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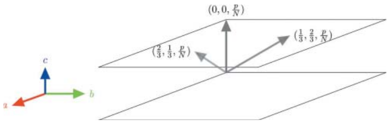

Diffraction enhancement of symmetry and modular structures

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Diffraction enhancement of symmetry (DES) is the phenomenon according to which the symmetry of the diffraction pattern of a crystal can be higher than the point symmetry of the structure that has produced it. The most well known example is that of Friedel's law, which is however violated in the presence of resonant scattering. This phenomenon is addressed in monoarchetypal modular structures and it is shown that a sufficient condition for DES is that both the module and the family of stacking vectors are invariant under an isometry that is not a symmetry operation for the structure. In general, DES is still observed in the presence of significant resonant scattering. The example of SiC polytypes, where the phenomenon has been confirmed experimentally, is studied in detail but the conclusions depend only on the symmetry of the layer and on the stacking vectors: the same applies therefore to all compounds sharing these features, like ZnS.

1. Introduction

The phenomenon called diffraction enhancement of symmetry (DES hereafter) is defined by its consequences: some structures may show a diffraction pattern whose point symmetry is higher than the point symmetry of the structure. DES occurs typically in modular structures, although not all structures giving rise to DES are modular structures: even purely artificial structures built by convolution of homometric objects can present DES. For example, Matsumoto simulated periodic structures with triclinic symmetry but tetragonal (Matsumoto, 2019*a*) or cubic (Matsumoto, 2019*b*) diffraction symmetry. DES has been investigated in the past in a series of papers which tried to develop a general approach (Iwasaki, 1972; Perez-Mato & Iglesias, 1977; Sadanaga & Ohsumi, 1975, 1979; Iglesias, 1979), but has received little attention since then.

Modular structures are built by juxtaposing one or more types of modules. The modules are three-dimensional components with periodicity in less than three independent directions (non-periodic bricks or blocks, monoperiodic rods or chains, diperiodic sheets or layers) that can ideally be described as cuts from structurally and chemically homogeneous parent structures (archetypes). Depending on whether the modules are obtained from a single archetype or from multiple archetypes, modular structures are classified as monoarchetypal (*e.g.* humite and lillianite, among many others) or polyarchetypal (*e.g.* saphirine-type compounds, built by layers of pyroxene and of spinel) (Ferraris *et al.*, 2008). Monoarchetypal modular structures are known as cell twins and include polytypes [for a recent review, see Umayahara & Nespolo (2020)]. A modular structure can ideally be analysed

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by a decomposition into its modules (of one or more types), their relative orientations (which are all equivalent in the example of SiC) and the set of vectors relating these modules. The complete symmetry of a modular structure is described by a groupoid, which is a more general algebraic structure than a group and includes the partial operations relating every pair of modules of the same kind (Nespolo *et al.*, 2020). DES occurs in modular structures when the point symmetry of the set of stacking vectors admits operations that do not occur in the point group of the structure. The purpose of this article is to give the basic principles of DES and apply them to simple modular structures where the phenomenon has been observed experimentally: silicon carbide polytypes. More complex structures will be analysed in the near future.

2. Preamble. Note on terminology

In the following we make reference to the interatomic vectors of a crystal structure, *i.e.* the collection of vectors relating each pair of atoms (of the same chemical species) in a crystal structure. A collection of vectors in which each vector occurs once is a *set*; if some vectors occur more than once, the collection is called a *multiset*; the number of times a vector occurs in the multiset is its *multiplicity*. The collection of vectors we consider is infinite (in the usual idealization of considering a crystal structure as infinite due to its periodicity) and each vector is associated with an ordered pair (i, j) of atoms or of modules. Such a collection is known as an *indexed family* or, for short, *family*. Therefore, in the following we adopt the term *vector family*, which is more precise than the term *vector set* introduced by Buerger (1950).

After fixing a coordinate system, an isometry is represented by a matrix-column pair $(\mathbf{R}, \mathbf{t})$, in which $\mathbf{R}$ is the 3×3 square matrix representing the linear part of the operation, and $\mathbf{t}$ is the 3×1 column representing its translation part.

3. Origin of DES

Sadanaga & Ohsumi (1975) reported that DES occurs when the family of all interatomic vectors in the crystal structure is invariant under a linear isometry that is not a symmetry operation of the structure. This conclusion results from the fact that, although the structure factor depends on the atomic positions, the measured intensities yield the square of the modulus of the structure factor, and this depends on the interatomic vectors.

The intensities measured in an X-ray diffraction experiment are indicated as $I(\mathbf{h})$, where $\mathbf{h}$ is the vector of coordinates in reciprocal space corresponding to the *hkl* reflection. Recall that the Laue indices *hkl* of a reflection are the integer coordinates of $\mathbf{h}$ with respect to the reciprocal basis (see Section 4). The intensity at a peak is actually distributed over a certain volume, the measured intensities are integrated over this volume and are then reduced to amplitudes $|F_{\rm o}(\mathbf{h})|$ of the (observed, indicated by the subscript) structure factors by the application of a number of experimental corrections, the phases being in general irretrievable. If $I(\mathbf{h}) = I(\mathbf{hR})$ for every $\mathbf{h}$, where $\mathbf{R}$ is the linear part of an isometry, then the diffraction pattern is invariant under $\mathbf{R}$. The intrinsic translation part of an isometry (*i.e.* the screw component of a screw rotation or the glide component of a glide reflection), if any, as well as possible centring translations, lead to systematic absences in the diffraction pattern. A translation of the whole structure influences only the phases, which are not retrieved from a conventional diffraction experiment. In the study of DES we thus only need to consider the linear parts of the isometries relating the modules.

