Ewald constants of silicon carbide polytypes and the role of hexagonality

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Ewald Constants of Silicon Carbide Polytypes
And the Role of Hexagonality

Dr. D. Lenstra et al.

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EWALD CONSTANTS OF SILICON CARBIDE POLYTYPES AND THE ROLE OF HEXAGONALITY

by

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Abstract

A novel decomposition scheme for the calculation of Ewald constants of SiC polytypes in terms of layer contributions is presented, which elucidates the explicit role played by the hexagonality. Simple formula's are presented which allow direct calculation of Ewald constants for any SiC polytype accurate to 1 in $10^6$. 
1. Introduction

This article deals with the determination of Ewald constants $\alpha$ for lattices coinciding with the class of polytypes of SiC (Silicon Carbide). Though the calculation of these constants is in principle straightforward if the well-known 3-dimensional Ewald procedure [1,2] for convergence acceleration is applied, we want to advocate a novel description scheme in terms of subsequent layer contributions, as it reveals and elucidates an almost linear dependence of $\alpha$ on the hexagonality parameter $h$. This yields an obvious and remarkably accurate means to determine $\alpha$ for any polytype. We are also able to describe systematically the slight deviations from this linear relation.

The relevance of the above Ewald constants shows up if one wants to compare total energies of the various SiC polytype crystals. We are currently engaged in such a comparison in the framework of a pseudopotential approach [3].

A significant contribution which can be split off from the total energy is the so-called Ewald energy, which is the electrostatic interaction energy due to point charges having the ionic change $q = -4e$ ($e$ is the electron charge) and situated at the ionic positions within a uniform neutralizing background charge density. The remaining contribution to the total energy is significantly smaller and can be calculated separately, for instance, in the framework of a pseudopotential approach [3]. In the present paper we will exclusively deal with the Ewald contribution to the total energy.

The Ewald energy $\gamma$ (per atom) and the dimensionless Ewald constant $\alpha$ are related according to

$$\gamma = \frac{-q^2}{8\pi \varepsilon_0 R_{\text{at}}} \alpha, \quad (1)$$

where $R_{\text{at}}$ is the radius of a sphere with volume $V_{\text{at}}$ equal to the volume occupied by each point charge. The Ewald constant $\alpha$ is given by

$$\alpha = \frac{2R_{\text{at}}}{NV_{\text{at}}} \sum_{i=1}^{N} \frac{d^3r}{|r - R_\text{i}|} - \frac{R_{\text{at}}}{V_{\text{at}}} \sum_{i=1}^{N} \int \frac{d^3r}{|r - R_\text{i}|} \int \frac{d^3r'}{V|r - r'|}$$  

$$- \frac{R_{\text{at}}}{N} \sum_{i=1}^{N} \sum' \frac{1}{|R_\text{i} - R_j|}. \quad (2)$$
In (2), $V$ is the total crystal volume; $N$ equals the number of atoms (point charges) per unit cell; $R_i$ runs through the point charge positions in the unit cell, while $R_j$ runs through all positions in $V$. The prime in the $j$-summation in (2) indicates exclusion of $R_i = R_j$. All three terms in the right-hand side of (2) have a divergency when the crystal volume $V$ tends to infinity, which divergencies, however, precisely cancel in the complete expression. The first two terms in (2) may be combined for $V \to \infty$ to yield one single term $\left(\frac{R_i}{V}\right) \int d^3r/r$. However, in view of the layer decomposition to be carried through in the sequel, we will use expression (2).

2. Polytype description

The various polytypes of SiC can be distinguished by the particular order in which double layers of silicon and carbon atoms are stacked above each other. The stacking sequence is generally such that after $N_L$ double layers a particular sequence is repeated, in that case leading to periodicity. All polytypes can be described with the help of hexagonal unit cells [4] spanned by the vectors $\mathbf{t}_1 = (a/2)(\sqrt{3} \mathbf{a}_1 - \mathbf{a}_2)$; $\mathbf{t}_2 = a \mathbf{a}_2$; $\mathbf{t}_3 = N_L c \mathbf{a}_2$, where $a$ is the distance between nearest-neighbour Si atoms (or C-atoms) and $c$ is the mutual distance between adjacent Si-layers (or C-layers). Within a specific double layer the lateral positions of both the Si and C atoms are either $n_1 \mathbf{t}_1 + n_2 \mathbf{t}_2$ (we call this an A-type layer); $(n_1+2/3)\mathbf{t}_1 + (n_2+1/3)\mathbf{t}_2$ (B-type) or $(n_1+1/3)\mathbf{t}_1 + (n_2+2/3)\mathbf{t}_2$ (C-type), where $n_1, n_2$ may be any integer. The $k$-th double layer extends from $(k-1)c \mathbf{a}_2$ to $(k+1)c \mathbf{a}_2$. The Si atoms in this layer are situated at $(kc - \frac{3u}{4}) \mathbf{a}_2$; the C atoms at $(kc + \frac{3u}{4}) \mathbf{a}_2$, where $u$ is close to $3c/4$. There is a sequential restriction in the $z$-direction in that AA, BB or CC-stacking is impossible.

