delta F_{vib}^{4H-3C}(T) \approx$ −0.9 meV/f.u. at 0 K and ≈ −3 meV/f.u. at 1200 K.[38]

Recently, Ramakers et al.[22] calculated the Helmholtz vibrational free energy differences between SiC polytypes using DFPT. Their values for $\Delta F_{vib}^{4H-3C}(T)$ are −0.3 meV/f.u. at 0 K and −1.7 meV/f.u. at 1200 K. The DFPT results of Ramakers et al.[22] are similar and validate the free energy differences obtained by Zywietz et al.[38] using BCM. The similar values obtained from BCM and DFPT imply that the

former implicitly includes the adiabatic component of the EPI contribution to the phonon energy.[31]

Because the adiabatic component of the EPI contribution to the free energy differences is very small and the nonadiabatic component of the phonon self-energy is negligible in large band gap semiconductors,[27,37] we can conclude that the EPI contribution to the vibrational free energy differences between SiC polytypes are very small or negligible.

With our results, we can assess the importance of the three correction terms, ZPVE, vdW, and EPI, to the DFT relative stability order of SiC polytypes. The ZPVE is relatively insensitive to crystal structure[18] which is also reflected in the similar Debye temperatures of SiC polytypes.[72,73] Its contribution to the energy differences between SiC polytypes is ∼0−1 meV/f.u. using DFPT and other methods.[22,38] The D3(BJ) correction is also relatively insensitive to crystal structure. It contributes ∼1−2 mev/f.u. to the energy differences between SiC polytypes. In contrast, EPI correction contributes ≥22 meV/f.u. to the energy differences (Figure 2), indicating much greater sensitivity to crystal structure. Clearly, the EPI term is the most important of the three correction terms to affect the relative stability of SiC polytypes. Hence, EPI contributions must be included in all studies of materials with polymorphs that differ marginally in energy where currently only ZPVE and vdW contributions are included.

After including vdW and EPI corrections to DFT, the relative stability order is SiC-4H, SiC-2H, and SiC-3C. The hexagonal SiC-4H is stable over the cubic SiC-3C by ∼25 meV/f.u. or ∼2.5 kJ/mol. Hence, by including EPI corrections, the stability of SiC-4H is significantly enhanced when compared to DFT studies, with or without the vdW approximation.

Our results are consistent with the experimental results of Kleykamp.[12] Our results also provide additional motivation to confirm (or contradict) Kleykamp's[12] results by independent electrochemical experimental studies. As discussed previously, electrochemical studies can provide a clear and unambiguous indication of the stable SiC polytype.

It is evident that including EPI contributions using the approximate eq 11 leads to a better match with the experimental results of Kleykamp[12] compared to earlier DFT-based studies.[15−22] Because eq 11 neglects the $1 - f_{k+Q}$ factor present in eq 9, our results imply that the neglect of the $1 - f_{k+Q}$ factor is not dominant in determining the differences in EPI contributions to the total energy. This is due to cancellation of errors, especially in structurally similar SiC polytypes where the errors due to the neglect of the $1 - f_{k+Q}$ factor are likely to be similar. However, eq 9 is the correct expression and must be used once its computation is included in software packages.

Our results have wide applicability. A significant EPI results in ZPR of VBM and other eigenstates in hundreds of meV in several materials.[47−57,59,60] It also leads to strong crystal structure dependence of the ZPR(VBM) with its differences in tens of meV in AlN, BN, and GaN polytypes.[51,55,57] Because the ZPR (VBM) contributes to $\Delta E_{av}^{ep}(0)$, it follows that differences in $\Delta E_{av}^{ep}(0)$ (and hence $\Delta E_{EP}(V,0)$) between polymorphs of order of tens of meV/f.u. is a distinct possibility that must be evaluated. Our results for C and SiC polytypes support this suggestion.

It is essential to obtain accurate energy differences between polymorphs to determine their pressure−temperature $(P-T)$ stability regions and phase boundaries. Thus, our results imply

that including EPI contributions to the total energy is essential to accurately determine the $P-T$ phase stability of materials in ab initio studies.

