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Analysis of one-dimensional disordered structures by simulation technique

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Herein, we report a study on one-dimensional disordered structures (ODDS) in close packed (cp) crystals by the Monte Carlo computer simulation technique. Calculations of diffraction intensity distributions along the 10.L reciprocal lattice row from: 5T, 8H(44) and 12R(31)$_3$ structures with deformation stacking faults (SFs) are presented. In particular, using the simple frequency function of fault to fault distances, both random and non-random distributions of SFs are considered. Distinctive features of the diffraction patterns corresponding to the chosen examples of transformations from the parent structures 5T, 8H(44) and 12R(31)$_3$ into other polytypes are discussed in detail.

Keywords: polytypes, stacking faults, one-dimensional disorder, solid-state transformation, Monte Carlo.

1. Introduction

The essentially small SF energy in cp and layered structures follows from both theoretical calculations and experimental data. The tendency for the formation of SFs is a common feature of a broad class of materials known as polytypes (cp and layer structures). Extensive work in last five decades confirmed that SFs do play a decisive role in the formation of polytypes and the solid-state transformation between them. The presence of SFs in cp structures destroys the periodicity along the stacking direction axis, thus resulting in one-dimensional disorder structures, and producing characteristic diffraction effects. Random SFs may give rise to the following effects: shift, broadening, asymmetry of diffraction maxima, and redistribution of integrated intensity. The general theory of X-ray diffraction by cp crystals with SFs (ODDS) has been developed since early 1940s. But conventional methods (random-walk technique, difference equation or matrix-equation methods) even if applied to the structures with a small concentration and/or random distribution of SFs proved to be mathematically cumbersome, and are applied to the limited number of rather simple cp structures.

However, a number of cp inorganic structures like SiC, ZnS, CdI$_2$ frequently contain a very high concentration of SFs, which are not distributed totally at random [1]. In such cases, the final results arrived at obtained by earlier workers (conventional methods) break down.

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Solid state transformation from one small period polytype into another, in materials like SiC, ZnS, CdI$_2$ [1], cobalt and its alloys [2, 3], and martensites of copper-based alloys [4], take place through nucleation and propagation of SFs on the basal plane. The diffraction intensity distributions from the intermediate states for few model transformations (2H→3C, 3C→2H, 2H→4H, 2H→6H) [1, and literature cited therein] were calculated. However, due to mathematical difficulties, in each case a separate analytical solution had to be elaborated. Thus, in the literature there is lack of appropriate solutions for high period polytypes undergoing phase transformations.

The diffraction intensity distributions from ODDS can be easily calculated due to development of Monte Carlo technique [5], first proposed in the earlier studies works [6-8]. The aim of this work is to demonstrate the value of the technique in the calculation of diffraction intensity distribution from high period polytypes with SFs, and from the intermediate states of phase transitions from these polytypes. Because of the limited scope of this article, three chosen structures, i.e., 5T, 8H(44), and 12R(13) (for polytypes notation see [1, 9]) with only one kind of SFs, viz., deformation SFs exemplify our recent results.

2. Calculation of Intensity Distribution

The proposed calculations of the intensity distributions for ODD structures are based upon the following widely commonly accepted assumptions:

1° The crystal is free of other distortions.
2° The scattering power is the same for all cp layers.
3° There is no change in the layer spacings at the faults.
4° The faults extend over entire cp planes.

The structure factor of the structure built with translationally equivalent cp layers is a product of two functions: $F(H,K,L) = F_o(H,K,L) \times S(H,K,L)$, where $F_o(HKL)$ is the normal structure factor for a unit layer. The $S(H,K,L)$ depends strictly and only on the layer stacking sequence, thus $S(H,K,L)$ functions for different materials, e.g. ZnS or SiC, but for the same polytype or a given sequence of layers are exactly the same. $|S(1,0,L)|^2$ values for N cp transitionally equivalent layers can be calculated in the following way:

$$|S(1,0,L)|^2 = A^2 + B^2; \quad A^2 = \Sigma \cos 2\pi \left( L \cdot k/N + m_k \cdot 1/3 \right) ; \quad B^2 = \Sigma \sin 2\pi \left( L \cdot k/N + m_k \cdot 1/3 \right)$$

