Acta Cryst. (1977). A33, 687–689,

Analysis of a Faulted 4*H* Structure of CdI_2

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(*Received* 11 *December* 1975; *accepted* 23 *March* 1977)

A faulted 4*H* structure of CdI_2 gives a diffraction pattern composed of sharp spots and diffuse streaks. The structure was solved by assuming that the sharp spots come from the 'average structure' and the diffuse streaks from one-dimensional disorder.

Introduction

Mitchell (1956) has reported that the most common polytype of CdI_2 is type 4*H* with the *ABC* sequence $(A\gamma B)$ $(A\beta C)$ and the second common type is type 2*H* with $(A\gamma B)$. However, faulted 4*H* structures appear more frequently than type 2*H* in as-grown crystals (Minagawa, 1976). This paper describes the structure of a faulted 4*H* structure in terms of a stacking disorder of *V* and *V'*, where *V* and *V'* stand for the layer units $(A\gamma B)$ and $(A\beta C)$, respectively.

Experimental

Crystals grown from aqueous solutions were hexagonal plates. All ten crystals examined revealed that one side of a crystal plate was of faulted 4*H*, while the other side was of type 4*H* or 2*H*. No single crystal of faulted 4*H* only was obtained. The crystal used for intensity measurement consisted of faulted 4*H* on one side and type 2*H* on the other and had dimensions 570 μm in width and 50 μm in thickness. The domain of the faulted 4*H* in the crystal was estimated to be 20 μm thick by comparing the intensities of back and penetrating reflexions. Since the linear absorption coefficient, μ, of CdI_2 is 1568 for Cu $K\alpha$, 99·7% of the intensity of a back reflexion comes from a surface layer 20 μm thick. Hence, the intensities of back reflexions may be considered to be given by the faulted 4*H* only.

With Cu $K\alpha$ radiation, intensity data of sharp spots and diffuse streaks were recorded on zero-layer Weissenberg photographs about **b**. The characteristics of the sharp spots and the diffuse streaks from the faulted 4*H* are as follows. (1) The positions of the sharp spots coincide with those of the corresponding spots for type 4*H*. The spot with $\zeta=l$ has an intensity between those of the corresponding spots for types 4*H* and 2*H* and the intensity of the spot with $\zeta=l+\frac{1}{2}$ is weaker than that for type 4*H*, where the thickness of one layer unit is chosen as the *c* axial length. (2) The diffuse intensities along **c*** are very strong at $\zeta=l+\frac{1}{2}$ and very weak at $\zeta=l$ and their distributions are almost the same for $h0\zeta$ rows with $h=3n\pm1$ (n an integer).

The intensities of the sharp spots were estimated visually and corrected for Lorentz and polarization effects, spot size and absorption (see Appendix). The photometrically measured diffuse intensities were corrected for absorption, the polarization effect and the geometrical factor with the formula given by Takaki, Kato & Sakurai (1975).

Table 1. *Stacking mode of the layer units*

	V	*V'*	*V*	*V'*
$\frac{1}{2}w_1$ *V*			β_1	$1-\beta_1$
$\frac{1}{2}w_2$ *V'*			β_2	$1-\beta_2$
$\frac{1}{2}w_1'$ *V*	α_1	$1-\alpha_1$		
$\frac{1}{2}w_2'$ *V'*	α_2	$1-\alpha_2$		

Structure of the faulted 4*H*

If the sharp spots found at $\zeta=l$ and $l+\frac{1}{2}$ are regarded as Bragg reflexions from the average structure, its period along **c** should be twice the thickness of one layer unit. A stacking mode of layer units in a faulted 4*H* structure with such an average structure is given in Table 1, where w_1, w_2 are the respective probabilities of finding *V*: $(A\gamma B)$ and *V'*: $(A\beta C)$ at the first site, and w_1', w_2' those for the second site. Therefore $w_1+w_2=1$ and $w_1'+w_2'=1$. β_1, β_2 are the respective probabilities of finding *V* at the second site after *V*, *V'* at the first site, and so on. The layer form factors for *V*, *V'* are given by

$$V=N_1N_2[f_I+f_{Cd}\varepsilon^*\exp(i\pi\zeta/2)+f_I\varepsilon\exp(i\pi\zeta)]$$
$$V'=N_1N_2[f_I+f_{Cd}\varepsilon\exp(i\pi\zeta/2)+f_I\varepsilon^*\exp(i\pi\zeta)],$$