Each possible periodic stacking yields a candidate for a polytype but not all stackings seem to occur in nature. Some examples are 2H SiC (AB stacking), 3C SiC (ABC), 4H SiC (ABCB), 15R SiC (ABCABCABABCABCB) where H, C, R stands for hexagonal, cubic and rhombohedral indicating the actual crystal symmetry of the polytype. The number in front is to be identified with $N_L$.

The hexagonality parameter $h$ is defined as the fraction of equal type layer combinations for layers lying 2 layers apart from each other. It is easily seen that $h=1$, 0, $\frac{1}{3}$ for 2H SiC, 3C SiC and 4H SiC, respectively. Recent experimental data show that the values of the crystal parameters $a$ and $c$ vary linearly with $h$. The data yield [5]
Fig. 1 Illustrating the linear and quadratic hexagonality effect, respectively. Black dots (left-hand scale) correspond to the calculated values of the Ewald constant for the ideal ratio $c/a = \sqrt{2/3}$ (fourth column of Table 1). The solid straight line connects the 3C ($h=0$) and 2H ($h=1$) values. Open dots (right-hand scale) indicate the vertical displacements of the non-ideal $a$ values (last column of Table 1) with respect to the solid line. The dashed curve is the quadratic form connecting the 3C ($h=0$) and 2H ($h=1$) values. Note that the right-hand scale has been enlarged with respect to the left-hand scale.
\[ a = 3.0827 - 0.0064\times h \quad (10^{-10}\text{m}), \quad (3a) \]
\[ c = 2.5170 + 0.0070\times h \quad (10^{-10}\text{m}), \quad (3b) \]
giving, for instance, \( a \ (3\text{C SiC}) = 3.0827 \ \text{Å} \) with \( h(3\text{C SiC}) = 0 \) and \( a(2\text{H SiC}) = 3.0763 \ \text{Å} \) with \( h(2\text{H SiC}) = 1 \) [6]. Unfortunately, it is to our best knowledge not known how the bondlength in the z-direction \( (u) \) will vary from one polytype to the other. In what follows we will invariably use values of \( u \) such that all nearest neighbour Si to C bond lengths are equal [7].

Adopting this it can easily be seen that \( u \) is given by

\[ u = \frac{1}{6} \frac{a^2}{c} + \frac{1}{2} c. \quad (4) \]

3. Ewald constants for ideal and non-ideal \( c/a \) ratio

In Table 1 some Ewald constants are given as calculated by means of the conventional Ewald procedure [2] for the cases of "ideal" ratio \( c/a = \sqrt{2/3} \) and non-ideal ratio in accordance with (3). In each case the bond length \( u \) was taken as in (4).

Table 1 Ewald constants \( \alpha \) calculated for a set of polytypes with increasing value of the hexagonality parameter \( h \). In the first \( \alpha \)-column it is assumed that \( c/a = \sqrt{2/3} \) and \( u = 3c/4 \); in the second \( \alpha \)-column the values of \( c/a \) and \( u \) are taken from (3) and (4). An asterisk indicates that the polytype has been found to exist.