where $m_k$ depends on the kind of the layers; $m_k = 0, 1, -1$ when A-, B-, C-type of layer (for notation see [9]) is on k positions in the given sequence of layers, respectively. $H, K$ and $L$ are hexagonal indices.
As previously [5], the crystal is considered to be an ensemble consisting of 500 to 5000 systems; each system being a sequence of $N=512$ cp layers. The layer sequences are ‘grown’ in the computer, layer by layer, using a random number generator. Faults are introduced in a sequential manner, i.e., from one end of the stuck of layers towards the other. Intensity distribution along $10.6 \leq L/N \leq 0.6$, is computed as an average intensity distribution scattered from all the systems in the ensemble in the following order. First, using the Monte Carlo procedure, systems composing a statistical ensemble are generated. For each system $|S(1,0,L)|^2$ are determined by formula equation (1), then $|S(1,0,L)|^2_{Avr}$ values are multiplied by $|F_0(L)|^2$ determined, as in the earlier work [5], for $Zn_{0.7}Cd_{0.3}Se$. Finally, the intensity is corrected by usual Lorentz-polarisation factor, and to account for the instrumental resolution, the calculated profiles are convoluted with Gaussians’ of full width at half maximum (FWHM) equal to 0.012.

3. Statement of the model

Deformation (or transformation) fault (DF) is introduced into the crystal when one part of structure is displaced with respect to the other (for SF classification systems, see [1]). The stacking sequences corresponding to the isolated-deformation faults in 5T, 8H(44) and 12R(13) structures in $hc$ symbolic notations [9] are shown in table 1.

Generally, in high period polytypes four different DF sites can be distinguished (see the table). Although by symmetry, the ‘$ch$’- and ‘$hc$’-types must be the same. The early diffraction theories do not differentiate DFs dependent upon fault sites. We will use denotation DF (as earlier) when following the conventional approach. However, deformation faults occurring between different pairs of layers ($cc$, $ch$, and $hh$) lead to layer configurations which are not equivalent energetically. Structure study of the low-temperature phase of lithium metal (9R($hhchhc$chhc$) structure with deformation SFs) showed that it is necessary to distinguish between ‘$hh$’- and ‘$ch$’- type DF in order to satisfactory match the calculated intensity distributions with those experimentally observed [6]. Following the approach in [6] we will denote the three kinds of faults as ‘$hh$’-type DF, ‘$ch$’- type DF, and ‘$cc$’-type DF, respectively.

The diffraction intensity distributions from modelled structures are based upon the frequency functions (FF) defined before [5]:

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\[ P(j) = \begin{cases} 
\gamma(1-\gamma)^{j-1} & \text{for } j < R \\
\beta(1-\gamma)^{R-1} & \text{for } j = R \\
\alpha(1-\beta)(1-\gamma)^{R-1}(1-\alpha)^{j-R-1} & \text{for } j \geq R 
\end{cases} \]  

(2)

where \( R \) is the most probable distance, in layer units, between the nearest SFs. The three parameters \( \beta, \alpha \) and \( \gamma \) define these probabilities: the probability of SFs at R-layer separation, the probability of SFs occurred at more than at R-layer separation, and the probability of SFs occurring at smaller than R-layer separation, respectively.

Using the above FF enables to embrace including, as special cases, conventional solutions known from earlier works ([5], and literature cited there). For example, parameters \( \alpha = \beta = \gamma \) give a model of a structure with random SFs. The simplest model of non-random SFs arises from assumptions \( R>1, \gamma = 0 \) and \( \alpha = \beta \). which means a strong repulsion between SFs at distances \( j<R \) and uniform SFs disposition, characterized by parameter \( \alpha \), at distances \( j \geq R \). The assumption \( \gamma > \alpha = \beta \) results in a model (not considered in this work) of strong attraction.

4. Application and discussion

4.1. Random stacking faults

The calculated variation of intensity distribution for 5T, 8H(44) and 12R(13)_3 structures with increasing content of random deformation SFs (conventional approach, equal probabilities of \('cc'-, \('ch'-, \('hc'-) and \('hh'\)-type DF) are shown in figure 1.