From the diffraction intensity one obtains $|F_{\rm o}(\mathbf{h})|^2$:

$$\begin{aligned}\left|F_{\rm o}(\mathbf{h})\right|^2 &= F_{\rm o}(\mathbf{h})F_{\rm o}^*(\mathbf{h})\\ &= \sum_j \sum_k f_j f_k \exp\left(2\pi i\mathbf{h}\cdot\mathbf{r}_j\right)\exp(-2\pi i\mathbf{h}\cdot\mathbf{r}_k)\\ &= \sum_j f_j^2 + \sum_j \sum_{k\neq j} f_j f_k \exp\left[2\pi i\mathbf{h}\cdot\left(\mathbf{r}_j - \mathbf{r}_k\right)\right], \qquad (1)\end{aligned}$$

where j and k are running over the atoms in the unit cell, and f_j and f_k are the real-valued atomic scattering factors of the jth and kth atoms, respectively (where for notational convenience we suppressed that f_j and f_k depend on $\mathbf{h}$ via $\sin\vartheta/\lambda$, for ϑ Bragg's angle and λ the wavelength of the incident radiation). The term f_j^2 comes from the fact that for $j = k$ the exponentials cancel. Therefore, $|F_{\rm o}(\mathbf{h})|$, obtained from $I(\mathbf{h})^{1/2}$ after applying the necessary corrections, actually contains information about the vector family of interatomic vectors $\mathbf{r}_j - \mathbf{r}_k$, which was termed *vector set* by Buerger (1950) (see Section 2), not about atomic position vectors $\mathbf{r}_j$. If the whole family of interatomic vectors is invariant under some linear isometries that are not contained in the point group of the structure, this opens the possibility of observing DES. The universally known example is that of Friedel's law: because $\mathbf{h}\cdot(\mathbf{r}_j - \mathbf{r}_k) = -\mathbf{h}\cdot(\mathbf{r}_k - \mathbf{r}_j)$ and $f_j f^*_k = f_k f^*_j$, an X-ray diffraction pattern was considered centrosymmetric even when the structure is not (old textbooks state that diffraction 'adds' an inversion centre). Resonant scattering makes this conclusion untrue for most crystals. In the following we investigate the conditions under which additional symmetry of the vector family beyond the inversion may lead to DES.

4. Point space versus vector space. Vector family and Patterson function

Crystallographers make extensive use of two different spaces, the point space $\mathbb{E}^n$ (E for Euclidean, n being its dimension; our analysis is worked out for the relevant case $n = 3$ but is valid for general n) and the vector space $\mathbb{V}^n$. The former is the affine space where atoms exist, the latter is a vector space *sensu strictu* (Nebe, 2011) that comes into play in different ways (Nespolo & Souvignier, 2009):

(i) As the vector space underlying the point space $\mathbb{E}^n$ in which we find the translation vectors and the interatomic vectors. Its elements are commonly written with respect to a basis $(\mathbf{a}_1, \ldots, \mathbf{a}_n)$.

(ii) As the vector space containing face normals and reciprocal-lattice vectors. In this case its elements are usually written with respect to the reciprocal basis ($\mathbf{a}_1^*, \ldots, \mathbf{a}_n^*$) of ($\mathbf{a}_1, \ldots, \mathbf{a}_n$) defined by the relations $\mathbf{a}_i \cdot \mathbf{a}_j^* = \delta_{ij}$ (in physics, the convention $\mathbf{a}_i \cdot \mathbf{a}_j^* = 2\pi\delta_{ij}$ is more common, which avoids the factor 2π in the Fourier transform).

To emphasize that the structure factors are defined on the space spanned by the reciprocal basis ($\mathbf{a}_1^*, \ldots, \mathbf{a}_n^*$), we can write them, as customary in many textbooks, as a continuous function $F(\mathbf{r}^*)$. Bragg peaks correspond to a discrete set of $\mathbf{r}^*$ and are centred about positions having integer coordinates with respect to the reciprocal basis.

The relation between a set of points in $\mathbb{E}^n$ and the vector family of interatomic vectors in $\mathbb{V}^n$ has been exploited since long ago for the solution of crystal structures, namely in the form of the Patterson function (Patterson, 1934, 1935*a*,*b*). The Patterson function is the inverse Fourier transform T^{-1} of $|F_o(\mathbf{r}^*)|^2$ and is defined in $\mathbb{V}^n$:

$$\begin{aligned} P(\mathbf{u}) &= \rho(\mathbf{r}) * \rho(-\mathbf{r}) = \int_V \rho(\mathbf{r})\rho(\mathbf{u}+\mathbf{r})\,\mathrm{d}\mathbf{r} \\ &= T^{-1}\Big[\big|F_o(\mathbf{r}^*)\big|^2\Big] = \int_{V^*} \big|F_o(\mathbf{r}^*)\big|^2 \exp(-2\pi i\mathbf{r}^* \cdot \mathbf{u})\,\mathrm{d}\mathbf{r}^* \\ &= \frac{1}{V}\sum_h \big|F_o(\mathbf{h})\big|^2 \exp(-2\pi i\mathbf{h} \cdot \mathbf{u}), \qquad (2) \end{aligned}$$

where V is the volume of the unit cell and the symbol $*$ denotes a convolution. The passage from integral to summation is justified by the fact that, if one ignores the diffuse scattering between pairs of Bragg peaks, then the reciprocal space can be sampled in a discrete way by considering only those $\mathbf{r}^*$ that correspond to integer values of Laue indices. The peaks of the Patterson function are located at positions for which $\mathbf{r} + \mathbf{u}$ is a vector $\mathbf{r}_k$ locating an atom of the original structure, so that the vector $\mathbf{u}$ sampling the $\mathbb{V}^n$ space is actually restricted to interatomic vectors $\mathbf{u} = \mathbf{r}_k - \mathbf{r}_j$. Summarizing, there are three quantities that we will use in the following:

(i) The vector family, defined as the multiset of all interatomic vectors and expressed with respect to the basis ($\mathbf{a}_1, \ldots, \mathbf{a}_n$) of $\mathbb{V}^n$.

(ii) The peaks of the Patterson function which are centred on positions that correspond to the vectors belonging to the vector family.

(iii) The squares of the moduli of the structure factors, which contain information about the vector family; being a function of $\mathbf{h} = (hkl)$, they are expressed with respect to the reciprocal basis.

An early attempt to relate the Patterson map to the electron-density map had been made by Wrinch (1939). She simplified the problem by considering a set of discrete points and its Patterson representation, which corresponds to the vector family scaled by the associated intensities. The developments of Buerger (1950) constitute an extension of some basic ideas in the paper by Wrinch.

