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Tentative Description of Close-Packed Structures with Stacking Faults*

BY B. PAŁOSZ AND J. PRZEDMOJSKI

Warsaw Technical University, Institute of Physics, Koszykowa 75, 00-662 *Warszawa, Poland*

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In this paper attention is drawn to the importance of layer blocks in disordered structures (*DS*) as the source of additional maxima on experimental photometric curves. So far these maxima have not been interpreted. On the basis of a *DS* structure a classification of structures with stacking faults has been proposed.

Introduction

The classification of stacking faults occurring in a close-packed structure is usually carried out on the basis of a regular 3*C* structure with two basic types of growth and deformation faults taken into account. According to this classification, growth faults are connected with the occurrence of single hexagonal *h* layers, while deformation faults are connected with the occurrence of single hexagonal cells, dividing the layer blocks in a regular 3*C* sequence.

This classification suggests the occurrence of specific types of faults connected with crystal growth and treatment: *h* layers are formed in the process of crystal growth, while deformation faults appear as the result of mechanical stresses. The actual crystals produced have a more complicated structure for which the above classification proves to be insufficient.

Several attempts to interpret structures with stacking faults by calculating theoretical curves of intensity distribution were undertaken. However, the theoretical intensity curves calculated from the Wilson (1942) and Paterson (1952) formulae for structures with growth and deformation faults do not agree satisfactorily with the experimental curves, the latter being more complicated in form.

The intensity curves of ZnS solid solution crystals obtained by the Bridgman method (Kozielski, 1975) have specific maxima, and similar maxima have been observed for ZnS crystals by Farkas-Jahnke (1973). The latter may be connected, in our opinion, with a *DS* structure.

The purpose of this paper is to analyse the observed intensity curves and to classify them on the basis of the assumption that structures with stacking faults are composed of simple polytype cells (*e.g.* 2*H*, 3*C*, 4*H*, 6*H*, 10*H* . . . *etc.*) and of *DS* fragments.

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Description of a structure with stacking faults using the notion of disordered structure

It is convenient to describe stacking faults with the help of a perfect regular 3*C* structure as a starting point, and applying the Zhdanov symbols (Zhdanov, 1945) and the *hc* notation (Jagodzinski, 1971). In accordance with Zhdanov notation the perfect regular structure may be denoted by $+\infty$ or $-\infty$ and in the *hc* notation as an infinite sequence of *c* or *c'* layers.

The occurrence of faults in the layer sequence will cause a division of the homogenous block of $\pm\infty$ layers into smaller blocks of alternating + and − sequences. This type of structure may be denoted according to Zhdanov by a set of symbols determining the number of + and − signs which appear alternately in the structure.

$$\ldots n_1 n_2 n_3 n_4 \ldots$$

The structure will be called *DS* (Disordered Structure) when the sequence of symbols $\ldots n_1 n_2 n_3 \ldots$ shows no periodicity. In the *hc* notation the occurrence of faults will correspond with the occurrence of hexagonal layers at the point where a sequence of plus signs passes into a sequence of minus signs or *vice versa*:

Zhdanov notation			4				3				4				5				
Hägg notation	+	+	+	+	−	−	−	+	+	+	+	−	−	−	−	−			
ABC sequence	*A*	*B*	*C*	*A*	*B*	*A*	*C*	*B*	*C*	*A*	*B*	*C*	*B*	*A*	*C*	*B*	*A*		
hc notation		*c*	*c*	*c*	*h'*	*c'*	*c'*	*h*	*c*	*c*	*c*	*h'*	*c'*	*c'*	*c'*	*c'*			

A full description of the structure should comprise the determination of the magnitude of blocks $n_1 n_2 n_3 \ldots$ *etc.* forming the structure and their respective distributions. In the case of the lack of periodicity in a finite sequence of layers, it is only possible to estimate the sizes of the blocks and their statistical distributions. For the description of the structure an additional parameter α determining the ratio of the number of layers in the positive (N_+) and negative (N_-) sequences $\alpha = N_+/(N_+ + N_-)$ proves to be useful. The positive and negative sequences are of course equivalent, thus it may be assumed that the difference $(N_+ - N_-)$ formed from the numbers of positive and negative sequences has random values unconnected with the

