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On the Structures of Rhombohedral Polytypes in CdI_2 Crystals

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A new polytype 18R[1212]$_3$ with space group $R\bar{3}m1$ has been discovered. When the layer sequence of each rhombohedral polytype, nR, reported so far is divided into three equal parts, they are found to have the same layer sequence as that of a frequently occurring polytype, 4H, 6H, 8H, 10H or 14H. A layer-slip process is considered, in which a rhombohedral polytype can be generated from a hexagonal polytype.

Introduction

Rhombohedral polytypes in CdI_2 crystals reported so far are 12R (Agrawal & Trigunayat, 1968), 24R and 36R (Jain, Chadha & Trigunayat, 1970), 30R and 42R (Chadha & Trigunayat, 1967) and 60R and 72R (Prasad & Srivastava, 1971). In this paper a new type 18R is reported and the layer sequences characteristic of rhombohedral polytypes are discussed.

A new polytype 18*R*

Crystals grown from aqueous solutions were thin hexagonal plates. 39 crystals were investigated by X-ray diffraction. Crystal plates frequently contained two or more polytypes in syntactic coalescence. Table 1 gives the frequency of occurrence of each polytype, the order of which qualitatively agrees with that of the frequencies reported by Mitchell (1956).

Table 1. *Frequencies of occurrence of various polytypes*

Types	Number observed	Percentage Present work	Percentage Mitchell (1956)
4H	27	48	48
Faulted 4H / Faulted 2H	11	20	8*
2H	5	9	3·8
6H	4	7	2·5
8H	0	0	1·9
10H	2	4	1·3
Others	7	13	34
Total	56	101 %	99·5 %

* This fraction also contains other faulted structures.

A new polytype 18R was identified from a zero-layer Weissenberg photograph taken with Cu $K\alpha$ radiation (Fig. 1). As seen from Fig. 1, the 18R was coalesced with 6H having the Zhdanov symbol (1122) and a very small amount of 4H. There are six possible structures for 18R: [15]$_3a$, b;* [24]$_3$; [1113]$_3a$, b; [1212]$_3$. Calculated intensities for the six structures were compared with observed intensities, and only those for [1212]$_3$ showed good agreement with observed intensities. Table 2 gives the detailed structure and a comparison between observed and calculated intensities.

* Two possible structures are represented by this Zhdanov symbol because, although the sequence of the I layers is given by the Zhdanov symbol, there are still two ways of arranging the Cd layers.

Table 2. *Structure and intensities of h0l reflexions of 18R polytype*

Space group $R\bar{3}m1$
Zhdanov symbol [1212]$_3$
ABC sequence
$(A\gamma B)$ $(A\gamma B)$ $(C\alpha B)$ $(C\beta A)$ $(C\beta A)$ $(B\gamma A)$ $(B\alpha C)$ $(B\alpha C)$ $(A\beta C)$
$a=4{\cdot}24$, $c=61{\cdot}51$ (hexagonal indexing)
Atomic coordinates

Iodine atoms at $00n_1z$, $\frac{1}{3}\frac{2}{3}n_2z$, $\frac{2}{3}\frac{1}{3}n_3z$; $n_1=0,4,14,18,22,32$; $n_2=2,6,10,20,24,28$; $n_3=8,12,16,26,30,34$.
Cadmium atoms at $00n_4z$, $\frac{1}{3}\frac{2}{3}n_5z$, $\frac{2}{3}\frac{1}{3}n_6z$; $n_4=9,25,29$; $n_5=13,17,33$; $n_6=1,5,21$.
$z=\frac{1}{36}$.

L	I_{obs}	I_{calc}	L	I_{obs}	I_{calc}
	10L		50	s.	222
43	m.	170	53	abs.	14
46	v.v.s.	1000	56	v.s.	542
49	abs.	38	59	abs.	31
52	v.s.	586	62	v.v.s.	760
55	abs.	15	65	w.	120
58	s.	191			
61	w.	111		$\bar{2}0L$	
64	v.s.	425	46	v.s.*	772
			49	abs.	32
	$\bar{1}0L$		52	v.s.	534
41	w.	53	55	abs.	14
44	v.s.	584	58	s.	207
47	m.	143	61	m.	133

* The absorption is high for this reflexion because of the plate-like shape of the crystal.