5. Modular structures that consist of translationally related modules

The electron-density map $\rho(\mathbf{r})$ of a modular structure which consists of translationally related identical modules with electron density $\rho_0(\mathbf{r})$ can be described as

$$\rho(\mathbf{r}) = \sum_n \delta(\mathbf{r} - \mathbf{o}_n) * \rho_0(\mathbf{r}), \qquad (3)$$

where $\mathbf{o}_n$ is the vector connecting the origin of the nth module to the origin of a common coordinate system (usually chosen as one of the $\mathbf{o}_n$). The sum $\Sigma_n\delta(\mathbf{r} - \mathbf{o}_n)$ is a sum of Dirac peaks with unit weight (*i.e.* the volume below each Dirac peak is 1). The Dirac function as the limiting case for a peak that is reduced to a single point is used here for convenience to simplify the forthcoming derivation. For the modular structure, the structure factor can be expressed as

$$\begin{aligned} \big|F(\mathbf{h})\big| &= \left|\int\left[\sum_n \delta(\mathbf{r} - \mathbf{o}_n) * \rho_0(\mathbf{r})\right] \exp(2\pi i\mathbf{h} \cdot \mathbf{r})\,\mathrm{d}\mathbf{r}\right| \\ &= \left|\int\left[\sum_n \delta(\mathbf{r} - \mathbf{o}_n) \exp(2\pi i\mathbf{h} \cdot \mathbf{r})\,\mathrm{d}\mathbf{r}\right]\right| \\ &\quad \times \left|\int \rho_0(\mathbf{r}) \exp(2\pi i\mathbf{h} \cdot \mathbf{r})\,\mathrm{d}\mathbf{r}\right|, \qquad (4) \end{aligned}$$

where the convolution theorem is used to obtain equation (4). Assuming that the origins $\mathbf{o}_n$ in the different modules are chosen in equivalent positions, an arbitrary interatomic vector $\mathbf{r}_j - \mathbf{r}_k$ can be written as $\mathbf{r}_j - \mathbf{r}_k = (\mathbf{r}_j - \mathbf{o}_j) - (\mathbf{r}_k - \mathbf{o}_k) + (\mathbf{o}_j - \mathbf{o}_k)$, which allows us to partition equation (4) in two terms, one, $F_T(\mathbf{h})$, containing the information about the stacking vectors, *i.e.* the vectors relating origins of each pair of modules in the structure, and the other, $F_M(\mathbf{h})$, related to the electron density of the module:

$$\begin{aligned} &\big|F(\mathbf{h})\big| = \big|F_T(\mathbf{h})\big| \times \big|F_M(\mathbf{h})\big| \\ &\begin{cases} F_T(\mathbf{h}) = \int \sum_n \delta(\mathbf{r} - \mathbf{o}_n) \exp(2\pi i\mathbf{h} \cdot \mathbf{r})\,\mathrm{d}\mathbf{r} = \sum_n \exp(2\pi i\mathbf{h} \cdot \mathbf{o}_n) \\ F_M(\mathbf{h}) = \int \rho_0(\mathbf{r}) \exp(2\pi i\mathbf{h} \cdot \mathbf{r})\,\mathrm{d}\mathbf{r}. \end{cases} \qquad (5) \end{aligned}$$

The Fourier transform of a monoarchetypal modular structure is given by the Fourier transform of the stacking sequence, which is a fringe function (Lipson & Taylor, 1958), modulated by the Fourier transform of the layer(s) (Takeda, 1967). The function can be non-zero for integral h and k (if the layer lattice is spanned by $\mathbf{a}$ and $\mathbf{b}$), *i.e.* on rods $(hk\nu)^*$ with $h, k \in \mathbb{Z}$, $\nu \in R$. It is possible to extract the Fourier transform of the module from the expression of the structure factor, which thus assumes the simple form of a product of the module transform and of the stacking sequence transform. Accordingly, the vector family can be factorized (in the sense of a direct product decomposition) into two components, the module vector family, which includes all the interatomic vectors within the module, and the stacking vector family, denoted by $\mathbf{S}$ in the following, which includes all the stacking vectors and is closed under taking opposites. For that, in an arbitrary interatomic vector $\mathbf{r}_j - \mathbf{r}_k$, $\mathbf{r}_j - \mathbf{o}_j$ and $\mathbf{r}_k - \mathbf{o}_k$ belong to the module vector family and $\mathbf{o}_j - \mathbf{o}_k$ to the stacking vector family $\mathbf{S}$. If both the module vector family and the stacking vector family are invariant under a linear isometry $\mathbf{R}$, then also the diffraction pattern of the modular structure is invariant under **R**, while **R** is not required to be a symmetry operation of the modular structure.

6. Resonant scattering

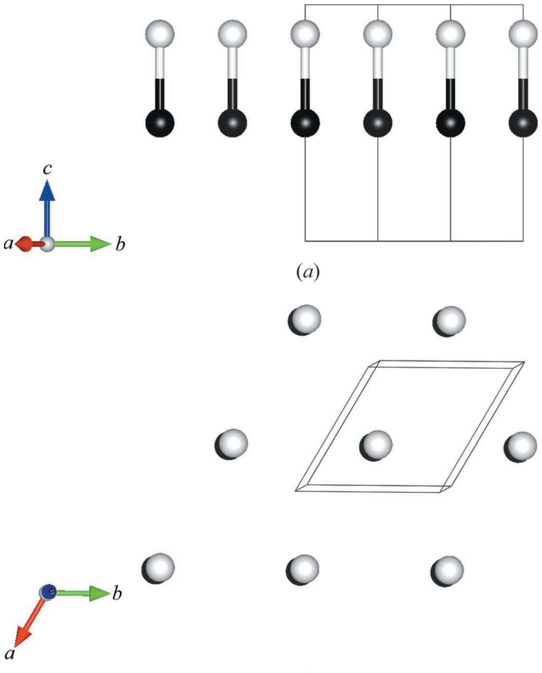
In the previous sections we have ignored the resonant scattering, whose contribution is significant for most crystal structures.