CONCLUSION

We propose and compute a new correction term, due to electron−phonon interactions, to the DFT total energy. We rely on Allen's general formalism that goes beyond the QHA and includes contributions from quasiparticle interactions to the free energy. We show that, for semiconductors and insulators, the EPI contributions to the free energies of electrons and phonons are the corresponding zero-point energy contributions. Using Allen's expression in combination with the Allen−Heine theory for the EPI calculations, we calculate the EPI corrections to the total energy for C, Si, and SiC polytypes. The EPI corrections alter the energy differences between polytypes; especially in C and SiC where the EPI strength is significant. Compared to the ZPVE and vdW correction, the EPI correction term is more important in determining the relative stability order of SiC polytypes due to its greater sensitivity to crystal structure. It clearly establishes that in ab initio studies SiC-3C is metastable and SiC-4H is the stable polytype, consistent with the experimental results of Kleykamp. Our study enables the inclusion of EPI contribution as a separate term in the free energy expression. This opens the way to go beyond QHA by including the contribution of EPI to all thermodynamic properties.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c08244.

> Proof of linearity for $\Delta E_{av}^{ep}(T)$ vs $1/N_q$ (section I) and results for Si and C poltypes (section II) and SiC polytypes (section III) using GGA.fhi and PSPNC pseudopotentials (PDF)

AUTHOR INFORMATION

Corresponding Author

Tiramkudlu R. S. Prasanna − *Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Mumbai 400076, India;* ⓞ orcid.org/0000-0001-5508-7164; Email: prasanna@iitb.ac.in

Authors

Arjun Varma Ramasimha Varma − *Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Mumbai 400076, India;* ⓞ orcid.org/0000-0002-5597-7383

Shilpa Paul − *Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Mumbai 400076, India*

Anup Itale − *Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Mumbai 400076, India*

Pranav Pable − *Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Mumbai 400076, India*

Radhika Tibrewala − *Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Mumbai 400076, India*

Samruddhi Dodal − *Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Mumbai 400076, India*

Harshal Yerunkar − *Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Mumbai 400076, India*

Saurav Bhaumik − *Department of Mathematics, Indian Institute of Technology Bombay, Mumbai 400076, India*

Vaishali Shah − *Department of Scientific Computing, Modeling and Simulation, Savitribai Phule Pune University, Pune 411007, India;* ⓞ orcid.org/0000-0002-3964-9435

Mogadalai Pandurangan Gururajan − *Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Mumbai 400076, India*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.2c08244

REFERENCES

(1) Takagi, M.; Taketsugu, T.; Kino, H.; Tateyama, Y.; Terakura, K.; Maeda, S. Global search for low-lying crystal structures using the artificial force induced reaction method: A case study on carbon. *Phys. Rev. B* **2017**, *95*, 184110.

(2) Mujica, A.; Pickard, C. J.; Needs, R. J. Low-energy tetrahedral polymorphs of carbon, silicon, and germanium. *Phys. Rev. B* **2015**, *91*, 214104.

(3) He, C.; Shi, X.; Clark, S. J.; Li, J.; Pickard, C. J.; Ouyang, T.; Zhang, C.; Tang, C.; Zhong, J. Complex low energy tetrahedral polymorphs of group IV elements from first principles. *Phys. Rev. Lett.* **2018**, *121*, 175701.

(4) Dmitrienko, V. E.; Chizhikov, V. A. Infinite family of bc8-like metastable phases in silicon. *Phys. Rev. B* **2020**, *101*, 245203.

(5) Haberl, B.; Strobel, T. A.; Bradby, J. E. Pathways to exotic metastable silicon allotropes. *Applied Physics Reviews* **2016**, *3*, 040808.

(6) Proserpio, D. M. Samara Carbon Allotrope Database; http://sacada.sctms.ru (accessed July 15, 2021).

(7) Lee, I.-H.; Lee, J.; Oh, Y. J.; Kim, S.; Chang, K.-J. Computational search for direct band gap silicon crystals. *Phys. Rev. B* **2014**, *90*, 115209.

(8) Riley, F. *Structural Ceramics*; Cambridge University Press: Cambridge, UK, 2009.

(9) Kimoto, T. Material science and device physics in SiC technology for high-voltage power devices. *Jpn. J. Appl. Phys.* **2015**, *54*, 040103.

(10) Greenberg, E.; Natke, C. A.; Hubbard, W. N. The enthalpy of formation of silicon carbide by fluorine bomb calorimetry. *J. Chem. Thermodyn.* **1970**, *2*, 193−201.

(11) Chase, M. W. JANAF thermochemical table. *J. Phys. Chem. Ref. Data* **1985**, *14*, Supplement No. 1, 633−634.

(12) Kleykamp, H. Gibbs energy of formation of SiC: A contribution to the thermodynamic stability of the modifications. *Berichte der Bunsengesellschaft für physikalische Chemie* **1998**, *102*, 1231−1234.