Structures of rhombohedral polytypes

On examination of layer sequences of rhombohedral polytypes (R polytypes) which are reported so far and listed in Table 3, it has been found that R polytypes are constructed of frequently occurring hexagonal polytypes (H polytypes), *i.e.*, let an R polytype, nR, be divided into three equal parts between two neighbouring I layers with no intervening Cd layer. As described in detail below, each of the three parts of 12R[13]$_3$ is

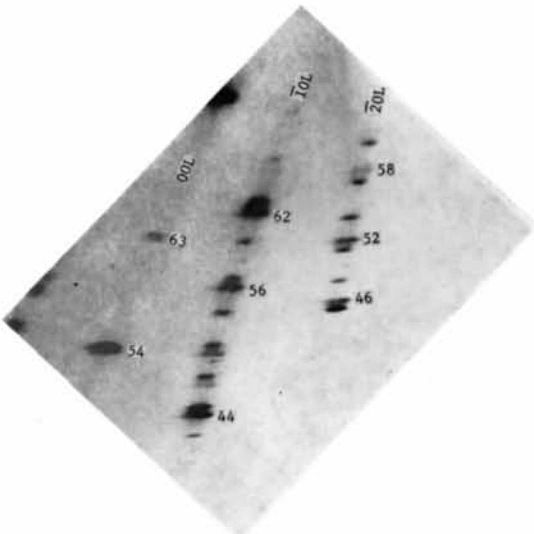

Fig. 1. An enlarged part of the Weissenberg photograph of 18*R* coalesced with 6*H* and a very small amount of 4*H*. The indexed spots and those with similar shape are reflexions from 18*R*, intense spots, excepting 18*R* spots, are reflexions from 6*H* and the remaining small spots are reflexions from 4*H*.

formed by one unit cell of $4H(22)$,* that of $24R[1322]_3$ formed by two unit cells of $4H$ or one unit cell of $8H(1232)$, that of $18R[1212]_3$ formed by one unit cell of $6H(1122)$, that of $36R[22112121]_3$ formed by two unit cells of $6H(1122)$, that of $30R[121222]_3$ formed by one unit cell of $10H(112222)$ and that of $42R[12122222]_3$ formed by one unit cell of $14H(11222222)$.† Both the three parts of $60R[(22)_3 1223]_3$ and that of $72R[(22)_4 1223]_3$ consist of the unit cell of $4H$. Table 3 gives these relations between R and H polytypes.

Table 3. *Rhombohedral polytype and its basic polytype*

All hexagonal polytypes in this table have been reported by Mitchell (1956) except $8H$ reported by Lal, Chadha & Trigunayat (1971).

$12R[13]_3$	$4H(22)$
$24R[1322]_3$	$4H(22)$,† $8H(1232)$†
$18R[1212]_3$	$6H(1122)$
$36R[22112121]_3$	$6H(1122)$†
$30R[121222]_3$	$10H(112222)$†
$42R[12122222]_3$	$14H(11222222)$†
$60R[(22)_3 1223]_3$	$4H(22)$†
$72R[(22)_4 1223]_3$	$4H(22)$†

† A syntactic coalescence of the rhombohedral polytype with its basic polytype is not yet reported in these cases.