[insert figure 1 about here]

For 5T, 8H, and 12R structures, for with a small content of SFs there is not any shift of peaks and all peaks are equally broadened. This agrees well with conventional theories of 8H(44) [10] and 12R(13)_3 [10, 11] structures (the two works assume small SFs content). However, as \( \alpha \) reaches to 0.05, reflections of parent 12R\(^+\) structure are accompanied by reflections of its twin 12R\(^-\) structure (three small but discernible peaks, at \( L/N=-5/12, -1/12, \) and \( 1/12 \), on the bottom intensity curve of figure 1c) while the conventional solutions do not predict their presence on the diffraction pattern. In literature, there is lack of relevant solutions for 5T structures. For all three considered structures, it is evident from figure 1 (middle rows), that as \( \alpha \) increases from 0.05 to 0.2, the background intensifies at the expense of broadening and decreasing peaks. The probability \( \alpha=0.5 \) results in the most disordered structure with hexagonality \( \alpha_h=0.5 \) (equal probability of occurrence of \( h \) and \( c \) layers). Note that the same calculated intensity distribution curve (symmetric with respect to zero layer and two widely broadened maxima) was obtained for 2H, 3C and 4H structures with DF for \( \alpha=0.5 \) [5]. As \( \alpha \)
increases from 0.5, there is reversal of the process, until at \( \alpha = 1 \) the structures become a perfect 5T, 8H and 12R, respectively (see top curves calculated for \( \alpha = 0.95 \)).

### 4.2. Correlated stacking faults

The simple model of non-random deformation SFs (FF with \( R \geq 2 \)) arises from assumption \( \gamma = 0 \) and \( \alpha = \beta \). The FF with \( R = 2 \) and \( \alpha \) increasing from 0 to 1 represent 5T\( \rightarrow \)10H(31131), 8H(44)\( \rightarrow \)8H(211211), and 12R\( ^+ \)\( \rightarrow \)12R\( ^+ \)+12R\( ^- \) transformations, respectively. Further, \( R = 3 \) in (2) results in 5T\( \rightarrow \)15T, 8H\( \rightarrow \)24H, and 12R\( \rightarrow \)36R transformations, while \( R = 4 \) give rise to 5T\( \rightarrow \)20T, 8H(44)\( \rightarrow \)8H(44)+8H(211211), and 12R\( \rightarrow \)2H+3C+4H transformations. The calculated variation of the intensity distributions for the 5T\( \rightarrow \)10H(31131) transformation by means of DF due to FF with \( R = 2 \) is shown in figure 2a.

[insert figure 2 about here]

For small \( \alpha \), there is no essential difference among intensity distributions for \( R = 1 \) and \( R = 2 \). But for \( \alpha \geq 0.2 \), the intensity curves corresponding to random and non-random SFs are substantially different. For \( 0.2 \leq \alpha \leq 0.8 \) and \( R = 2 \) (middle rows in figure 2a), the intensity distribution curves have rather complex shapes; i.e., strongly diffused intensities with maxima not corresponding to reflections of any type of simple polytypes. As \( \alpha \) increases from 0.8 to 0.9, the diffused background decreases and broadened peaks become sharper. The top curve in figure 2a shows almost sharp and slightly broaden reflections of the 10H structure.

Generally, due to non-random DFs a polytype undergoes transformation into another polytype with the same or higher period. On the other hand, increasing content of SFs for each of the three types of fault, i.e., ‘cc’-, ‘ch’- or ‘hh’-type DF, can lead to transformation from a parent polytype to a lower period polytype. It follows from the table, that when two parts of a crystal preferentially slip across between the same two layers like ‘hh’, layers the 5T structure undergoes transformation into 3C structure. Calculated intensity distribution for 5T structures with ‘hh’-type DF and \( \alpha \) varying from 0.1 to 0.9 are shown on figure 2b. As \( \alpha \) increases from 0.1 to 0.9, reflection at \( L/N = 0.4 \) shifts towards regular position of 3C reflection and intensifies at the expense of broadening and decreasing peaks at \( L/N = -0.4, -0.2, 0, \) and \( 0.2 \). The ‘ch’ and ‘cc’-type DF give rise to 5T\( \rightarrow \)15R(23)\( _3 \) and 5T\( \rightarrow \)15R(2111)\( _3 \) transformations, respectively. The calculated intensity distributions from the 5T\( \rightarrow \)15R(23)\( _3 \) transformation are depicted in figure 2c.