<table>
<thead>
<tr>
<th>polytype</th>
<th>layer sequence</th>
<th>( h )</th>
<th>( \alpha(c/a = \sqrt{2/3}) )</th>
<th>( \alpha(c/a \text{ from (3)}) )</th>
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<tbody>
<tr>
<td>3C*</td>
<td>ABC</td>
<td>0</td>
<td>1.670 851 405 5</td>
<td>1.670 851 405 5</td>
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<tr>
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<td>ABCABAC</td>
<td>2/7</td>
<td>1.670 152 539 6</td>
<td>1.670 162 948 6</td>
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<tr>
<td>6H*</td>
<td>ABCACB</td>
<td>1/3</td>
<td>1.670 036 064 9</td>
<td>1.670 050 227 0</td>
</tr>
<tr>
<td>5H</td>
<td>ABCAB</td>
<td>2/5</td>
<td>1.669 871 688 6</td>
<td>1.669 892 105 4</td>
</tr>
<tr>
<td>4H*</td>
<td>ABCB</td>
<td>1/2</td>
<td>1.669 628 385 8</td>
<td>1.669 660 177 2</td>
</tr>
<tr>
<td>7H</td>
<td>ABCBCAC</td>
<td>4/7</td>
<td>1.669 451 807 4</td>
<td>1.669 493 361 0</td>
</tr>
<tr>
<td>7H</td>
<td>ABCACAC</td>
<td>4/7</td>
<td>1.669 450 865 4</td>
<td>1.669 492 460 0</td>
</tr>
<tr>
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<td>ABACAB</td>
<td>2/3</td>
<td>1.669 218 532 3</td>
<td>1.669 274 994 7</td>
</tr>
<tr>
<td>2H*</td>
<td>AB</td>
<td>1</td>
<td>1.668 398 807 6</td>
<td>1.668 525 274 2</td>
</tr>
</tbody>
</table>
The $\alpha$-values in Table 1 were calculated up to 20 significant decimal figures; the displayed figures were rounded off in the last decimal. The suggested high accuracy of the $\alpha$-values has numerical significance only.

Fig. 1 reveals the almost linear dependence of $\alpha$ on $h$ in the case of the ideal ratio $c/a = \sqrt{2}/3$ (black dots). The explanation for this will be given in the next section by analyzing successive layer contributions to $\alpha$. The open dots in Fig. 1 represent the $\alpha$-values from the last column in Table 1. The deviations from the linear plot are almost perfectly quadratic in $h$ which is the result of applying (3).
4. Decomposition of $\alpha$ into layer contributions

We divide the crystal into layers $L_k$ defined by $(k-1)c < z < (k+1)c$ with $k = 0, \pm 1, \pm 2, \ldots$. The position vectors of the point charges in these layers are chosen as

$$\begin{align*}
\mathbf{R}_{n_1n_2k} &= \begin{cases} 
(n_1+2/3)t_1 + (n_2+1/3)t_2 + (kc-\lambda u)\hat{z}, & \text{if } L_k \text{ is B-type;} \\
(n_1+1/3)t_1 + (n_2+2/3)t_2 + (kc-\lambda u)\hat{z}, & \text{if } L_k \text{ is C-type;}
\end{cases}
\end{align*}$$

where $n_1, n_2 = 0, \pm 1, \pm 2, \ldots$. Expression (2) can now be written

$$\alpha = \frac{\text{Rat}}{V} \left. \left. \sum_{k=-\infty}^{+\infty} \right|_{k=\infty} \int d^3r \left\{ \frac{1}{|\mathbf{r} - \mathbf{R}_{000}|} + \frac{1}{|\mathbf{r} - \mathbf{R}_{000}|} \right\} \right|_{x, y \text{ in cell}}$$

$$- \frac{\text{Rat}}{2V^2} \sum_{k=-\infty}^{+\infty} \int d^3r \int d^3r' \left|z < c/2\right| \left|\mathbf{L}_k \left|\mathbf{r} - \mathbf{r}'\right| \right|_{x, y \text{ in cell}}$$

$$- \frac{\text{Rat}}{N_d} \sum_{k'=-\infty}^{+\infty} \left\{ \sum_{n_1n_2k} \frac{1}{|\mathbf{R}_{\text{Occ}, n_1n_2k'} + \mathbf{R}_{\text{Occ}, n_1n_2k} + \mathbf{R}_{\text{Occ}, n_1n_2k'} + \mathbf{R}_{\text{Occ}, n_1n_2k}|} \right\}.$$

(6)
The prime in one of the summations in (6) excludes \( n_1 = n_2 = k = 0 \). In the following a layerwise Ewald-type procedure will be carried through leading to an expression for \( \alpha \) of the form

\[
\alpha = \sum_{k=0}^{\infty} \alpha_k,
\]

where \( \alpha_0 \) refers to contributions from the central layer \( L_0 \), while \( \alpha_k \) \((k > 0)\) refers to contributions originating from the two layers \( L_k \) and \( L_{-k} \). Before turning to this evaluation we want to emphasize the necessity of our special choice for the position coordinates of the \( \text{Si} \) and \( \text{C} \) atoms (point charges) with respect to the boundaries of the successive layers. In fact, it can easily be verified that the point charge-background interaction contribution to \( \alpha \) (first term in (6)) for any finite crystal extending from \( z = (-k - \frac{1}{2})c \) to \( z = (k+\frac{1}{2})c \) will come out differently if a non-symmetric choice for the position coordinates is made [8]. The reason is that in such a crystal a net polarization in the \( z \)-direction exists. The accompanying uniform electric field in the \( z \)-direction survives in the limit \( k \to \infty \). As the Ewald energy refers to a polarization-free crystal we are obliged to make the symmetric choice.

