X-ray Diffraction Study of the Structural Change from 2H to 4H in CdI₂ Crystals

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The structural changes, 2H → faulted 2H → faulted 4H → 4H, in CdI₂ crystals, which are caused by successive heat treatments, were studied by X-ray diffraction. The faulted 2H and faulted 4H structures, which give diffraction patterns composed of sharp spots and diffuse streaks, were solved on the assumption that sharp spots arise from the 'average structure' and diffuse streaks from a stacking disorder of layers. It was revealed that (1) each of the faulted 2H and faulted 4H structures is maintained unchanged over a certain range of heating temperature and (2) when two kinds of layer, V and V', are stacked in the faulted structures, a small number of V' layers are always followed by a large number of V layers.

**Introduction**

The most common structure found in as-grown crystals of CdI₂ is type 4H with the layer sequence (AyB) (Minagawa, 1976). Here, 'faulted 4H' and 'faulted 2H' represent the faulted structures having average structures with c axial lengths identical to those of types 4H and 2H. In a preliminary experiment to investigate structural changes among these common structures, we found that by heating, the 2H structure changes into 4H via faulted 2H and faulted 4H, and faulted 2H structures found in as-grown crystals change into 4H via faulted 2H. In the present X-ray diffraction study, the faulted 2H and faulted 4H structures appearing in the course of the structural changes were analysed in terms of a stacking disorder of two kinds of layers, V and V', where V and V' denote the compound layers consisting of a Cd layer sandwiched between two I layers, (AyB) and (AB'C), respectively, and the process of the 2H (VV... → 4H (VV'VV'...)) structural change was studied.

**Experimental**

Crystals were grown from aqueous solutions. Of two 2H crystals used, one (crystal 1) was a hexagonal plate 600 μm across and 50 μm thick and the other (crystal 2) a rectangular thin plate 2 mm long, 725 μm wide and 40 μm thick. Crystals 1 and 2 were heated in air in an electric furnace. Crystal 1 was subjected to the successive heat treatments, (a) as-grown → (d) 80 °C → (d') 90 °C → (e) 100 °C → (e') 110 °C → (f) 130 °C → (f') 150 °C → (g) and (g) being the same as for crystal 1. Both crystals were quenched from each temperature to room temperature in the course of the successive heat treatments and each time intensity data of sharp spots and diffuse streaks from the crystals were recorded on multiple-film zero-layer Weissenberg photographs about b taken with Ni-filtered Cu Kα radiation.

On the Weissenberg photographs about b, which lies on a wide plane of crystal plate 1 or 2, back reflections can be distinguished from penetrating ones because of the small thickness and high absorption of the crystals; so that one side of crystal plates was found to have the 2H structure and the other the faulted 4H structure. It may be concluded that the intensities of back reflections coming from the 2H side originate from the 2H structure only, because we know the following two facts: (1) 99.7% of the intensity of back reflection comes from a surface layer 20 μm thick, since μ = 1568 cm⁻¹ for Cu Kα, and (2) the domains of 2H in crystals 1 and 2 were estimated to be about 30 and 20 μm thick respectively, from comparison of the intensities of the penetrating reflexions from the 2H and faulted 4H structures. By analysis of the variation of the intensities of back reflections from the 2H side after the heat treatments mentioned above, the 2H → 4H structural change was investigated.

Fig. 1 (1) to (9) gives 10 reflected Weissenberg photographs of crystals 1 and 2 quenched after each heat treatment. Throughout (1) to (9), sharp spots are observed at ζ = l/an integer, where ζ is the coordinate along c*, c* = 1/c₀. Here, c₀ is the c axial length of the 2H structure. Diffuse streaks are also observed along ζ. Their intensities are strong at ζ = l + ½ and weak at ζ = l and gradually concentrate at ζ = l + ½ with increasing heating temperature. On the Weissenberg photographs corresponding to (4) to (9) a core of intensity is recognized at ζ = l + ½ on the diffuse streaks; on the other hand, no core is perceived at the positions on the photographs corresponding to (2) and (3) (Fig. 1 obscurely reproduces the feature). The feature was also confirmed by microdensitometer measurement. There-
fore we supposed the core of intensity recognized at \( \zeta = l + \frac{1}{2} \) in (4) to (9) to be a sharp spot similar to that at \( \zeta = l \). Then the diffraction patterns in (2) and (3) and those in (4) to (9) can be considered as due to faulted 2H and faulted 4H respectively. Intensities of the sharp spots at \( \zeta = l + \frac{1}{2} \) become stronger with increasing heating temperature. Characteristics of intensity distributions of the sharp spots and diffuse streaks along \( h0\zeta \) rows with \( h = 3n + 1 \) (\( n \) an integer) are the same as those along the \( 10\zeta \) row.