(13) Jacobson, N.; Putnam, R.; Navrotsky, A. In *Measurement of the Thermodynamic Properties of Multiple Phases*; Weir, R., De Loos, T., Eds.; Experimental Thermodynamics; Elsevier, 2005; Vol. 7; pp 307−325.

(14) Drüe, M.; Kozlov, A.; Seyring, M.; Song, X.; Schmid-Fetzer, R.; Rettenmayr, M. Phase formation in the ternary system Li−Si−C. *J. Alloys Compd.* **2015**, *653*, 474−479.

(15) Park, C. H.; Cheong, B.-H.; Lee, K.-H.; Chang, K.-J. Structural and electronic properties of cubic, 2H, 4H, and 6H SiC. *Phys. Rev. B* **1994**, *49*, 4485.

(16) Käckell, P.; Wenzien, B.; Bechstedt, F. Electronic properties of cubic and hexagonal SiC polytypes from ab initio calculations. *Phys. Rev. B* **1994**, *50*, 10761.

(17) Kawanishi, S.; Mizoguchi, T. Effect of van der Waals interactions on the stability of SiC polytypes. *J. Appl. Phys.* **2016**, *119*, 175101.

(18) Scalise, E.; Marzegalli, A.; Montalenti, F.; Miglio, L. Temperature-Dependent Stability of Polytypes and Stacking Faults in Si C: Reconciling Theory and Experiments. *Physical Review Applied* **2019**, *12*, 021002.

(19) Heine, V.; Cheng, C.; Needs, R. J. The preference of silicon carbide for growth in the metastable cubic form. *J. Am. Ceram. Soc.* **1991**, *74*, 2630−2633.

(20) Rutter, M. J.; Heine, V. Energetics of stacking boundaries on the {0001} surfaces of silicon carbide. *J. Phys.: Condens. Matter* **1997**, *9*, 8213.

(21) Heine, V.; Cheng, C.; Needs, R. A computational study into the origin of SiC polytypes. *Materials Science and Engineering: B* **1992**, *11*, 55−60.

(22) Ramakers, S.; Maruszczyk, A.; Amsler, M.; Eckl, T.; Mrovec, M.; Hammerschmidt, T.; Drautz, R. Effects of thermal, elastic, and surface properties on the stability of SiC polytypes. *Phys. Rev. B* **2022**, *106*, 075201.

(23) Cazorla, C.; Gould, T. Polymorphism of bulk boron nitride. *Science Advances* **2019**, *5*, eaau5832.

(24) Nikaido, Y.; Ichibha, T.; Hongo, K.; Reboredo, F. A.; Kumar, K. C. H.; Mahadevan, P.; Maezono, R.; Nakano, K. Diffusion Monte Carlo Study on Relative Stabilities of Boron Nitride Polymorphs. *J. Phys. Chem. C* **2022**, *126*, 6000−6007.

(25) van Setten, M. J.; Uijttewaal, M. A.; de Wijs, G. A.; de Groot, R. A. Thermodynamic stability of boron: The role of defects and zero point motion. *J. Am. Chem. Soc.* **2007**, *129*, 2458−2465.

(26) Bhat, S. S.; Gupta, K.; Bhattacharjee, S.; Lee, S.-C. Role of zero-point effects in stabilizing the ground state structure of bulk Fe2P. *J. Phys.: Condens. Matter* **2018**, *30*, 215401.

(27) Giustino, F. Electron-phonon interactions from first principles. *Rev. Mod. Phys.* **2017**, *89*, 015003.

(28) Ponce, S.; Antonius, G.; Gillet, Y.; Boulanger, P.; Laflamme Janssen, J.; Marini, A.; Cote, M.; Gonze, X. Temperature dependence of electronic eigenenergies in the adiabatic harmonic approximation. *Phys. Rev. B* **2014**, *90*, 214304.

(29) Allen, P. B. Theory of thermal expansion: Quasi-harmonic approximation and corrections from quasi-particle renormalization. *Modern Physics Letters B* **2020**, *34*, 2050025.

(30) Allen, P. B. Second Erratum — Theory of thermal expansion: Quasi-harmonic approximation and corrections from quasi-particle renormalization. *Modern Physics Letters B* **2022**, *36*, 2292002.

(31) These comments are based on feedback received from Prof. P. B. Allen as part of the review of this manuscript.