way stacking faults form in the crystal. The perfect regular structure is known to give asymmetric reflexions with respect to the zero layer (10.1 and $10.\bar{2}$ for $+\infty$ sequence, $10.\bar{1}$ and 10.2 for $-\infty$ sequence) thus the difference between the intensities of the 10.L and 10.$\bar{L}$ reflexions may serve as the basis for the determination of α. The model of a structure where *DS* occurs in fragments of the crystal and is separated by polytype cells, has been presented in Fig. 1. Let us assume two areas of crystal are simultaneously exposed to an X-ray beam (Fig. 1). If a multilayer 3*C* block ($+\infty$) represents a perfect structure and if for the structure *DS* $\alpha=0{\cdot}5$, then on the X-ray pattern a symmetric background originating from the *DS* structure should appear together with a difference in the intensity of the 10.L and 10.$\bar{L}$ reflexions resulting from the 3*C* structure. The photometric curve presented in Fig. 2 exhibits such a structure (in this structure fragments of 4*H* sequence appear as well).

Finding the intensity distribution which results from a *DS* structure presents the main problem in interpreting the structure according to the model presented.

Method of calculating theoretical curves

The theoretical intensity distribution curves were determined on the basis of the 10.L reflexions of the structural models. The intensities were calculated according to the formula given by Brafman, Alexander & Steinberger (1967). The shape of the general *DS* structure model is given by the sequence $\ldots n_1 n_2 n_3 \ldots$. Taking into account the experimentally determined width of the reflexion connected with the width of the crystal fragment analysed by X-rays, the points for plotting the intensity distribution curve were obtained by summation of the intensities of overlapping reflexions for the consecutive values of the L/m coordinate. (A more detailed description of the procedure is given in another paper by Pałosz & Przedmojski, 1975). The intensity curves were plotted in the coordinate system L/m, where L stands for the 10.L reflexion index and m for the number of layers in the corresponding structural model.

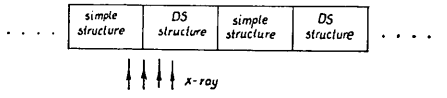

Fig. 1. Structural model with stacking faults.

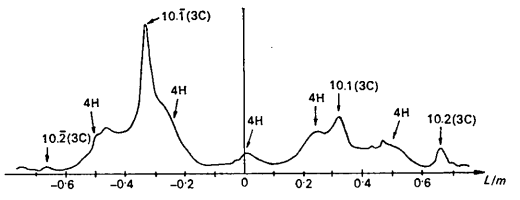

Fig. 2. Photometric curve measured along 10.L row of spots of an X-ray oscillation photograph (Cu $K\alpha$ radiation) for a crystal with $3C+4H+DS$ structure.

The basic assumption for constructing the *DS* model was the lack of periodicity in the arrangement of the layer blocks. The model was built from about 200–250 layers. The analysis of theoretical curves for models with a different number of layers has led to the conclusion that the optimum-sized model should comprise about 200 layers. 100–150 layers proved to be insufficient, whereas increasing the number of layers to over 250 did not improve agreement with experiment.

The average size of the layer blocks forming the structure, along with the percentage of hexagonal layers in the structure, has been chosen as the measure of the degree of disorder. In Table 1 those figures are presented.

Table 1. *Measure of the degree of disorder*

Average size of blocks	%*h*
20	5
10	10
6·67	15
5	20
4	25
*	
3·33	30
2·88	35
2·5	40
2·22	45
2	50

* A 3*C* structure cell requires three layers, hence its size is of at least a three-layer block.

Table 1 shows that a *DS* structure may be considered as a 3*C* structure with stacking faults to the point of about 25% *h*, whereas above this point, the dominating order of layers in the 3*C* cell will decrease. Therefore the intensity distribution obtained for a structure containing more than 25% *h* will differ substantially from the distribution obtained for a 3*C* structure with a small number of stacking faults (*e.g.* 5% *h*). Assuming that the layer blocks forming the structure are similar in size to the average size of the block (for 25% *h* the average block size amounts to four layers and the structure will be formed mainly by three, four and five-layer blocks with two- and six-layer blocks occurring), the lack of periodic order of the layer blocks does not exclude the repetition of certain sequences in the structure *e.g.* 34, 35, 45 *etc.* These sequences are not formed by cells of separate polytypes, and show characteristic interference patterns. In the case of 50% *h* *DS* structure with the average block size amounting to two, the model has to be built almost from one-, two- and three-layer blocks only. The sequences 13, 12, 23, 121, 123 *etc.* must appear frequently and the interference pattern then

suggests the presence of periods in the structure to give the characteristic maxima (and not reflexions).