The first and second terms \( I_1 \) and \( I_2 \) in the right-hand side of (6) will be written

\[
I_1 = \frac{2R}{V} \sum_{k=0}^{\infty} \frac{\int_{-\infty}^{c} dz \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy}{\frac{1}{[x^2+y^2+(z+c/2)^2]^{1/2}}}^{(k+1/2)c},
\]

and

\[
I_2 = \frac{R}{cV} \sum_{k=0}^{\infty} \frac{\int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dy}{\frac{1}{[x^2+y^2+(z'+-c/2)^2]^{1/2}}}^{(k-1/2)c},
\]

respectively. Quite similar to the procedure outlined in the paper by Coldwell-Horsfall and Maradudin [9] (see also Appendix), we want to express the occurring divergent \( xy \) integrals with the help of the identity

\[
g^{-1/2} = \pi^{-1/2} \int_0^\infty dt \ t^{-1/2} \exp(-gt). \]

We find
\[
\int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dy \frac{1}{(x^2+y^2+w^2)^{3/4}} = 2\sqrt{\pi} |\omega| \int_0^{+\infty} dt e^{-t^2}. \tag{9}
\]

Applying this to (8a) and (8b), performing the layerwise \( z \)-integrations, using \( v_{at} = a^2 c^3/4 = 4\pi R_{at}^3 \) we obtain

\[
I_1 + I_2 = \frac{4\sqrt{\pi}}{ac\sqrt{3}} \sum_{k=-\infty}^{+\infty} \left\{ \frac{1}{3}c^2 + u^2 \right\} \delta_{ko} + 2c^2 |x| \int_0^{+\infty} dt e^{-t^2}. \tag{10}
\]

Let us now turn to the remaining term \( I_3 \) contributing to \( \alpha \) in (6). In evaluating this term it is readily verified that only two types of Si-Si distances occur. Namely

\[
\left| R_{\text{Si}}^{\text{ook'}}, - R_{n_1 n_2, k'+k} \right|^{-1} = a^{-1} \left[ n_1^2 + n_2^2 - n_1 n_2 + k^2 c^2/a^2 \right]^{-1}, \tag{11a}
\]

if the layers are of equal type, while

\[
\left| R_{\text{Si}}^{\text{ook'}}, - R_{n_1 n_2, k'+k} \right|^{-1} = a^{-1} \left[ (n_1+1/3)^2 + (n_2+2/3)^2 - (n_1+1/3) (n_2+2/3) \right. \\
+ k^2 c^2/a^2 \left. \right]^{-1}, \tag{11b}
\]

if the layers are of different type. Quite similar expressions follow for the Si-C distances. The result is that only two types of summations survive:

\[
s_{AA}(\xi) = \sum \frac{1}{n_1 n_2 \left[ n_1^2 + n_2^2 - n_1 n_2 + \xi \right]^{1/2}}, \tag{12a}
\]

and

\[
s_{AB}(\xi) = \sum \frac{1}{n_1 n_2 \left[ (n_1+1/3)^2 + (n_2+2/3)^2 - (n_1+1/3) (n_2+2/3) + \xi \right]^{1/2}}. \tag{12b}
\]

The prime in the summation in (12a) indicates that for \( \xi = 0 \) the term with \( n_1 = n_2 = 0 \) is excluded. In the Appendix expressions for \( s_{AA}(\xi) \) and \( s_{AB}(\xi) \) are derived, showing quite similar divergencies as in eqs. (9) and (10).