Intensities of the sharp spots were estimated visually and corrected for Lorentz and polarization effects and spot size. Corrections for absorption of X-rays by crystal 1 (a hexagonal plate) and crystal 2 (a rectangular plate) were made with the formulae given by Minagawa (1977) and Takaki, Sakata & Watanabe (1961), respectively. Intensities of the diffuse streaks were measured by microdensitometer and corrected for absorption, polarization and a geometrical factor given by Takaki, Kato & Sakurai (1975).

As to the structural changes, the following two facts are to be mentioned. First, although crystals 1 and 2 passed through the different heating processes, \( a \rightarrow d \rightarrow d' \rightarrow e \rightarrow e' \rightarrow f \rightarrow f' \rightarrow g \) and \( a \rightarrow b \rightarrow c \rightarrow d \rightarrow g \) respectively, the two crystals quenched from the same temperature \( (d \) or \( g) \) gave nearly equal diffraction intensities. This indicates that the faulted structures are governed not by the heating process but by the maximum heating temperature. Secondly, no appreciable differences were observed among three diffraction patterns obtained after heating a 2H crystal at 50°C for different periods, one, two and three weeks. Furthermore, no appreciable difference was observed between the two diffraction patterns obtained after heating a faulted 2H crystal at 150°C for two and four days. Each heating period in the successive heat treatments for crystals 1 and 2, therefore, may be long enough for the structural changes to be completed.

**Faulted 4H and faulted 2H structures**

Faulted structures were solved by using the theory of Takaki & Sakurai (1976). If the sharp spots are regarded as Bragg reflexions from an average structure, the

![Fig. 1. The 10\zeta rows of Weissenberg photographs of crystal 1 [(1),(4),(5),(6),(7)] and crystal 2 [(2),(3),(8),(9)] after successive heat treatments (a) to (i) (see text).](image)
spots at $\zeta = l$ observed in Fig. 1 (2) and (3) should be given by the average structure in faulted 2H with $c$ equal to $c_0$, and the spots at $\zeta = l$ and $l + \frac{1}{2}$ observed in Fig. 1 (4) to (9) by the average structure in faulted 4H with the $c$ equal to $2c_0$. When layer sites occupied by the layers $V$ and $V'$ in the 4H structure, $V' V' V' V'\ldots$, are called 'first layer site' and 'second layer site' respectively, the average structure in faulted 4H is given schematically as follows:

$$\begin{bmatrix} w_1 & V \\ w_2 & V' \end{bmatrix}$$

First layer site

$$\begin{bmatrix} w'_1 & V \\ w'_2 & V' \end{bmatrix}$$

Second layer site

$$\begin{bmatrix} w_1 & V \\ w_2 & V' \end{bmatrix}$$

First layer site

where $w_1$ and $w_2$ are the probabilities of finding the layers $V$ and $V'$ at the first layer site respectively, and $w'_1$ and $w'_2$ those at the second layer site respectively. Therefore $w_1 + w_2 = 1$ and $w'_1 + w'_2 = 1$. In the average structure in faulted 2H, the second layer site is identical with the first, namely, $w'_1 = w_1$ and $w'_2 = w_2$. A stacking mode of layers in faulted 4H can be represented as follows:

$$\begin{array}{c}
\beta_1 \\
V\\
\alpha_1 \\
V'
\end{array}$$

$$\begin{array}{c}
1 - \beta_1 \\
V\\
\alpha_2 \\
V'
\end{array}$$

where $\beta_1$ ($\beta_2$) is the probability of finding $V$ at the second layer site when the preceding first layer site is occupied by $V(V')$ and $\alpha_1$ ($\alpha_2$) that at the first layer site when the preceding second layer site is occupied by $V(V')$. In the stacking of layers in faulted 2H and faulted 4H structures appearing in the course of the 2H $\rightarrow$ 4H structural change can be solved with the average structure and stacking mode of layers described above.