Results

The results of calculations of theoretical curves for *DS* structures with different % *h* values are presented in Fig. 3. It is seen that the curves for the models with more than 20% *h* differ substantially from the curves obtained for a 3*C* structure with a small number of stacking faults (5–10% *h*), in that they exhibit characteristic maxima. It has been found that theoretical curves obtained for different models of the same % *h* are similar in general shape proving the description by means of the parameter % *h* to be applicable.

Confirmation of the actual occurrence of a *DS*-type structure in real crystals is expected to be found in two cases: (*a*) in separate crystals consisting exclusively of *DS* structures and (*b*) for a *DS* structure accompanying the occurrence of polytypes. The investigations carried out by us have lead to the conclusion that simple polytypes, $2H, 4H, 6H, 10H$ *etc.*, represent the preferred order of layers. We therefore expect mainly polytype structure and rarely larger separate fragments of *DS* structure. Furthermore the condition of forming a structure from layer blocks of a size comparable with the average size of the block structure allows synonymous structural models to be built. However, this condition should not be expected to hold strictly in the case of real crystals.

The occurrence of a simultaneous 'mixture' of several *DS* structures and thus of intensity curves combining several curves of the type shown in Fig. 3 is more probable. The structure corresponding with the photometric curve shown in Fig. 4 may be seen as an example of a 'mixed' structure. This curve may be considered as a combination of intensity curves of *DS* 40–50% *h* structures. (The overlapping of the curves causes strengthening of the maxima in *L*/*m* positions of about 0·4 and 0·6 and a more regular shape within whole *L*/*m* value interval).

DS structures are expected to occur much more frequently when together with polytypes. Among the investigated crystals of ZnS solid solutions a few cases of pure *DS* structures were examined, but more frequently we observed maxima resulting from a *DS* structure accompanying the diffuse reflexions of the polytypes. Fig. 5(*a*) shows the photometric curve, on which the broadened reflexions of 2*H* and 3*C* structures and the maxima resulting from the *DS* structure of about 50% *h* (type $2H+3C+DS$ structure) may be distinguished.

Fig. 5(*b*) shows the photometric curve of a $6H+DS$ structure. The positions of additional maxima enable one to conclude the presence of areas of *DS* structure in the crystal with 35–40% *h*.

Precise determination of the ratio of the number of layers occurring in the *DS* structure to the number ordered in polytype cells can be carried out by further comparison of the size of broadened reflexions with the shape and size of the background. In the case where layers ordered in polytype cells prevail in the crystal, the maxima corresponding to the *DS* structure are broadened and lead to a continuous and regular background causing a corresponding broadening of the polytype reflexions (Fig. 2).

Utilizing the results of the intensity curve calculation of structures with $\alpha \neq 0{\cdot}5$ we have found that a relatively precise determination of the parameter α is possible by measuring the integral intensities of the parts of the curve corresponding to L and $\bar{L}$. In Table 2 are given the values of α calculated on the basis of

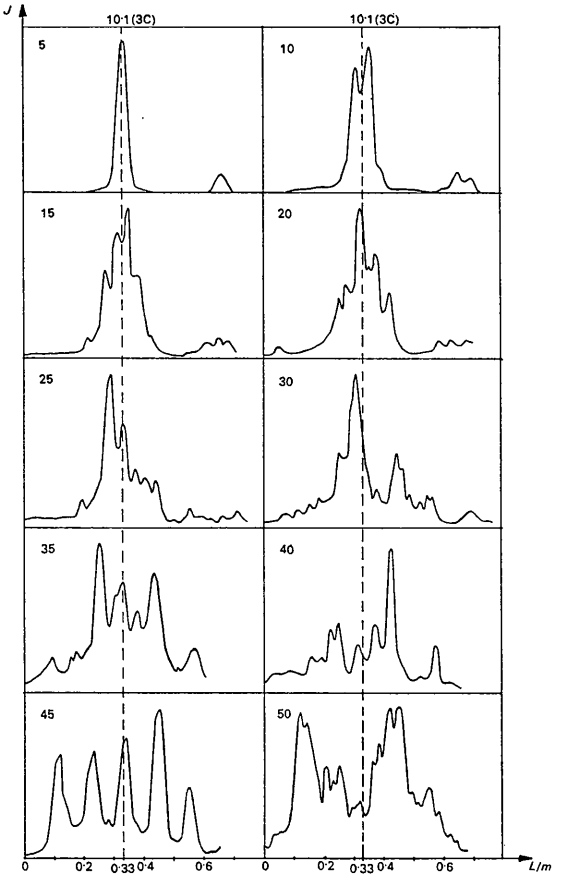

Fig. 3. Diagram of theoretical curves of intensity distribution along a row of 10.*L* reflexions obtained for *DS* structures with 5 to 50% *h* layers.