As a matter of course all divergencies in \( I_1 + I_2 \) due to \( I_3 \) have to cancel. The remaining expression for \( \alpha \) can best be given in terms of the convergent quantities
\[ S_{AA}(\zeta) = \frac{4\sqrt{\pi}}{\sqrt{3}} \zeta \int_0^\infty dt e^{-1/t^2} - S_{AA}(\zeta), \ (\zeta > 0); \]  
(13a)

\[ S_{AA}(0) = \frac{4\sqrt{\pi}}{ac\sqrt{3}} \left( \frac{1}{3} c^2 u^2 - uc \right) \int_0^\infty dt e^{-1/t^2} - S_{AA}(0); \]  
(13b)

\[ S_{AB}(\zeta) = \frac{4\sqrt{\pi}}{\sqrt{3}} \zeta \int_0^\infty dt e^{-1/t^2} - S_{AB}(\zeta), \ (\zeta > 0). \]  
(13c)

In terms of layer contributions \( \alpha \) can now be written as

\[
\alpha = \alpha_0^{AA} + \alpha_1^{AB} + \sum_{k=2}^{\infty} \left[ h_k^{AA} \alpha_k^{AA} - (1 - h_k^{AA}) \alpha_k^{AB} \right], \quad (14)
\]

where

\[
\alpha_0^{AA} = \frac{R\zeta}{a} \left[ S_{AA}(0) + S_{AA} \left( \frac{u}{a} \right) \right]; \quad (15a)
\]

\[
\alpha_1^{AB} = \frac{R\zeta}{a} \left[ 2S_{AB} \left( \frac{c}{a} \right) + S_{AB} \left( \frac{c-u}{a} \right) + S_{AB} \left( \frac{c+u}{a} \right) \right]; \quad (15b)
\]

\[
\alpha_k^{AB} = \frac{R\zeta}{a} \left[ 2S_{AB} \left( \frac{kc}{a} \right) + S_{AB} \left( \frac{kc-u}{a} \right) + S_{AB} \left( \frac{kc+u}{a} \right) \right], \quad (15c)
\]

\((\beta = A, B; \ k = 2, 3, 4, \ldots ).\)

In (14), \( h_k^{AA} \) is equal to the fraction of equal type layer combinations for layers lying a distance \( kc \) apart. As a matter of course, \( h_2^{AA} \) coincides with our earlier hexagonality parameter \( h \). The quantities \( S_{AA}(\zeta) \) and \( S_{AB}(\zeta) \) can be calculated for any \( \zeta \). Because of the rapid exponential decrease of the \( S_{AB}(\zeta) \) for \( \zeta \to \infty \), only a few \( k \) terms in (14) are relevant.

Eq. (14) shows that explicit dependence of \( \alpha \) on the particular polytype neither shows up in \( \alpha_0 \) nor in \( \alpha_1 \). Differences in \( \alpha \) among the various polytypes are due mainly to differences in the \( \alpha_2^{AB} \) which explains the almost linear behaviour observed in Fig.1 for the ideal ratio \( c/a = \sqrt{2}/3 \).

The third column in Table 2 displays the first few \( \alpha_k^{AB} \) constants up to 10 decimal places accuracy for the "ideal" ratio \( c/a = \sqrt{2}/3 \). These data, when substituted in (14), reproduce all values given in Table 1 correctly up to 10 decimal places. In order to illustrate the effect of small deviations \( \Delta \) of \( c/a \) from the ideal ratio \( \sqrt{2}/3 \), the 4th and 5th column of Table 2 give the first and second derivative respectively, of each layer contribution with respect to \( c/a \), assuming equal bond length, i.e., eq. (4).
It is easily seen from these data that the Ewald constant for 3C SiC (i.e. add the 0AA, 1AB, 2AB and 3AA-data) has a minimum at the ideal c/a ratio equal to $\sqrt{2/3}$. An optimum to occur here is indeed expected for the highly symmetric 3C case. We have verified that it is a minimum with respect to variations of u/a also. Note, however, that this implies a maximum for the electrostatic energy, so that, if the Ewald energy would be decisive for the stability, the zincblende and diamond structures would be unstable configurations.

Using the data of Table 2 for the 2H SiC polytype (i.e., add the 0AA, 1AB, 2AA and 3AB data), we find

$$\alpha_{2H}^2 \approx 1.66840 + 0.0317 \times \Delta + 0.89 \times \Delta^2/2,$$

from which we may extract the minimal value $\alpha_{2H}^2 = 1.66784$, reached at $c/a = \sqrt{2/3} - 0.0356 = 0.7807$. Note, however, that the experimental c/a ratio for 2H SiC is slightly larger than $\sqrt{2/3}$, which demonstrates another inadequacy of the Ewald energy to set a trend with respect to the stability of a crystal.