The 3C\( \rightarrow \)12R, 2H\( \rightarrow \)12R and 4H\( \rightarrow \)12R transformations due to non-random deformation faults and \( R = 4 \) in equation (2) were studied in [5]. When in 12R structure deformation SF
occurs between two like \( hh \) or \( cc \) layers, it introduces ‘cccccc’ or ‘hhhhhh’ lamellae into the structure, respectively. Thus non-random insertion of only one type, viz., ‘cc’- or ‘hh’- type DF, after four layers corresponds to growth of thick 3C or 2H regions, respectively. Similarly, when two parts of a crystal can slip across between unlike \( hc \) or \( ch \) layers and the process is repeated after four layers it results in a ‘…chchchchchchhc…’ sequence, i.e., the perfect sequence of the 4H(22) structure. The intensity distribution variations for the 12R→3C, 12R→2H and 12R→4H transformations by means of consecutive insertion of only one kind of ‘hh’-, ‘ch’- or ‘cc’-type DF are depicted on figure 3.

It should be noted that intensity curves calculated for 5T polytype with ‘hh’-type DF (0≤\( \alpha \)≤1) are similar to those calculated for the 12R polytype with the same ‘hh’-type DF (see figures 2b and 3a). However, the difference between both sets of diffraction patterns consists in the number and positions of the reflections. Five and four reflections are present on the intensity diffraction curves (\( \alpha = 0.1 \)) for parent 5T and 12R structures, respectively. It is evident from the bottom curves of figure 3 that there is substantial difference between intensity distributions of the 12R structure with the equal content of, ‘cc’-, ‘ch’- and ‘hh’-type DFs, even for a comparatively small faults probability (\( \alpha = 0.1 \)). On the bottom curve from column c reflections (merged by diffuse intensity) are much more broadened than those ones on the curves from columns b and a. Contrary to both ‘hh’-type and ‘ch’-type DF the ‘cc’-type DF causes the presence of small additional reflection which accompany the four reflections of parent 12R structure. For both ‘ch’- and ‘cc’-type DF and 0.3≤\( \alpha \)≤0.7 (middle rows, figure 3b and figure 3c), the intensity distributions have rather complex shapes; i.e., strongly diffused intensities with maxima not corresponding to the reflections of any type of simple polytypes. As \( \alpha \) increases from 0.7 to 0.9, the diffused background decreases and broadened peaks become sharper. Top curves in figure 3b and figure 3c show almost sharp and slightly broaden reflections of 2H and 4H structures, respectively.

In conclusion, the value of the Monte Carlo technique for calculating diffraction intensity distributions at intermediate stages of solid-state transformations has been demonstrated. First explicit calculations of diffraction intensity distributions variations corresponding to solid-state transformations from 5T, 8H(44) and 12R(13)\(_3\) structures due to the random and non-random deformation SFs have been presented.

**Acknowledgment**

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References


Figure Caption:

Figure 1. Calculated intensity distributions along 10.L reciprocal lattice row for plytypes with random DFs, $\gamma = 0$, $\alpha = \beta$. From bottom: $\alpha = 0.05$, 0.20, 0.50, 0.80, 0.95. a) 5T parent polytype. b) 8H parent polytype. c) 12R parent polytype.

Figure 2. Calculated intensity distributions along 10.L reciprocal lattice row for 5T parent structure with deformation SFs, $\alpha = \beta$, $\gamma = 0$. From bottom: $\alpha = 0.1$, 0.3, 0.5, 0.7, 0.9. a) DF, $R = 2$. b) ‘hh’-type DF c) ‘ch’-type DF.

Figure 3. Calculated intensity distributions along 10.L reciprocal lattice row for 12R parent structure with SFs, $\alpha = \beta$, $\gamma = 0$. From bottom: $\alpha = 0.1$, 0.3, 0.5, 0.7, 0.9. a) ‘hh’-type DF b) ‘hh’-type DF. c) $R = 4$, ‘ch’-type DF.

Table Caption:

Table 1. Stacking sequences for the 5T, 8H(44) and 12R(13) lattices with isolated deformation SFs in $hc$ notation. The sequences corresponding to DFs at different fault sites in comparison to perfect-crystals. The vertical bar indicates the plane across which the two parts
of the crystal have slipped. The notation ‘ch’-type DF, for instance, denotes the fact that the slip occurs between the $c$ and $h$ layers of the perfect crystal.
Table 1

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Figure 2.
Figure 3.