(32) Nath, P.; Plata, J. J.; Usanmaz, D.; Al Rahal Al Orabi, R.; Fornari, M.; Nardelli, M. B.; Toher, C.; Curtarolo, S. High-throughput prediction of finite-temperature properties using the quasi-harmonic approximation. *Comput. Mater. Sci.* **2016**, *125*, 82−91.

(33) Togo, A.; Tanaka, I. First principles phonon calculations in materials science. *Scripta Materialia* **2015**, *108*, 1−5.

(34) Allen, P. B.; Heine, V. Theory of the temperature dependence of electronic band structures. *Journal of Physics C: Solid State Physics* **1976**, *9*, 2305.

(35) Heid, R. Density Functional Perturbation Theory and Electron Phonon Coupling. In *Emergent Phenomena in Correlated Matter*; Pavarini, E., Koch, E., Schollwöck, U., Eds.; Jülich, 2013.

(36) Saitta, A. M.; Lazzeri, M.; Calandra, M.; Mauri, F. Giant nonadiabatic effects in layer metals: Raman spectra of intercalated graphite explained. *Physical review letters* **2008**, *100*, 226401.

(37) Calandra, M.; Profeta, G.; Mauri, F. Adiabatic and nonadiabatic phonon dispersion in a Wannier function approach. *Phys. Rev. B* **2010**, *82*, 165111.

(38) Zywietz, A.; Karch, K.; Bechstedt, F. Influence of polytypism on thermal properties of silicon carbide. *Phys. Rev. B* **1996**, *54*, 1791.

(39) Li, Y.; Kerr, W.; Holzwarth, N. Continuity of phonon dispersion curves in layered ionic materials. *J. Phys.: Condens. Matter* **2020**, *32*, 055402.

(40) Allen, P. B.; Hui, J. C. K. Thermodynamics of solids: Corrections from electron-phonon interactions. *Zeitschrift für Physik B Condensed Matter* **1980**, *37*, 33−38.

(41) Allen, P. B. Solids with thermal or static disorder. I. One-electron properties. *Phys. Rev. B* **1978**, *18*, 5217.

(42) Allen, P. B.; Cardona, M. Temperature dependence of the direct gap of Si and Ge. *Phys. Rev. B* **1983**, *27*, 4760.

(43) Allen, P. B. Zero-point and isotope shifts: relation to thermal shifts. *Philosophical Magazine B* **1994**, *70*, 527−534.

(44) Fan, H. Y. Temperature dependence of the energy gap in semiconductors. *Phys. Rev.* **1951**, *82*, 900.

(45) Migdal, A. B. Interaction between electrons and lattice vibrations in a normal metal. *Soviet Physics—JETP* **1958**, *7*, 996−1001.

(46) Antončík, E. On the theory of temperature shift of the absorption curve in non-polar crystals. *Czech. J. Phys.* **1955**, *5*, 449−461.

(47) Marini, A. Ab initio finite-temperature excitons. *Phys. Rev. Lett.* **2008**, *101*, 106405.

(48) Giustino, F.; Louie, S. G.; Cohen, M. L. Electron-phonon renormalization of the direct band gap of diamond. *Phys. Rev. Lett.* **2010**, *105*, 265501.

(49) Antonius, G.; Poncé, S.; Boulanger, P.; Côté, M.; Gonze, X. Many-body effects on the zero-point renormalization of the band structure. *Phys. Rev. Lett.* **2014**, *112*, 215501.

(50) Poncé, S.; Antonius, G.; Boulanger, P.; Cannuccia, E.; Marini, A.; Côté, M.; Gonze, X. Verification of first-principles codes: Comparison of total energies, phonon frequencies, electron−phonon coupling and zero-point motion correction to the gap between ABINIT and QE/Yambo. *Comput. Mater. Sci.* **2014**, *83*, 341−348.

(51) Poncé, S.; Gillet, Y.; Laflamme Janssen, J.; Marini, A.; Verstraete, M.; Gonze, X. Temperature dependence of the electronic structure of semiconductors and insulators. *J. Chem. Phys.* **2015**, *143*, 102813.

(52) Antonius, G.; Poncé, S.; Lantagne-Hurtubise, E.; Auclair, G.; Gonze, X.; Côté, M. Dynamical and anharmonic effects on the electron-phonon coupling and the zero-point renormalization of the electronic structure. *Phys. Rev. B* **2015**, *92*, 085137.