The data in Table 2 can be used to calculate the k-th layer contribution to $\alpha$ for any polytype for which $\Delta = \sqrt{2/3} - c/a$ is known. The latter value varies between 0(3C) and approximately $4 \times 10^{-3}$ (2H), as follows from the experimental result (3). The $\alpha_{2H}^{AB}$ in (14) can be calculated using

$$\alpha_{k}^{AB} = \left\{ \begin{array}{c} \alpha_{k}^{AB} \\ \frac{c}{a} = \sqrt{\frac{2}{3}} \\ \frac{\partial \alpha_{k}^{AB}}{\partial (c/a)} |_{\frac{c}{a} = \sqrt{\frac{2}{3}}} \end{array} \right\} \Delta + \left\{ \begin{array}{c} \frac{\partial^2 \alpha_{k}^{AB}}{\partial (c/a)^2} |_{\frac{c}{a} = \sqrt{\frac{2}{3}}} \end{array} \right\} \Delta^2/2, \quad (16)$$

with the constants taken from Table 2.

A simple formula for the Ewald constant of an arbitrary polytype with accuracy of 1 in $10^6$ can be derived from the data given in Table 2 together with (14) and (16), and reads

$$\alpha = 1.670851 - 0.002459 \times h_2^{AA} + 0.000007 \times (1 - h_3^{AA})$$

$$+ 0.0318 \times h_2^{AA} \times \Delta. \quad (17)$$
Here, $h_2^{AA}$ is the usual hexagonality $h$, introduced before, and $1-h_3^{AA}$ can be viewed upon as a generalized hexagonality, that is, the hexagonality with respect to third nearest neighbour layers. Finally, if we substitute the explicit $c/a$ dependence on hexagonality which follows from (3), we can write (17) as

$$\alpha = 1.670851 - 0.002459 \times h_2^{AA} + 0.000007 \times (1 - h_3^{AA})$$

$$+ 0.000126 \times (h_2^{AA})^2. \quad (18)$$

The formula's (17) or (18) will be useful for a direct determination of Ewald constants of SiC-polytypes in all applications which require no higher accuracy than $1 \text{ in } 10^6$.

Table 2 The constants $\alpha_k^{AB}, \partial \alpha_k^{AB}/\partial (c/a)$ and $\partial^2 \alpha_k^{AB}/\partial (c/a)^2$ for the "ideal" value $c/a = \sqrt{2/3}$. All digits shown are significant. Equal bond length, i.e., eq. (4), has been assumed. Contributions $\alpha_k^{AB}$ for $k > 5$ are smaller than $3 \times 10^{-11}$

<table>
<thead>
<tr>
<th>$k$</th>
<th>combination</th>
<th>$\alpha_k^{AB}$</th>
<th>$\partial \alpha_k^{AB}/\partial (c/a)$</th>
<th>$\partial^2 \alpha_k^{AB}/\partial (c/a)^2$</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>AA</td>
<td>1.437 436 889 8</td>
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<td>- 3.00</td>
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<td></td>
<td>AB</td>
<td>0.000 000 005 9</td>
<td>0.0000</td>
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</tr>
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Conclusion

The decomposition method here presented yields successive layer contributions to the Ewald constants ($\alpha$) of SiC polytypes and reveals explicit information about the influence of typical layers stackings to the electrostatic energy of the point-charge crystal with uniform compensating charge background. It is demonstrated that $\alpha$ is in good approximation a linear function of hexagonality only. The small deviations from linearity are due to (i) variations in $c/a$, leading in lowest order to a quadratic hexagonality effect, and (ii) third and higher nearest neighbour layer effects. The contribution to $\alpha$ due to $k$-th nearest-neighbour layers is of the order of $10^{+2-2.5k}$ $(k \geq 2)$.

Simple formula's have been given wich allow immediate calculation of $\alpha$ for any polytype with known $c/a$ ratio accurate up to $1$ in $10^6$. If higher accuracies are needed, the method of layer decomposition is an attractive alternative to the conventional Ewald procedure, especially for polytypes with increasingly large hexagonal unit cells, in which the latter method requires three-dimensional summations over an increasingly large set of reciprocal lattice vectors. In the method here presented, the reciprocal lattice summation is performed layerwisely and the number of terms needed for a given accuracy is independent of polytype. The final summation is a layer summation in direct space, whose speed of convergence is independent of polytype either.