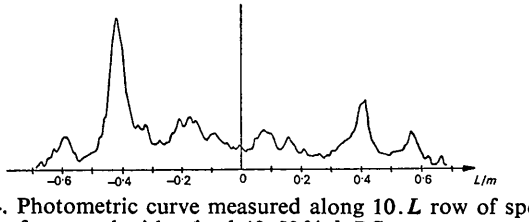

Fig. 4. Photometric curve measured along 10.*L* row of spots of a crystal with mixed 40–50% *h* *DS* structures.

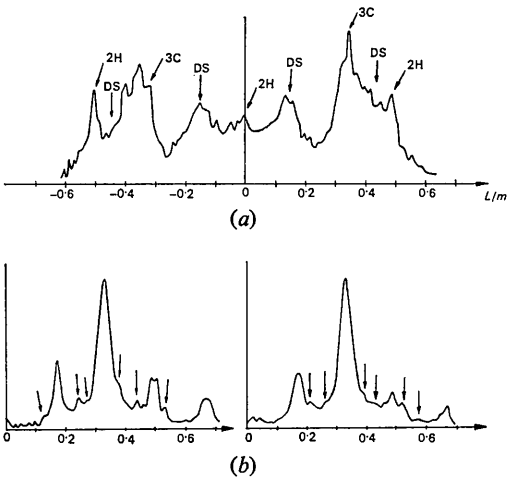

Fig. 5. Photometric curve measured along 10.L row of spots for (*a*) a crystal with $2H+3C+DS$ 50% h structure. (*b*) a crystal with $6H+DS$ 35–40% h structure.

Table 2. *Values of the parameter* α

α calculated from integral intensity	α calculated from models
0·45	0·43
0·35	0·34
0·30	0·29

the measured integral intensities compared with the values from theoretical curves calculated for the described models.

Conclusion

The introduction of the concept of a *DS* structure deduced from a characteristic intensity distribution leads to the classification of structures with stacking faults as a combination of fragments of layers ordered in simple polytype cells, occurring in numbers of a few to several dozens, and of *DS* structure fragments.

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Un Nouvel Exemple d'Empilement Ordonné à Très Longue Période dans le Système Or–Manganèse; la 'Phase X' ($Au_{11}Mn_4$)

PAR B. BELBÉOCH, H. FRISBY, N. GAIGNEBET, R. KLEINBERGER ET M. ROULLIAY

Service de Physique du Solide et de Résonance Magnétique, Centre d'Etudes Nucléaires de Saclay, BP n°2 – 91190 Gif-sur-Yvette, France

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A new example of long-period stacking order is described in the Au–Mn system for the composition $Au_{11}Mn_4$ (26·7 at. % Mn). The structure was determined by X-ray and electron diffraction and confirmed by neutron diffraction. The stacking order is the so-called 3R type in Sato's nomenclature [Sato, Toth & Honjo, *J. Phys. Chem. Solids*, (1967). **28**, 137–160]. The structure includes 27 layers, building up a giant monoclinic cell containing 810 atoms. This phase undergoes a magnetic transition at about 140 K. As opposed to examples given by Sato *et al.* (1967), the $Au_{11}Mn_4$ structure is not based on a long-period superlattice with antiphase boundaries.

I. Introduction

Humble (1964) au cours de son étude de la phase ordonnée monoclinique Au_5Mn_2 a caractérisé par diffraction des rayons X, une nouvelle phase de structure inconnue dénommée par lui 'phase X' et de teneur en manganèse légèrement inférieure à celle de Au_5Mn_2 (26,7 at.% Mn au lieu de 28,7 at.% Mn).

Pour des alliages dont la teneur en manganèse est comprise entre 22 at.% et 28 at.% et sur des échantillons massifs, Sato, Toth & Honjo (1967) ont trouvé des structures à longue période basées sur des modulations du réseau c.f.c. par des défauts d'empilement dans une direction [111], structures dénommées 1R,5H,6H,3R selon le mode d'empilement. En fait les structures décrites sont ordonnées et proviennent toutes de la