where N_1 and N_2 are the numbers of unit cells along **a**, **b**, respectively, f_I and f_{Cd} are the atomic scattering factors for the I and Cd ions, respectively, and $\varepsilon=\exp[2\pi i(h-k)/3]$, the phase factor corresponding to the displacement $A\rightarrow B$. The structure factor for the Bragg reflexion from the average structure and the diffuse intensity $I_D(\varphi)$ are given by [Takaki & Sakurai (1976), equations (5*a*) and (5*b*)]

$$F=F_1+F_2\exp(2\pi i\zeta),$$

where $F_1=w_1V+w_2V'$ and $F_2=w_1'V+w_2'V'$;

$$I_D(\varphi)=\tfrac{1}{2}N(w_1w_2+w_1'w_2')|V-V'|^2 \times[(1-x^2)/(1+x^2-2x\cos 2\varphi)](1+U\cos\varphi),$$

where

$$|V-V'|^2=3[f_I^2+f_{Cd}^2-2f_If_{Cd}\cos(\varphi/4)],$$

$$U=\frac{2[w_1w_2(\beta_1-\beta_2)+w_1'w_2'(\alpha_1-\alpha_2)]}{[(w_1w_2+w_1'w_2')(1+x)]},$$

$x=(\alpha_1-\alpha_2)(\beta_1-\beta_2)$, $\varphi=2\pi\zeta$ and N is the number of layer units [Takaki & Sakurai (1976), equations (39*a*) and (39*b*)]. The structure factors for $hk\zeta$ reflexions are listed in Table 2. The distribution of diffuse intensities is the same for $hk\zeta$ rows with $h-k=3n\pm1$.

Table 2. *Structure factors for $hk\zeta$ reflexions*

$h-k$ / ζ	$3n$	$3n\pm1$
l	$2V$	$(w_1+w_1')V+(w_2+w_2')V'$
$l+\frac{1}{2}$	0	$(w_1-w_1')(V-V')$

The values of w_i and w_i' are given by solving the average structure. The values of α_i and β_i are given by solving diffuse intensities; then only two parameters, say α_2 and β_2, are independent, since there are the relations $w_1\beta_1+w_2\beta_2=w_1$ and $w_1'\alpha_1+w_2'\alpha_2=w_1$.

The best agreement was obtained between the observed and calculated structure factors by putting $w_1=0{\cdot}90$, $w_2=0{\cdot}10$, $w_1'=0{\cdot}28$, $w_2'=0{\cdot}72$, $B=1{\cdot}5$ for the I ion and $B=3{\cdot}0$ for the Cd ion, where B is the isotropic temperature factor. Table 3 gives the observed and calculated structure factors. The R index ($R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$) is 0·12. As for the diffuse streaks, the best intensity agreement was obtained with the values of w_i, w_i' given above and the values $\alpha_1=0{\cdot}64$, $\alpha_2=1{\cdot}00$, $\beta_1=0{\cdot}20$ and $\beta_2=1{\cdot}00$. A comparison of observed and calculated intensities is shown in Fig. 1.

Table 3. *Observed and calculated structure factors*

Observed reflexions marked with an asterisk have a geometry of incident and reflected beams different from that in Fig. 2, so that they were corrected with the corresponding formula for the absorption factor. This case is not common; and so the formula is not given here.

ζ	F_o	F_c	ζ	F_o	F_c	ζ	F_o	F_c
	0 0 ζ		6	46.6	37.0		2 0 ζ	
			6.5	30.1	31.3			
2	121	99.0	7	43.6	50.0	5	60.4	61.2
3	82.9	65.6	7.5	11.1	12.4	5.5	33.2	32.2
4	183	182				6	33.9	30.5
5	49.4	40.1		$\bar{1}$ 0 ζ		6.5	22.2	26.1
6	62.6	60.9				7	39.5*	50.0
7	21.7	22.0	4.5	23.4	21.3	7.5	8.5*	10.9
8	54.8	75.9	5	68.2	72.3			
			5.5	39.1	39.3		$\bar{2}$ 0 ζ	
	1 0 ζ		6	40.9	37.0			
			6.5	27.1	31.3	5	65.9	72.5
4.5	24.0	21.3	7	45.3	58.3	5.5	33.5	32.2
5	88.9	87.0	7.5	12.2	12.4	6	33.4	30.5
5.5	41.6	39.3				6.5	22.6	26.1
						7	30.8*	43.3
						7.5	8.1*	10.9

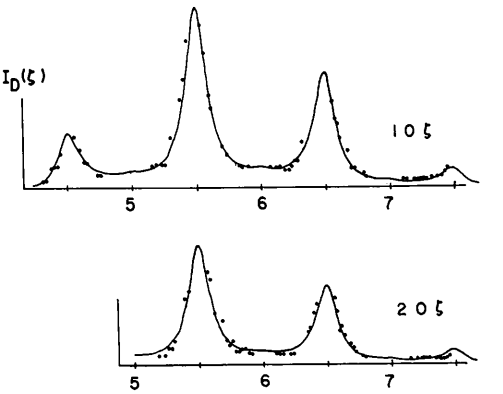

Fig. 1. Comparison of observed (dots) and calculated (full lines) diffuse intensities.