In the numerical results presented it was assumed that (i) the thickness $c$ of each layer is constant over the polytypic hexagonal unit cell; and (ii) all nearest-neighbour Si to C distances are equal. To our best knowledge there are as yet no indications that either of these assumptions is wrong.
References

2. J.T. Devreese and F. Brosens, Basic concepts in dielectric response and pseudopotentials, publication of the International Advanced Study Institute, University of Antwerp (1984), Appendix A.
7. See Ref. 4, section 4.6.
Appendix. Evaluation of $S_{AA}(\xi)$ and $S_{AB}(\xi)$

We start with (12a) for $S_{AA}(\xi)$ which can alternatively be written as (using $m_1 = n_1 + n_2$ and $m_2 = n_1 - n_2$):

$$s_{AA}(\xi) = 2 \sum_{m_1 + m_2 \text{ even}} (m_1^2 + 3m_2^2 + 4\xi^2)^{-1/2}, \quad (A-1)$$

where $\sum$ indicates summations over all integers $m_1$ and $m_2$ such that $m_1 + m_2$ is even. By using the identity

$$\omega^{-1} = \pi^{-1} \int_0^\infty dt \, t^{-1/2} e^{-\omega t} + \pi^{-1} \int_0^\infty dt \, t^{-1/2} e^{-\omega t}, \quad (A-2)$$

where $\varepsilon$ is an arbitrary positive number, we can express (A-1) as

$$s_{AA}(\xi) = 2 \sum_{m_1 + m_2 \text{ even}} \frac{\operatorname{erfc} [\sqrt{\varepsilon (m_1^2 + 3m_2^2 + 4\xi^2)}]}{\sqrt{m_1^2 + 3m_2^2 + 4\xi^2}},$$

$$+ \frac{2}{\sqrt{\pi}} \sum_{m_1 + m_2 \text{ even}} \int_0^t dt \, t^{-1/2} e^{-(m_1^2 + 3m_2^2 + 4\xi^2)t}. \quad (A-3)$$

The first summation in the right-hand side of (A-3) is convergent for any finite value of $\varepsilon$. The second summation is split into two summations by putting $m_1 = 2u_1$, $m_2 = 2u_2$ and $m_1 = 2u_1 + 1$, $m_2 = 2u_2 + 1$, respectively, where $u_1, u_2$ are integers. Then we apply a variant of the theta-transformation [10], i.e.,

$$\sum_{n=-\infty}^{\infty} e^{-(n-y)^2/x} = (\pi/x)^{1/4} \sum_{n=-\infty}^{\infty} e^{-2in\pi y - n^2 \pi^2 / x}, \quad (A-4)$$

where $x > 0$ and $y$ real, to each summation separately. The second summation in (A-3) can now be expressed as

$$(\pi/12)^{1/4} \sum_{u_1 u_2} (1 + e^{(u_1 + u_2)\pi / 2}) \int_0^t dt \, t^{-3/2} e^{-2\pi^2 (3u_1^2 + u_2^2)/(12t) - 4\xi^2 t}. \quad (A-5)$$
The singular $u_1 = u_2 = 0$ term should in fact be considered as a proper limit in which the lower boundary of the $t$-integration goes to zero representing the effect of the layer area tending to infinity [9].

The nonvanishing terms are the ones with $u_1 + u_2$ even. Introducing the new integration variable $x = t^{-1}$ and treating the singular $u_1 = u_2 = 0$ term separately, we can rewrite (A-5) as

\[ 2 \left( \frac{\pi}{3} \right)^{-1} \int_{-\infty}^{\infty} \frac{-4\zeta^2/x^2}{e} \, dx + 2 \left( \frac{\pi}{3} \right)^{-1} \sum \int_{\text{even}}^{\infty} \frac{-\pi^2 (3n_1^2 + n_2^2)x^2/12 - 4\zeta^2/x^2}{e^{-1}} \, dx \]

where the accent over the summation symbol indicates exclusion of $n_1 = n_2 = 0$.

The first term in (A-6) can also be written as

\[ 2 \left( \frac{\pi}{3} \right)^{-1} \int_{0}^{\infty} \frac{-4\zeta^2/x^2}{e} \, dx - 2 \left( \frac{\pi}{3} \right)^{-1} \int_{0}^{\infty} \frac{-4\zeta^2/x^2}{e} \, dx \]

\[ = 4 \left( \frac{\pi}{3} \right)^{-1} |\zeta| \int_{0}^{\infty} \frac{-1/x^2}{e} \, dx + 4 \pi 3^{-1/2} |\zeta| \text{erfc}(2\zeta^3 |\zeta|) \]

\[ - 2 \pi (3\zeta)^{-1} e^{-4\zeta^2} \]

where it is understood that $\zeta \neq 0$. If $\zeta = 0$, the singularity in the first term of (A-6) is undetermined. Namely, it can then be written

