Supplementary information for

**Electron-phonon interaction contribution to the total energy of group IV semiconductor polymorphs: evaluation and implications**

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Supporting Information Available

The supplementary information contains: i) Proof of linearity for $\Delta E_{av}^{ep}(T)$ vs. $1/N_q$ (Section I) and ii) Results for Si and C poltypes (Section II) and SiC polytypes (Section III) using GGA.fhi and PSPNC pseudopotentials.

Proof that $\Delta E_{av}^{ep}(T)$ varies linearly with $1/N_q$

For brevity, we represent $\Delta \epsilon_{nk}(T)$ as $\Delta \epsilon_{nk}$. Given that $\Delta \epsilon_{nk}$ is linear in $x$ ($= 1/N_q$) for all $n$, $k$, there are constants, $a_{nk}$ and $b_{nk}$ such that:

$$\Delta \epsilon_{nk}(x) = a_{nk}x + b_{nk}$$  \hspace{1cm} (S1)

The converged eigenvalue, $\Delta \epsilon_{nk}^c$, is given by:

$$\Delta \epsilon_{nk}^c = \lim_{x \rightarrow 0^+} \Delta \epsilon_{nk}(x) = b_{nk}$$  \hspace{1cm} (S2)

Substituting Eq. (S1) in Eq. (S2), we get:

$$\Delta E_{av}^{ep}(x) = 2x \sum_{nk} w_k a_{nk} + 2 \sum_{nk} w_k b_{nk}$$  \hspace{1cm} (S3)

The converged value of the EPI correction to the total energy, $\Delta E_{av}^{ep,c}$, is given by:

$$\Delta E_{av}^{ep,c} = \sum_{nk} w_k \Delta \epsilon_{nk}^c = 2 \sum_{nk} w_k b_{nk}$$  \hspace{1cm} (S4)

Therefore,

$$\Delta E_{av}^{ep,c} = \lim_{x \rightarrow 0^+} E_{av}^{ep}(x)$$  \hspace{1cm} (S5)

It follows from Eq. (S3) and Eq. (S5) that $\Delta E_{av}^{ep}(T)$ varies linearly with $1/N_q$ and the converged value can be obtained by linear extrapolation.
Si and C polymorphs

Figure S1 shows the convergence behavior of the EPI correction to the total energy with q-point grid density, using the GGA.fhi pseudopotential.

Figure S1: Convergence of electron-phonon interaction correction to the total energy at 0 K with q-point grid density for smearing parameter value of 100 meV for carbon and silicon polytypes for GGA.fhi pseudopotential.

Table S1 gives the lattice parameters, band gaps and the relative energy stability with and without EPI corrections for the C and Si polymorphs. The increase in relative stability of C-dia and Si-dia is clearly seen when the EPI corrections to the total energies are included.

Table S1: The lattice parameters, band gaps and the energy differences for carbon and silicon polytypes for GGA.fhi pseudopotential

| Material | a,c (Bohr) | Band gaps (Indirect/ Direct) (eV) | ΔE (DFT) (meV/f.u.) | ΔE (DFT+EPI) (meV/f.u.) |
|----------|------------|-----------------------------------|---------------------|------------------------|
| C-dia    | 6.73       | 4.21, 5.62                        | 0                   | 0                      |
| C-hex    | 4.732, 7.876 | 3.38, 5.0                        | 24.9                | 68.7                   |
| Si-dia   | 10.33      | 0.614, 2.56                       | 0                   | 0                      |
| Si-hex   | 7.27, 12.017 | 0.45, 0.98                      | 9.8                 | 17.4                   |
Figure S2 shows the convergence behavior of the EPI correction to the total energy with q-point grid density using the pspnc pseudopotential.

![Graph showing convergence behavior of EPI correction to total energy](image)

Figure S2: Convergence of electron-phonon interaction correction to the total energy at 0 K with q-point grid density for smearing parameter value of 100 meV for carbon and silicon polytypes for pspnc (LDA) pseudopotential.

Table S2 gives the lattice parameters, band gaps and the relative energy stability with and without EPI corrections for the C and Si polymorphs. The increase in relative stability of C-dia and Si-dia is clearly seen when the EPI corrections to the total energies are included.

**Table S2: The lattice parameters, band gaps and the energy differences for carbon and silicon polytypes for pspnc pseudopotential**

| Material | a,c (Bohr) | Band gaps (Indirect/ Direct) (eV) | ΔE (DFT) (meV/f.u.) | ΔE (DFT+EPI) (meV/f.u.) |
|----------|------------|-----------------------------------|---------------------|------------------------|
| C-dia    | 6.69       | 4.22, 5.63                        | 0                   | 0                      |
| C-hex    | 4.706, 7.838 | 3.12, 4.99                        | 24.8                | 68.5                   |
| Si-dia   | 10.20      | 0.43, 2.52                        | 0                   | 0                      |
| Si-hex   | 7.180, 11.875 | 0.26, 0.95                      | 8.4                 | 15.1                   |

The above results are similar to those for ONCV pseudopotential in the main paper.
Table S3: The lattice parameters and the energy stability of SiC polytypes relative to SiC-3C for DFT, DFT-D2 and DFT-D3(BJ) conditions for GGA.fhi pseudopotential.

| Polytype | a,c (Bohr) | ΔE (meV/SiC) |
|----------|-----------|-------------|
| **3C-SiC** |           |             |
| DFT      | 8.26      | 0           |
| DFT-D2   | 8.21      | 0           |
| DFT-D3(BJ) | 8.20   | 0           |
| **4H-SiC** |           |             |
| DFT      | 5.834, 19.099 | -2.11    |
| DFT-D2   | 5.799, 19.014 | 2.54     |
| DFT-D3(BJ) | 5.788, 18.498 | -1.84   |
| **2H-SiC** |           |             |
| DFT      | 5.831, 9.568 | 4.98     |
| DFT-D2   | 5.795, 9.537 | 14.5    |
| DFT-D3(BJ) | 5.784, 9.491 | 6.02    |

**SiC polytypes**

We first present results for SiC polytypes obtained using GGA.fhi pseudopotential.