As the wavelength of the incident beam approaches the absorption edge of a particular element, the scattering power of that atom needs to be described by a physical model corresponding to a forced damped harmonic oscillator. The full, complex, scattering factor is written as

$$f = f_0 + \Delta f' + \mathrm{i}\Delta f'', \tag{6}$$

where f_0 is the classical scattering factor, *i.e.* the Fourier transform of the electron density, strongly dependent on $\sin\vartheta/\lambda$; the real and imaginary correction terms, $\Delta f'$ and $\Delta f''$, can for practical purposes be regarded as being independent of $\sin\vartheta/\lambda$ and in general small compared with f_0, at least for conventional diffraction experiments. The values of $\Delta f'$ and $\Delta f''$ change most at the absorption edge of the element in question. To simplify the notation, in the following we gather the real part of the scattering factor in a single term, $f' = f_0 + \Delta f'$, and drop the Δ from the imaginary part. The structure factor corresponding to the reciprocal vector **h** then reads

$$F(\mathbf{h}) = \sum_j \left(f'_j + \mathrm{i}f''_j\right) \exp 2\pi\mathrm{i}\mathbf{h}\cdot\mathbf{r}_j. \tag{7}$$



(*a*)

(*b*)

Figure 1
The SiC layer shown in projection along [210] (*a*) and (*b*) slightly off the [001] direction. The two crystallographic orbits of silicon and of carbon atoms have the same *x* and *y* coordinates but differ for the *z* coordinate; each Si–C pair forms therefore a dumbbell (*a*). In the (001) projection, they are exactly overlapped (*b*).

The observed structure factors obtained from the diffraction intensities, equation (1), are modified accordingly:

$$\begin{aligned}
\left|F(\mathbf{h})\right|^2 &= F(\mathbf{h})F*(\mathbf{h}) \\
&= \sum_j \sum_k \left(f'_j + \mathrm{i}f''_j\right)\left(f'_k - \mathrm{i}f''_k\right) \exp\left(2\pi\mathrm{i}\mathbf{h}\cdot\mathbf{r}_j\right) \\
&\quad\times \exp(-2\pi\mathrm{i}\mathbf{h}\cdot\mathbf{r}_k) \\
&= \sum_j \sum_k \left[\left(f'_j f'_k + f''_j f''_k\right) - \mathrm{i}\left(f'_j f''_k - f'_k f''_j\right)\right] \\
&\quad\times \exp\left[2\pi\mathrm{i}\mathbf{h}\cdot\left(\mathbf{r}_j - \mathbf{r}_k\right)\right] \\
&= \sum_j \left|f_j\right|^2 + \sum_j \sum_{k\neq j} \left[\left(f'_j f'_k + f''_j f''_k\right) - \mathrm{i}\left(f'_j f''_k - f'_k f''_j\right)\right] \\
&\quad\times \exp\left[2\pi\mathrm{i}\mathbf{h}\cdot\left(\mathbf{r}_j - \mathbf{r}_k\right)\right].
\end{aligned} \tag{8}$$

The vector family **S** consists of all the vectors of the form $\mathbf{r}_j - \mathbf{r}_k$. Let us now assume that **R** is a point group operation for the vector family **S**, but not for the structure. In other words, it is an isometry that maps a vector $\mathbf{r}_j - \mathbf{r}_k$ to another one $\mathbf{r}_l - \mathbf{r}_m \in \mathbf{S}$ and we now consider its effect on equation (8). By introducing $\mathbf{R}(\mathbf{r}_j - \mathbf{r}_k) = \mathbf{r}_l - \mathbf{r}_m$ in equation (8) we get

$$\begin{aligned}
\left|F(\mathbf{hR})\right|^2 &= \sum_j \left|f_j\right|^2 + \sum_j \sum_{k\neq j} \left[\left(f'_j f'_k + f''_j f''_k\right) - \mathrm{i}\left(f'_j f''_k - f'_k f''_j\right)\right] \\
&\quad\times \exp\left[2\pi\mathrm{i}\mathbf{h}\cdot\mathbf{R}\left(\mathbf{r}_j - \mathbf{r}_k\right)\right] \\
&= \sum_j f_j^2 + \sum_j \sum_{k\neq j} \left[\left(f'_j f'_k + f''_j f''_k\right) - \mathrm{i}\left(f'_j f''_k - f'_k f''_j\right)\right] \\
&\quad\times \exp\left[2\pi\mathrm{i}\mathbf{h}\cdot(\mathbf{r}_l - \mathbf{r}_m)\right].
\end{aligned} \tag{9}$$

Because $\mathbf{R}(\mathbf{r}_j - \mathbf{r}_k) = \mathbf{r}_l - \mathbf{r}_m$, atoms *j* and *l* are of the same chemical species, and the same holds for atoms *k* and *m*. Therefore, the corresponding scattering factors in equation (9) become

$$\begin{aligned}
\left|F(\mathbf{hR})\right|^2 &= \sum_l \left|f_j\right|^2 + \sum_l \sum_{m\neq l} \left[\left(f'_l f'_m + f''_l f''_m\right) - \mathrm{i}\left(f'_l f''_m - f''_l f'_m\right)\right] \\
&\quad\times \exp\left[2\pi\mathrm{i}\mathbf{h}\cdot(\mathbf{r}_l - \mathbf{r}_m)\right],
\end{aligned} \tag{10}$$

which is identical to equation (8), the only difference being the symbol used for the running indices (*l*,*m* instead of *j*,*k*). Therefore, DES is still observed in the presence of significant resonant scattering.