The structure factors $F_V$ and $F_{V'}$ for the layers $V$ ($A\gamma B$) and $V'$ ($A\beta C$) are given by

$$F_V = N_1 N_2 \{ f_1 + f_{Ca} \epsilon * \exp(\imath \pi \zeta / 2) + f_{a} \exp(\imath \pi \zeta) \}$$

$$F_{V'} = N_1 N_2 \{ f_1 + f_{Ca} \epsilon * \exp(\imath \pi \zeta / 2) + f_{a} \exp(\imath \pi \zeta) \},$$

where $\epsilon = \exp \{ 2\pi \imath h - k \}/3 \}, N_1$ and $N_2$ are the numbers of unit cells along $a$ and $b$ respectively, and $f_i$ and $f_{Ca}$ the atomic scattering factors for I and Cd ions respectively. The structure factor, $F$, for the average structure in faulted 4H is given by

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

where $F_1 = w_1 F_V + w_2 F_{V'}$ and $F_2 = w'_1 F_V + w'_2 F_{V'}$. The structure factors for h0$^\zeta$ reflections are as follows: $F = 2F_V$ for $h = 3n$ and $\zeta = l$, $F = (w_1 + w'_1)F_V + (w_2 + w'_2)F_{V'}$ for $h \neq 3n$ and $\zeta = l$, and $F = (w_1 - w'_1)(F_V - F_{V'})$ for $h \neq 3n$ and $\zeta = l + \frac{1}{2}$. These equations can be used under the conditions $w'_1 = w_1$ and $w'_2 = w_2$ for the average structure in faulted 2H. The diffuse intensity from faulted 4H, $I_D(\phi)$, is given by [Takaki & Sakurai (1976), equation (39)]

$$I_D(\phi) = \frac{1}{2}N \{ w_1 w_2 + w'_1 w'_2 \} |F_V - F_{V'}|^2$$

$$\times \left( (1 - \gamma^2)/(1 + \gamma^2 - 2 \gamma \cos \phi) \right) (1 + U \cos \gamma),$$

where

$$|F_V - F_{V'}|^2 = 3(N_1 N_2)^2 \left[ f_1^2 + f_{Ca}^2 - 2 f_1 f_{Ca} \cos(\phi / 4) \right],$$

$$x = (\alpha_1 - \alpha_2) (\beta_1 - \beta_2),$$

$$U = 2 \left[ w_1 w_2 (\beta_1 - \beta_2) + w'_1 w'_2 (\alpha_1 - \alpha_2) \right]$$

$$\left[ (w_1 w_2 + w'_1 w'_2) (1 + x) \right],$$

$$\phi = 2\pi \zeta$$

and $N$ is the number of layers. The $I_D(\phi)$ for faulted 2H is obtained by substituting the relations $w'_1 = w_1$, $w'_2 = w_2$, $\beta_1 = \alpha_1$, and $\beta_2 = \alpha_2$ into the above equations and becomes

$$I_D(\phi) = N w_1 w_2 |F_V - F_{V'}|^2$$

$$\times \left( (1 - \gamma^2)/(1 + \gamma^2 - 2 \gamma \cos \phi) \right),$$

where $\gamma = x - y$. Each of equations (2) and (3) gives the same intensity distribution along the two h0$^\zeta$ rows with $h = 3n + 1$ and $3n - 1$.

**Determination of faulted structures**

First the average structures were determined by analysing the intensities of sharp spots. The structure factors for h0$^\zeta$ reflexions were calculated for various sets of $w_1$ and $w'_1$ values, and the set which gave the best agreement between calculated structure factors and observed ones of sharp spots was selected.

<table>
<thead>
<tr>
<th>Heating condition</th>
<th>$w_1$</th>
<th>$w'_1$</th>
<th>$w_2$</th>
<th>$w'_2$</th>
<th>$R$</th>
<th>$\alpha_1$</th>
<th>$\alpha_2$</th>
<th>$\beta_1$</th>
<th>$\beta_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H</td>
<td>0.66</td>
<td>0.66</td>
<td>0.34</td>
<td>0.34</td>
<td>0.15</td>
<td>0.44</td>
<td>0.48</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Faulted 2H</td>
<td>0.66</td>
<td>0.66</td>
<td>0.34</td>
<td>0.34</td>
<td>0.15</td>
<td>0.44</td>
<td>0.48</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Faulted 4H</td>
<td>0.66</td>
<td>0.66</td>
<td>0.34</td>
<td>0.34</td>
<td>0.15</td>
<td>0.44</td>
<td>0.48</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Note: The asterisks indicate the values determined from diffuse intensities.
Table 2. Observed and calculated structure factors (× 10) of sharp spots in the cases of the heating conditions (a), (b), (c), (d), (f) and (h).