Table S3 shows the lattice parameters and the energy stabilities relative to the SiC-3C polytype for DFT condition and also when dispersion approximations are included. We see that SiC-4H is more stable than SiC-3C for DFT conditions. When vdW-D2 approximation is included, SiC-3C is the stable structure, similar to literature results. However, when vdW-D3(BJ) approximation is used, SiC-4H is more stable. This is similar to the results for the ONCV pseudopotential reported in the main paper.
Figure S3 shows the convergence behaviour of the EPI correction to the total energy with q-point grid density for SiC polytypes for different smearing parameters. For 100 meV smearing parameter, the $\Delta E_{\text{ep}}^{(0)}$ was calculated only up to $\frac{1}{N_q} \approx 0.043$ due to computational limitations. For 50 meV smearing parameter, only the results for the highest q-point grid density were calculated (due to computational limitations.)

Table S4 shows the final stability of SiC-polytypes obtained by combining the EPI corrections in Figure S3 with the relative stability data in Table S3. For SiC-3C and SiC-2H we consider the last value to be the converged value. However, for SiC-4H, the last calculated value ($\frac{1}{N_q} \approx 0.043$) is not the converged value as it varies by $\lesssim 6$ meV/f.u. compared to
the previous value. Therefore, for SiC-4H, we report two values in Table S4; the first is the difference between the last values for SiC-3C and SiC-4H and the second is the difference at $\frac{1}{N_q} \approx 0.043$ for SiC-4H and the nearest value for SiC-3C, $\frac{1}{N_q} \approx 0.039$. The actual stability value of for SiC-4H is likely to be between these two values.

The results using GGA.fhi pseudopotential are similar to those from ONCV-PBE pseudopotential presented in the main paper.

Table S5 shows the lattice parameters and the energy stabilities relative to the SiC-3C polytype using the pspnc pseudopotential. The vdW corrections were not performed because ABINIT package does not support DFT-D2 and DFT-D3(BJ) corrections for LDA pseudopotentials.

Table S5: The lattice parameters and the energy stability (DFT) in meV/f.u. of SiC polytypes relative to SiC-3C for DFT lattice parameters for pspnc pseudopotential.

| Polytype | a,c (Bohr) | $\Delta E$ (DFT) (meV/SiC) |
|----------|------------|--------------------------|
| 3C-SiC   | 8.18       | 0                        |
| 4H-SiC   | 5.782, 18.931 | -3.17                   |
| 2H-SiC   | 5.778, 9.485 | 4.33                     |

Figure S4 shows the convergence behaviour of the EPI correction to the total energy with q-point grid density for SiC polytypes for different smearing parameters. For 100 meV smearing parameter, the $\Delta E_{\text{av}}^{ep}(0)$ was calculated only up to $\frac{1}{N_q} \approx 0.043$ due to computational limitations. For 50 meV smearing parameter, only the results for the highest q-point grid density was calculated (due to computational limitations.)
Figure S4: Convergence of electron-phonon interaction correction to the total energy at 0 K with q-point grid density for different values of the smearing parameter for SiC polytypes for pspnc (LDA) pseudopotential.

Table S6: Relative stability (in meV/f.u.) of SiC polytypes using pspnc pseudopotential in non-adiabatic condition-100 meV and 50 meV smearing parameters.

| Polytype | SiC-3C | SiC-4H | SiC-2H |
|----------|--------|--------|--------|
| DFT      | 0      | -3.2   | 4.3    |
| DFT + EPI (100 meV) | 0   | -33.1/-25.8 | -5.7    |
| DFT + EPI (50 meV) | 0    | -35.2  | -7.3   |

Table S6 shows the final stability of SiC-polytypes obtained by combining the EPI corrections with the relative stability data in Table S5. For SiC-3C and SiC-2H we consider the last value to be the converged value. However, for SiC-4H, the last calculated value ($\frac{1}{N_q} \approx 0.043$) is not the converged value as it varies by \( \lesssim 6 \) meV/f.u. compared to the previous value. Therefore, for SiC-4H, we report two values in Table S4; the first is the difference between the last values for SiC-3C and SiC-4H and the second is the difference at $\frac{1}{N_q} \approx 0.043$ for SiC-4H and the nearest value for SiC-3C, $\frac{1}{N_q} \approx 0.039$. The actual stability value of for SiC-4H is likely to be between these two values.
The results using pspnc pseudopotential are similar to those from the ONCV pseudopotential presented in the main paper.

Our results from both the GGA.fhi and the pspnc pseudopotentials are similar to those from ONCV pseudopotential. This suggests that the results are stable and independent of the choice of the pseudopotential.