7. Symbolic representation of SiC polytypes

SiC polytypes are built by the stacking of SiC layers with symmetry *P*(6)*mm* [notation after Dornberger-Schiff (1959)] or *p*6*mm* [notation after Kopský & Litvin (2010)], and fractional atomic coordinates Si$(\frac{2}{3},\frac{1}{3},\frac{1}{2})^{\mathrm{T}}$ and C$(\frac{2}{3},\frac{1}{3},\frac{7}{8})^{\mathrm{T}}$ (Fig. 1), where the superscript T means that the coordinates have to be written as a column vector, according to the crystallographic standards. Because of the tetrahedral coordination of each type of atom ($\mathrm{SiC_4}$ and $\mathrm{CSi_4}$), projection of the carbon and silicon atoms along the [001] direction gives the same positions in the (001) plane, hence the partial operation $\tau_{k+1,k}$ mapping a layer onto the next one, $\mathrm{L}_k \Rightarrow \mathrm{L}_{k+1}$, can be taken as a translation which has $(\frac{1}{3},\frac{2}{3})$ or $(\frac{2}{3},\frac{1}{3})$ as its components in the (001)

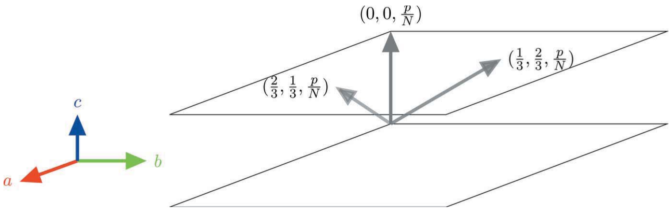


Figure 2
The three possible values of $t_{p,0}$. The (001) components can only be (0,0), $(\frac{1}{3},\frac{2}{3})$ or $(\frac{2}{3},\frac{1}{3})$, and the component along [001] is p/N, where N is the number of layers in the polytype.

plane. The symbol $\Rightarrow$ emphasizes that $\tau_{k+1,k}$ is a partial operation, *i.e.* an operation that is applied only to the layer L_k, but not to layers L_m for $m \neq k$. The order of the indices in $\tau_{k+1,k}$ is chosen such that composition is only possible if matching indices meet, *e.g.* $\tau_{k+2,k+1} \circ \tau_{k+1,k} = \tau_{k+2,k}$. In the concrete situation $\tau_{k+1,k}$ is the translation by a translation vector $t_{k+1,k}$ so that composition corresponds to the addition of the translation vectors. The partial operation mapping a layer L_k to a layer L_{k+p} that is p positions apart ($L_k \Rightarrow L_{k+p}$) is therefore the translation by the vector $t_{k+p,k}$ obtained as the vector sum of the stacking vectors relating adjacent modules:

$$t_{k+p.k} = \sum_{i=k}^{k+p-1} t_{i+1,i}. \tag{11}$$

The resulting vector can be adjusted by lattice vectors in the plane of periodicity, which leaves only the three possibilities (0,0), $(\frac{1}{3},\frac{2}{3})$ and $(\frac{2}{3},\frac{1}{3})$ for the (001) components of $t_{p,0}$ (see Fig. 2). Assuming a periodic stacking in which the stacking sequence repeats itself after N layers (so that layers N positions apart perfectly project on each other along the direction perpendicular to the layer plane) the component of $t_{k+p,k}$ along [001] is p/N. A stacking vector will be said to be of type 0, type 1 or type 2 according to whether its fractional component is $0, \frac{1}{3}$ or $\frac{2}{3}$ along [100].[1] An N-layer polytype is identified by the stacking symbol $x_0x_1x_2\ldots x_{N-1}$, where x_i is the type of stacking vector; each x_i can only take the values 1 or 2 because type 0 would interchange carbon and silicon atoms. Since the type of a stacking vector is determined by the [100] component, the type of $t_{k+p,k}$, denoted by $T_{k+p,k}$, is then simply the sum of the x_i in the stacking symbol, reducing the result to the remainder of division by 3:

$$T_{k+p.k} = \sum_{i=k}^{k+p-1} x_{i+1,i} \bmod 3. \tag{12}$$

The stacking vector family **S** can be subdivided into three subfamilies, by the type of translation. The members of the subfamily **S**(0) of type 0 stacking vectors, together with the vectors obtained from them by layer lattice vectors, point to the corners of a hexagonal unit cell; in that way, the full vector family generated by **S**(0) through full lattice translations exhibits hexagonal symmetry. On the other hand, the subfamilies **S**(1) and **S**(2) correspond to vectors pointing to the nodes rhombohedrally centring a hexagonal unit cell, again adjusting by layer lattice translations; the two full vector families generated by **S**(1) and by **S**(2), respectively, through full lattice translations each exhibit trigonal symmetry. Concretely, the subfamily **S**(1) contains stacking vectors $t(\frac{1}{3},\frac{2}{3},p/N)$, $t(-\frac{2}{3},-\frac{1}{3},p/N)$ or $t(\frac{1}{3},-\frac{1}{3},p/N)$ which are related by a threefold rotation, whereas the subfamily **S**(2) contains stacking vectors $t(\frac{2}{3},\frac{1}{3},p/N)$ or $t(-\frac{1}{3},\frac{1}{3},p/N)$ or $t(-\frac{1}{3},-\frac{2}{3},p/N)$.

For a structure built from N layers which then repeat periodically, the sum over the symbols x_i in the stacking sequence must be 0 when reduced modulo 3, because we distinguish three types of layers A, B and C depending on whether the fractional component of the origin is $0, \frac{1}{3}$ or $\frac{2}{3}$ along [100] (where it is customary to choose the origins such that the period starts with an A layer). Denote by $M_1(1)$ and $M_1(2)$ the number of x_i in the stacking symbol with $x_i = 1$ and $x_i = 2$, respectively, and let $\Delta = M_1(1) - M_1(2)$ be the difference between the number of type 1 stacking vectors and the number of type 2 stacking vectors. Then due to $2\ M_1(2) = -M_1(2) \pmod 3$ we must have $M_1(1) + 2\ M_1(2) = M_1(1) - M_1(2) = \Delta = 0 \pmod 3$. For example, a structure with stacking sequence 112112112 ($N = 9$), abbreviated as $(112)_3$, is valid with layer period ABCBCACAB (the next layer being again A) but cannot be reduced to the sequence 112 ($N = 3$) with $T_{2,0} = 1+1+2 = 1 \pmod 3$ [equation (12)] which does not represent a periodic structure (the second block BCA of three layers differs from the first block ABC). The only polytypes with $N = 3$ layers are those whose stacking sequence is 1_3 or 2_3, corresponding to the periods ABC and ACB.