(53) Friedrich, M.; Riefer, A.; Sanna, S.; Schmidt, W.; Schindlmayr, A. Phonon dispersion and zero-point renormalization of LiNbO3 from density-functional perturbation theory. *J. Phys.: Condens. Matter* **2015**, *27*, 385402.

(54) Nery, J. P.; Allen, P. B.; Antonius, G.; Reining, L.; Miglio, A.; Gonze, X. Quasiparticles and phonon satellites in spectral functions of semiconductors and insulators: Cumulants applied to the full first-principles theory and the Fröhlich polaron. *Phys. Rev. B* **2018**, *97*, 115145.

(55) Tutchton, R.; Marchbanks, C.; Wu, Z. Structural impact on the eigenenergy renormalization for carbon and silicon allotropes and boron nitride polymorphs. *Phys. Rev. B* **2018**, *97*, 205104.

(56) Querales-Flores, J. D.; Cao, J.; Fahy, S.; Savić, I. Temperature effects on the electronic band structure of PbTe from first principles. *Physical Review Materials* **2019**, *3*, 055405.

(57) Miglio, A.; Brousseau-Couture, V.; Godbout, E.; Antonius, G.; Chan, Y.-H.; Louie, S. G.; Côté, M.; Giantomassi, M.; Gonze, X. Predominance of non-adiabatic effects in zero-point renormalization of the electronic band gap. *Npj Computational Materials* **2020**, *6*, 167.

(58) Cannuccia, E.; Gali, A. Thermal evolution of silicon carbide electronic bands. *Physical Review Materials* **2020**, *4*, 014601.

(59) Patrick, C. E.; Giustino, F. Unified theory of electron–phonon renormalization and phonon-assisted optical absorption. *J. Phys.: Condens. Matter* **2014**, *26*, 365503.

(60) Zacharias, M.; Giustino, F. One-shot calculation of temperature-dependent optical spectra and phonon-induced band-gap renormalization. *Phys. Rev. B* **2016**, *94*, 075125.

(61) Gonze, X.; Amadon, B.; Anglade, P.-M.; Beuken, J.-M.; Bottin, F.; Boulanger, P.; Bruneval, F.; Caliste, D.; Caracas, R.; Côté, M.; et al. ABINIT: First-principles approach to material and nanosystem properties. *Comput. Phys. Commun.* **2009**, *180*, 2582−2615.

(62) Gonze, X.; Jollet, F.; Abreu Araujo, F. A.; Adams, D.; Amadon, B.; Applencourt, T.; Audouze, C.; Beuken, J.-M.; Bieder, J.; Bokhanchuk, A.; et al. Recent developments in the ABINIT software package. *Comput. Phys. Commun.* **2016**, *205*, 106−131.

(63) ABINIT, Tutorial TDepES, Temperature-DEPendence of the Electronic Structure; https://docs.abinit.org/tutorial/tdepes/ (accessed March 3, 2020).

(64) Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* **2006**, *27*, 1787−1799.

(65) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **2011**, *32*, 1456−1465.

(66) Van Troeye, B.; Torrent, M.; Gonze, X. Interatomic force constants including the DFT-D dispersion contribution. *Phys. Rev. B* **2016**, *93*, 144304.

(67) Hamann, D. R. Optimized norm-conserving Vanderbilt pseudopotentials. *Phys. Rev. B* **2013**, *88*, 085117.

(68) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865−3868.

(69) Raffy, C.; Furthmüller, J.; Bechstedt, F. Properties of hexagonal polytypes of group-IV elements from first-principles calculations. *Phys. Rev. B* **2002**, *66*, 075201.

(70) Fan, Q.; Chai, C.; Wei, Q.; Wong, K.; Liu, Y.; Yang, Y. Theoretical investigations of group IV alloys in the Lonsdaleite phase. *J. Mater. Sci.* **2018**, *53*, 2785−2801.

(71) Stöhr, M.; Van Voorhis, T.; Tkatchenko, A. Theory and practice of modeling van der Waals interactions in electronic-structure calculations. *Chem. Soc. Rev.* **2019**, *48*, 4118−4154.

(72) Xu, W.-W.; Xia, F.; Chen, L.; Wu, M.; Gang, T.; Huang, Y. High-temperature mechanical and thermodynamic properties of silicon carbide polytypes. *J. Alloys Compd.* **2018**, *768*, 722−732.

(73) Moruzzi, V. L.; Janak, J. F.; Schwarz, K. Calculated thermal properties of metals. *Phys. Rev. B* **1988**, *37*, 790.