\[ 2 \left( \frac{\pi}{3} \right)^{-1} \lim_{Q \to \infty} \int_{Q}^{\infty} dx = 2 \left( \frac{\pi}{3} \right)^{-1} \eta \lim_{Q \to \infty} \int_{0}^{Q} dx - 2 \pi (3\zeta)^{-1} \]

\[ = 2 \left( \frac{\pi}{3} \right)^{-1} \eta \lim_{Q \to \infty} \int_{0}^{Q} \frac{-1/x^2}{e} \, dx + 2 \pi 3^{-1/2} \eta - 2 \pi (3\zeta)^{-1} \]

for any nonnegative constant $\eta$. The integration in the second term of (A-6) can easily be carried out [11] and the resulting expression for $S_{\text{AA}}(\zeta)$ with $\zeta \neq 0$ can be substituted in (13a). The singularities are then seen to cancel each other precisely and the final result for $S_{\text{AA}}(\zeta)$ is
For $\zeta = 0$, we must, in agreement with (12a), subtract the $m_1 = m_2 = 0$ term in (A-1). Furthermore, the constant $\eta$ in (A-8) should be chosen such that the first term in the right-hand side of (13b) is canceled. Hence, we must have

$$\eta = \frac{2c}{3a} + \frac{2u^2}{ca} - \frac{2}{a} u.$$

The expression for $S_{AA}(0)$ can now be obtained from (A-9) by performing the limit $\zeta \to 0$, adding the quantity $-2\pi\eta/\sqrt{3}$ with $\eta$ as in (A-10) and omitting the $1/|\zeta|$ term. Thus we find

$$S_{AA}(0) = -\frac{4\pi}{\sqrt{3}} \left( \frac{c}{3a} + \frac{u^2}{ca} - \frac{u}{a} \right) + 2\sqrt{\frac{2}{3c}} + \eta \sqrt{\frac{\pi}{3}}$$

$$-2 \sum_{n_1 + n_2 \text{ even}} \frac{\text{erfc}\left[ \sqrt{c(n_1^2 + 3n_2^2)} \right] + \text{erfc}\left[ \pi \sqrt{n_1^2 + 3n_2^2} / (12\pi) \right]}{\sqrt{n_1^2 + 3n_2^2}}.$$ (A-11)

The evaluation of $S_{AB}(\zeta)$ proceeds along lines very similar to $S_{AA}(\zeta)$ and will not be repeated. The final expression for $S_{AB}(\zeta)$ is given by
In (A-9), (A-11) and (A-12) the parameter $\varepsilon$ can still be chosen, since, by construction, $S_{AA}(\zeta)$ and $S_{AB}(\zeta)$ are independent of $\varepsilon$. We have not attempted to find an optimal value for $\varepsilon$ in the sense of obtaining the fastest speed of convergence. Putting $\varepsilon = 1$ results in convergence up to 10 decimals for $n_1$ and $n_2$ combinations such that $(n_1^2 + 3n_2^2)^{1/2} < 10$. 

$$S_{AB}(\zeta) = -\frac{4\pi}{\sqrt{3}} |\zeta| \text{erfc}(2|\zeta|\sqrt{\varepsilon}) - \frac{2\text{erfc}[\sqrt{\varepsilon(4/3 + 4\zeta^2)}]}{\sqrt{4/3 + 4\zeta^2}}$$

$$+ 2\sqrt{\frac{\pi}{3\varepsilon}} e^{-4\varepsilon^2} - \sum_{n_1, n_2 \text{ even}} \left\{ \frac{2\text{erfc}[\sqrt{\varepsilon(n_1^2 + 3(n_2+2/3)^2 + 4\zeta^2)}]}{\sqrt{n_1^2 + 3(n_2+2/3)^2 + 4\zeta^2}} \right\}$$

$$+ \frac{\cos(2n_1 \pi/3)}{\sqrt{n_1^2 + 3n_2^2}^{1/2}} \left( e^{2\pi\zeta\sqrt{n_1^2 + 3n_2^2}/3} \text{erfc}[\pi\sqrt{(n_1^2 + 3n_2^2)/(12\varepsilon)} + 2\zeta\sqrt{\varepsilon}] \right)$$

$$- e^{-2\pi\zeta\sqrt{n_1^2 + 3n_2^2}/3} \text{erfc}[\pi\sqrt{(n_1^2 + 3n_2^2)/(12\varepsilon)} - 2\zeta\sqrt{\varepsilon}] \right\} \right). \quad (A-12)$$