The four possible types of space groups in which SiC polytypes crystallize ($F\bar{4}3m$, $R3m$, $P3m1$ and $P6_3mc$) consist of non-centrosymmetric groups.

(*a*) $F\bar{4}3m$ is realized only for the sequence 1_3 or its equivalent 2_3.

(*b*) Stacking sequences corresponding to a space group of type $R3m$ contain three subsequences of length $N/3$, where N is the number of layers in the period of the polytype. In the subsequences the difference Δ between the number of 1's and the number of 2's is not a multiple of 3, otherwise the period would only consist of $N/3$ layers.

(*c*) A space group of type $P6_3mc$ is realized when $t_{p+1,p} + t_{p+N/2+1,p+N/2} = 0 \pmod 3$, *i.e.* stacking vectors half a period apart are of opposite types. This is because of the action of the 6_3 screw rotation. For example, for $N = 10$, the three sequences 1111122222, 1112122212 and 1121122122 all correspond to structures with space groups of type $P6_3mc$. In the following we will refer to this restriction as the '(p, $p+N/2$) rule'.

(*d*) All the other sequences result in a space group of type $P3m1$.

8. DES in SiC polytypes

All four possible types of space groups in which SiC polytypes crystallize are non-centrosymmetric. Two of them ($F\bar{4}3m$ and $P6_3mc$) are hemihedral and cannot be extended beyond the holohedry, because these holohedries do not possess a crys-

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[1] Type 1 and type 2 correspond, respectively, to + and − in Hägg's notation (Hägg, 1943), ∇ and Δ in Nabarro-Frank's notation (Frank, 1951) or 1 and 0 symbols used by Dornberger-Schiff & Farkas-Jahnke (1970).

tallographic supergroup. For these two types of space group the only additional isometry is the inversion, but the layers are not centrosymmetric so that DES cannot occur. A third type of space group, $R3m$, is also hemihedral but in principle could be enhanced to cubic symmetry by a specialized metric (α = 60° or 109.47°). This is not realized in any SiC polytype. The last type of space group, $P3m1$, is tetartohedral; polytypes crystallizing in a space group of this type can therefore show DES to hexagonal symmetry. The additional isometry is a rotation of order two (or of order six, with its square being a threefold rotation already present in the point group of the polytype); consequently, a necessary condition for an additional isometry to show up in the vector family is that the number of layers must be even.

Previous studies have shown that most structures where DES occurs correspond to either of two conditions on the stacking sequence:

(i) The Ramsdell condition. According to Ramsdell & Kohn (1951), the diffraction pattern of a trigonal polytype of SiC has hexagonal symmetry if its stacking sequence is made up of two parts which are mirror images of each other.

(ii) The two-layers condition. SiC polytypes which do not satisfy the Ramsdell condition can still exhibit hexagonal symmetry of their diffraction pattern if the stacking sequence is composed from two subsequences, each satisfying the Ramsdell condition. One example is shown in Fig. 3, where the two subsequences indicated as X and Y both satisfy the Ramsdell condition although the whole sequence built as XYXYYX from the subsequences does not. The precise mechanism of how the two-layers condition causes DES is explained by Sadanaga (1973) and Marumo & Saito (1972).

These two conditions do not exhaust all the possibilities. Tsukimura (1980) identified an example of DES which does not satisfy either condition, indicating that necessary conditions for DES are difficult to formulate. Below we present a generalization of the results obtained by previous researchers.

As seen above, a sufficient condition for DES is the existence of an isometry **R** which is a symmetry operation for the stacking vector family **S** and the module, but not for the polytype structure itself. In the case of SiC structural models of space group type $P3m1$ this means that the stacking vector family **S** and the module both present sixfold rotational symmetry. The SiC layer does have symmetry $P(6)mm$; we have to identify the conditions under which the stacking vector family **S** shows hexagonal symmetry too. This corresponds to finding the conditions on the sequence of symbols which result in hexagonal symmetry of the stacking vector family. Due to the factorization of the structure factor into the part $F_{\rm M}(\mathbf{h})$ for the module and the part $F_{\rm T}(\mathbf{h})$ for the stacking vector family, in this case the sufficient condition is also a necessary condition, since $F_{\rm M}(\mathbf{h})$ is known to be invariant under the sixfold rotation. In general, one could imagine situations (most likely artificially constructed) in which neither the module nor the stacking vector family **S** is invariant under a symmetry operation **R**, but the product $|F_{\rm M}(\mathbf{h})| \cdot |F_{\rm T}(\mathbf{h})|$ is.

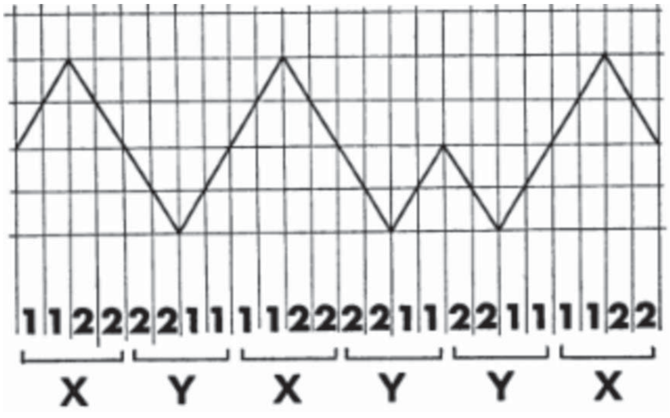

Figure 3
Example of a stacking sequence in which two subsequences, indicated as X and Y, both satisfy the Ramsdell condition although the whole sequence does not.

The stacking vector mapping layers which are p positions apart has been defined in equation (11). For each value of p, the multiplicity of stacking vectors of type 0, 1 and 2 is hereafter indicated as $\mathrm{M}_p(0)$, $\mathrm{M}_p(1)$, $\mathrm{M}_p(2)$, respectively.