| Indices L | f₁ | f₂ | c₁ | f₁ | f₂ | c₁ | f₁ | f₂ | c₁ | f₁ | f₂ | c₁ | f₁ | f₂ | c₁ | f₁ | f₂ | c₁ | f₁ | f₂ | c₁ | f₁ | f₂ | c₁ | f₁ | f₂ | c₁ | f₁ | f₂ | c₁ | f₁ | f₂ | c₁ |
|-----------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| L         | f₀ | f₁ | c₀ | f₀ | f₁ | c₀ | f₀ | f₁ | c₀ | f₀ | f₁ | c₀ | f₀ | f₁ | c₀ | f₀ | f₁ | c₀ | f₀ | f₁ | c₀ | f₀ | f₁ | c₀ | f₀ | f₁ | c₀ | f₀ | f₁ | c₀ | f₀ | f₁ | c₀ |
| (a)       |     |    |    |     |    |    |     |    |    |     |    |    |     |    |    |     |    |    |     |    |    |     |    |    |     |    |    |     |    |    |     |    |    |     |    |
| 0 0 L     | 15 | 69 | 66 | 15 | 69 | 66 | 15 | 69 | 66 | 15 | 69 | 66 | 15 | 69 | 66 | 15 | 69 | 66 | 15 | 69 | 66 | 15 | 69 | 66 | 15 | 69 | 66 | 15 | 69 | 66 |
| 1 0 L     | 14 | 416 | 508 | 14 | 416 | 508 | 14 | 416 | 508 | 14 | 416 | 508 | 14 | 416 | 508 | 14 | 416 | 508 | 14 | 416 | 508 | 14 | 416 | 508 | 14 | 416 | 508 | 14 | 416 | 508 |
| 0 1 L     | 6 | 653 | 656 | -1 0 L | 10 | 366 | 392 | 13 | 169 | 143 | 13 | 252 | 211 | 13 | 375 | 329 | 15 | 583 | 659 | 15 | 451 | 418 | 15 | 48 | 60 | 15 | 83 | 88 | 15 | 110 | 137 |
| 1 0 L     | 6 | 653 | 656 | -1 0 L | 10 | 800 | 807 | 9 | 770 | 12 | 146 | 151 | 12 | 239 | 250 | 12 | 332 | 360 | 15 | 548 | 590 | 15 | 448 | 473 | 15 | 91 | 98 | 15 | 138 | 146 |

w₁ and w₂ values thus obtained are given in Table 1, together with the R values, where $R = \frac{\sum |F_{\text{obs}} - |F_{\text{calc}}|}{\sum F_{\text{obs}}}$. Table 1 leads to the following results. (1) The 2H structure changes into the most common 4H structure via faulted 2H and faulted 4H. The faulted 2H and faulted 4H appear when the crystals are heated at temperatures below 65 °C and above 80 °C respectively. (2) The w₁ and w₂ values in Table 1 are plotted against the heating temperature in Fig. 3. In the figure they change stepwise with the heating temperature. In addition, within a temperature range where the w₁ and w₂ values are nearly constant the $\alpha_i$ and $\beta_i$ values are also nearly constant. These facts suggest that each of faulted structures appearing in the course of the structural changes remains unchanged over a certain range of heating temperature. (3) $\alpha_2 = \beta_2 = 1$ throughout the structural changes. This fact indicates that when the

![Fig. 2](image-url)  
Fig. 2. Comparison of observed (circles) and calculated (solid lines) diffuse intensities along 10~ and 20~ rows in the cases of the heating conditions (b), (c), (d) and (f).

![Fig. 3](image-url)  
Fig. 3. The $w_1$ (open circles) and $w_2$ (full circles) values versus heating temperature (see Table 1).
layers $V$ and $V'$ are stacked in the faulted structures, a small number of $V'$ layers are always followed by a large number of $V$ layers. The structural changes, faulted $2H$ (found in as-grown crystals) $\rightarrow$ faulted $4H \rightarrow 4H$, were also studied with the same technique, and the above three results were confirmed.

To investigate whether the faulted structures finally change into the $4H$ structure with or without faults, many crystals with faulted structures were heated repeatedly at temperatures above $300^\circ$C. After heating most of the crystals still contained a small number of faults. This was found from the fact that on their Weissenberg photographs the spot at $\zeta = l + \frac{1}{2}$ is broader along $\zeta$ than that at $\zeta = l$ because of overlapping of narrow diffuse intensities. On the other hand, a few crystals changed into the $4H$ structure with no faults.

Such a difference in the structural change may possibly be due to strain in the crystals.

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References