Discussion

In the above result the value of w_2 is small. Suppose $w_2=0$; then the case becomes that of a stacking disorder of two kinds of double layer units VV and $V'V$ given in Table 4, where g_1 and g_2 are the probabilities of finding VV and $V'V$ in the crystal respectively. The structure factors of the average structure for this model showed a good agreement ($R=0{\cdot}12$) with the observed values by putting $g_1=0{\cdot}36$ and $g_2=0{\cdot}64$. The diffuse intensities for this model are given by:

$$I_D'(\varphi)=\tfrac{1}{2}Ng_1g_2|V-V'|^2[(1-y^2)/(1+y^2-2y\cos 2\varphi)],$$

where $y=\alpha-\beta$. $I_D'(\varphi)$ does not contain the factor $1+U\cos\varphi$ in $I_D(\varphi)$ and $U=-0{\cdot}77$ for the present result, so that $I_D'(\varphi)$ gives quite different intensities from those observed. This suggests that the analysis of diffuse intensities is an important key in justifying a model for the faulted structure.

Table 4. *Stacking mode of two kinds of double layer units*

	VV	$V'V$
g_1 VV	α	$1-\alpha$
g_2 $V'V$	β	$1-\beta$

It is interesting that in the present result the relations $w_1(1-\beta_1)=w_2'\alpha_2$ and $w_2\beta_2=w_1'(1-\alpha_1)$ are satisfied, *i.e.* the number of the pair VV' is equal to that of $V'V$. These relations have also been found in a disordered structure of *o*-chlorobenzamide (Takaki, Kato & Sakurai, 1975).

In other crystal samples with faulted 4*H* structures, the intensity distributions of sharp spots and diffuse streaks vary from crystal to crystal. They could also

be explained in terms of the stacking mode of layer units given in Table 1.

The author wishes to thank Dr Y. Takaki for valuable discussions and Professor K. Sakurai for reading the manuscript. This work was financially supported by the Sakkokai Foundation.

APPENDIX

Absorption factor for back reflexions from a disc-shaped crystal

Let us calculate the absorption factor for zero-layer back reflexions from a disc-shaped crystal when the crystal is rotated about an axis parallel to a diameter and which passes through the centre of the disc. Fig. 2 shows a cross-section perpendicular to the rotation axis, together with the geometry of the incident and reflected beams for the reflexions given in Table 3 (two extreme cases are $\gamma=81{\cdot}3$, $\delta=8{\cdot}0°$ for 205 and $\gamma=8{\cdot}0$, $\delta=81{\cdot}3°$ for $\bar{2}05$). The absorption factor A for the disc is obtained by using the formula for the absorption factor of a right-prismatic crystal given by Takaki, Sakata & Watanabé (1961) and by assuming that the diameter r is fairly large compared with the thickness b ($b/r=1/11{\cdot}4$ in the present case):

$$A=(4/\pi rb\mu^2)(A_1+A_2+A_3),$$

where μ is the linear absorption coefficient,

$$A_1=(\operatorname{cosec}\gamma+\operatorname{cosec}\delta)^{-1}[(\mu\pi r/4)(1-C_1C_2)+\mu b(\cot\gamma+\cot\delta)C_1C_2-(1-C_1C_2)(\cot\gamma+\cot\delta)/(\operatorname{cosec}\gamma+\operatorname{cosec}\delta)],$$

$$A_2=\cos\gamma[\sin\delta(1-C_2)-(1-C_1C_2)/(\operatorname{cosec}\gamma+\operatorname{cosec}\delta)],$$

$$A_3=\cos\delta[\sin\gamma(1-C_1)-(1-C_1C_2)/(\operatorname{cosec}\gamma+\operatorname{cosec}\delta)],$$

$$C_1=\exp(-\mu b\operatorname{cosec}\gamma),$$

$$C_2=\exp(-\mu b\operatorname{cosec}\delta)$$

and γ and δ are the angles given in Fig. 2.

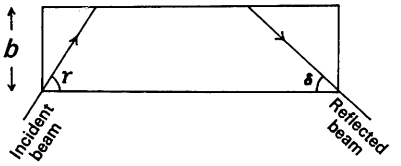

Fig. 2. A cross-section of a disc-shaped crystal perpendicular to the rotation axis, illustrating the geometry of the incident and reflected beams.

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