The stacking vector subfamily $\mathbf{S}(0)$ already exhibits hexagonal symmetry, independently from the multiplicity $\mathrm{M}_p(0)$. On the other hand, the stacking vector subfamilies $\mathbf{S}(1)$ and $\mathbf{S}(2)$ exhibit only trigonal symmetry. In order for the stacking vector family **S** to exhibit hexagonal symmetry it is therefore necessary that the union $\mathbf{S}(1) \cup \mathbf{S}(2)$ shows hexagonal symmetry. Two stacking vectors, one of type 1 and one of type 2, are oriented $(2n+1)60°$ apart ($n \in \mathbb{Z}$); if $\mathrm{M}_p(1) = \mathrm{M}_p(2)$ for every value of p, then $\mathbf{S}(1) \cup \mathbf{S}(2)$ includes a twofold rotation interchanging type 1 and type 2 stacking vectors. This means that under the condition $\mathrm{M}_p(1) = \mathrm{M}_p(2)$ for all p, the stacking vector family **S** exhibits hexagonal symmetry.

9. Polytypes exhibiting DES

In order to identify polytypes exhibiting DES one has to find the stacking sequences satisfying the condition $\mathrm{M}_p(1) = \mathrm{M}_p(2)$ for all p. To find the values of $\mathrm{M}_p(X)$, $X = 0$, 1 or 2, one has to compute the stacking symbols $\mathrm{T}_{k+p,k}$ corresponding to the stacking vectors $\mathrm{t}_{k+p,k}$ [equation (12)] for each value of k going from 0 to $N-1$. By definition, $\mathrm{M}_N(0) = N$, $\mathrm{M}_N(1) = \mathrm{M}_N(2) = 0$, because N is the number of layers in the period. Let us work out a simple example, a six-layer polytype with stacking sequence $x_0x_1x_2x_3x_4x_5 = 111222$, for the case $p = 3$ layers apart. Note that all computations with the stacking symbols are performed modulo 3, but to simplify notation we omit the (mod 3) in this section. It is convenient to imagine the stacking sequence being extended into a second period $x_0x_1x_2x_3x_4x_5x_0x_1x_2x_3\ldots$ so that also the stacking vectors $\mathrm{t}_{k+p,k}$ can be easily read off by reducing $k+p$ modulo N. The six stacking vectors of this type are then found to be:

$$\mathrm{t}_{3,0} = \mathrm{t}_{1,0}+\mathrm{t}_{2,1}+\mathrm{t}_{3,2},\ \mathrm{T}_{3,0} = x_0 + x_1 + x_2 = 1+1+1 = 0;$$
$$\mathrm{t}_{4,1} = \mathrm{t}_{2,1}+\mathrm{t}_{3,2}+\mathrm{t}_{4,3},\ \mathrm{T}_{4,1} = x_1 + x_2 + x_3 = 1+1+2 = 1;$$
$$\mathrm{t}_{5,2} = \mathrm{t}_{3,2}+\mathrm{t}_{4,3}+\mathrm{t}_{5,4},\ \mathrm{T}_{5,2} = x_2 + x_3 + x_4 = 1+2+2 = 2;$$
$$\mathrm{t}_{6,3} = \mathrm{t}_{0,3} = \mathrm{t}_{4,3}+\mathrm{t}_{5,4}+\mathrm{t}_{0,5},\ \mathrm{T}_{0,3} = x_3 + x_4 + x_5 = 2+2+2 = 0;$$
$$\mathrm{t}_{7,4} = \mathrm{t}_{1,4} = \mathrm{t}_{5,4}+\mathrm{t}_{0,5}+\mathrm{t}_{1,0},\ \mathrm{T}_{1,4} = x_4 + x_5 + x_0 = 2+2+1 = 2;$$
$$\mathrm{t}_{8,5} = \mathrm{t}_{2,5} = \mathrm{t}_{0,5}+\mathrm{t}_{1,0}+\mathrm{t}_{2,1},\ \mathrm{T}_{2,5} = x_5 + x_0 + x_1 = 2+1+1 = 1.$$

Table 1
Number of stacking sequences of SiC polytypes exhibiting DES.

No. of layers	No. of distinguishable stacking sequences	No. of sequences with space group of type $P6_3mc$	No. of $P3m1$ models where DES occurs	% of polytypes showing DES	No. of stacking sequences that are missed by Ramsdell condition and two-layers condition
2	1	1	0	0.00%	0
4	1	1	0	0.00%	0
6	3	1	2	66.67%	0
8	8	2	4	50.00%	0
10	25	3	12	48.00%	0
12	75	5	26	34.67%	2
14	245	9	60	24.49%	4
16	800	16	124	15.50%	12
18	2700	28	282	10.44%	40
20	9225	51	562	6.09%	78
22	32065	93	1152	3.59%	148
24	112632	170	2452	2.18%	460
26	400023	315	4716	1.18%	(not computed)
28	1432613	585	9762	0.68%	(not computed)
30	5170575	1091	19712	0.38%	(not computed)

The result is $M_3(1) = M_3(2) = 2$. In the same way, one obtains $M_1(1) = M_1(2) = 3$, $M_2(1) = M_2(2) = 2$, $M_4(1) = M_4(2) = 2$, $M_5(1) = M_5(2) = 3$. The stacking vector family for this polytype possesses sixfold rotational symmetry.

The number of possible polytypes increases rapidly with N. The necessary calculations are however reduced by showing that only half of the stacking sequence needs to be taken into account. The type of stacking vector corresponding to a full period, $T_{N,0}$, is 0 by definition. Therefore

$$T_{N,0} = \sum_{i=0}^{N-1} x_i = M_1(1) + 2M_1(2) = 0.$$

By putting $p = 1$ in the condition $M_p(1) = M_p(2)$ for DES, and remembering that $1+2 = 0 \pmod 3$ (the sum of a stacking vector of type 1 and one of type 2 is a stacking vector of type 0), we obtain

$$\begin{aligned} T_{N,0} &= \sum_{i=0}^{N-1} x_i = M_1(1) + 2M_1(1) = M_1(1)(1+2) \\ &= M_1(1)0 = 0. \end{aligned} \tag{13}$$

Let us break up the sequence into two subsequences of lengths p and $N-p$. These two subsequences can correspond, respectively, to the layers in the intervals $(0, p-1)$ and $(p, N-1)$; $(1, p)$ and $(p+1, N)$; $(2, p+1)$ and $(p+2, N+1)$ and so on; the general term is $(n, p+n-1)$ and $(n+p, N+n-1)$. The type of stacking vectors for the two subsequences is immediately obtained by remembering equation (13):

$$\begin{aligned} T_{N,0} &= T_{n+p,n} + T_{N+n,n+p} = 0 \\ T_{n+p,n} &= \sum_{i=n}^{n+p-1} x_i \\ T_{N+n,n+p} &= \sum_{i=n+p}^{N+n-1} x_i. \end{aligned} \tag{14}$$

The two subsequences can therefore be either one of type 1 and the other of type 2, or both of type 0. Hence, for every value of n, $T_{n+p,n} = -T_{N+n,n+p}$. As a consequence, for a given p the number of stacking symbols $T_{n+p,n} = 1$ is equal to the number of stacking symbols $T_{N+n,n+p} = 2$. But the number of stacking symbols $T_{n+p,n}$ when n runs from 0 to $N-1$ is simply M_p and the number of stacking symbols $T_{N+n,n+p}$ when n runs from 0 to $N-1$ is M_{N-p}. The result is therefore that $M_p(1) = M_{N-p}(2)$, $M_p(2) = M_{N-p}(1)$ and $M_p(0) = M_{N-p}(0)$. This result allows us to restrict the calculation of $M_p(0)$, $M_p(1)$, $M_p(2)$ to values up to $N/2$. Therefore calculating through $p = 2$ to $N/2$ is sufficient to examine the condition for DES to occur ($p = 1$ is simply the sequence $x_0x_1x_2\ldots x_{N-1}$ which has to contain equally many 1's and 2's for the structure to have period N). Geometrically, the property expresses that going p layers up by a type 1 stacking vector is the same as going p layers down by a type 2 stacking vector.

Concretely, the procedure to identify stacking sequences of polytypes exhibiting DES is the following:

(i) Identify the stacking sequences that satisfy the condition $M_1(1) = M_1(2)$.

(ii) Pick up those stacking sequences that satisfy the condition $M_p(1) = M_p(2)$ for all p.

(iii) Eliminate the candidates that correspond to a space group of type $P6_3mc$.

The results are stacking sequences corresponding to a space group of type $P3m1$ that show sixfold diffraction symmetry. It is mainly a combinatorial computation where sequences which differ by a choice of the origin or correspond to shorter periods have to be eliminated beforehand. For example, in the case of $N = 10$, sequences 1111122222, 1111222221, 1112222211 *etc*. actually belong to one and the same stacking, presented with a different choice of the origin. Sequences like 1212121212 are actually repetitions of a short period (in this example five periods of the sequence 12). One can select a distinguished origin by choosing the cyclic shift of the sequence which is lexicographically smallest. At the same time, a sequence coinciding with one of its cyclic shifts is seen to have a shorter period and is thus removed. Polytypes and their images by $2_{[001]}$ have been separately counted here: for example, sequences 1112211222 and 2221122111 are considered as distinguishable. Filtering the sequences in this way, one obtains 25 genuine stacking sequences of length $N = 10$. Of these, 15 present sixfold symmetry in the diffraction pattern, of which only three have the sixfold symmetry also in their structural model. Therefore, 12 of the 25 stacking sequences do exhibit DES, a surprisingly high proportion. The results (up to 30 layers) are shown in Table 1. If we compute the function $\ln(D)/N$, where D is the number of polytypes showing DES and N the number of layers, we find a trend showing a rapid

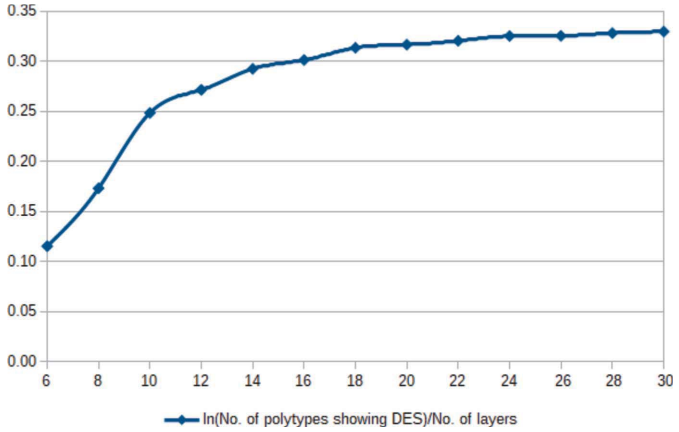

Figure 4
Representation of the function $\ln(D)/N$, where D is the number of polytypes showing DES and N the number of layers (data from Table 1). The trend shows a rapid convergence towards a constant value, indicating an asymptotically exponential growth for the number of polytypes exhibiting DES.

convergence towards a constant value, indicating an asymptotically exponential growth for the number D of polytypes exhibiting DES (Fig. 4). In Table 1, we have also listed the number of stacking sequences that are missed by the Ramsdell condition and the two-layers condition. Just as the total number of polytypes showing DES, the number of stacking sequences missed by these two well known conditions increases exponentially with the number of layers.

10. Conclusions

Diffraction enhancement of symmetry in modular structures is observed when an isometry is a symmetry operation for the module vector family and for the stacking vector family but not for the structure itself. SiC polytypes are modular structures built by the stacking of polar layers with the topology of close packings and hexagonal symmetry. Diffraction enhancement of symmetry is still observed in the presence of significant resonant scattering. It turns out that only polytypes crystallizing in one of the four possible space-group types, namely $P3m1$, can exhibit DES. Identifying stacking sequences of these polytypes is essentially a combinatorial problem; results indicate that both the total number of polytypes and the number of polytypes exhibiting DES increase exponentially with the number of layers, but with a smaller base for the polytypes with DES so that their percentage decreases rapidly. The results obtained depend only on the symmetry of the layer and on the stacking vectors: they apply therefore to all the compounds sharing these features, like *e.g.* ZnS.

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