R polytypes therefore can be generated from H polytypes as follows. The $12R$ and $24R$ are generated from $4H$ by the slip:

$$\begin{array}{c}
\qquad\qquad [\mathrm{cyc}]_p \qquad\qquad\qquad [\mathrm{cyc}]_p \\
\qquad\qquad \uparrow \qquad\qquad\qquad\quad \uparrow \\
\ldots [4H]_p[4H]_p[4H]_p[4H]_p[4H]_p[4H]_p[4H]_p \ldots, \\
\downarrow \qquad\qquad\qquad\quad \downarrow \qquad\qquad \\
[\mathrm{ant}]_p \qquad\qquad\quad [\mathrm{ant}]_p \qquad\qquad
\end{array}$$

where $[4H]$ represents the ABC sequence of $4H$, $(AB)(CB)$, and $[4H]_p$ indicates that $[4H]$ is repeated p times. Here (AB), (CB),..., *etc.* are abbreviations of $(A\gamma B)$, $(C\alpha B)$, ..., *etc.* respectively. [cyc] represents $(BC)(AC)$ which is obtained by the slipping of $[4H]$ in a cyclic ($A \rightarrow B \rightarrow C \rightarrow A$) manner and [ant] represents $(CA)(BA)$ which is obtained by the slipping of $[4H]$ in an anticyclic ($A \rightarrow C \rightarrow B \rightarrow A$) manner. The case of $p=1$ stands for a generation of $12R$ from $4H$ and that of $p=2$ stands for a generation of $24R$ from $4H$. The $24R$ is also generated from $8H$ by the slip:

$$\begin{array}{c}
\qquad [\mathrm{cyc}] \\
\qquad \uparrow \\
\ldots [8H]\,[8H]\,[8H]\,[8H] \ldots, \\
\downarrow \qquad \\
[\mathrm{ant}] \qquad
\end{array}$$

where $[8H]$ represents the ABC sequence of $8H$, $(AB)(AC)(AB)(CB)$,* and both [cyc] and [ant] have the same meanings as above.† The $18R$ and $36R$ are generated from $6H$ by the slip:

$$\begin{array}{c}
\qquad [\mathrm{cyc}]_p \\
\qquad \uparrow \\
\ldots [6H]_p[6H]_p[6H]_p[6H]_p \ldots, \\
\downarrow \qquad \\
[\mathrm{ant}]_p \qquad
\end{array}$$

where $[6H]$ represents the ABC sequence of $6H$, $(AB)(AB)(CB)$. The case of $p=1$ stands for a generation of $18R$ from $6H$ and that of $p=2$ stands for a generation of $36R$ from $6H$.‡ The $30R$ is generated from $10H$ by the slip:

$$\begin{array}{c}
\qquad [\mathrm{cyc}] \\
\qquad \uparrow \\
\ldots [10H]\,[10H]\,[10H]\,[10H] \ldots, \\
\downarrow \qquad \\
[\mathrm{ant}] \qquad
\end{array}$$

where $[10H]$ represents the ABC sequence of $10H$, $(AB)(AB)(CB)(AB)(CB)$. The $42R$ is generated from $14H$ by the slip:

$$\begin{array}{c}
\qquad [\mathrm{cyc}] \\
\qquad \uparrow \\
\ldots [14H]\,[14H]\,[14H]\,[14H] \ldots, \\
\downarrow \qquad \\
[\mathrm{ant}] \qquad
\end{array}$$

where $[14H]$ represents the ABC sequence of $14H$, $(AB)(AB)(CB)(AB)(CB)(AB)(CB)$. The above slip process by which an R polytype is generated from an H polytype is called a 'single slip process' (s.s.p.) in contrast to the 'periodic slip process' proposed by Mardix, Kalman & Steinberger (1968). The $60R$ and $72R$ are generated from $4H$ by the slip:

$$\begin{array}{c}
\qquad\qquad\qquad\qquad\qquad (BC) \\
\qquad\qquad\qquad\qquad\qquad \uparrow \\
\ldots [4H]_p(AB)\,(CB)\,[4H]_p(AB) \\
\qquad \downarrow \qquad\qquad \downarrow \\
\qquad (CA) \qquad\quad [\mathrm{ant}]_p \\
[\mathrm{cyc}]_p \qquad (AC) \qquad\qquad\qquad \\
\uparrow \qquad\quad \uparrow \qquad\qquad\qquad \\
(CB)\,[4H]_p(AB)\,(CB)\,[4H]_p \ldots. \\
\downarrow \qquad\qquad\qquad\qquad\qquad \\
(BA) \qquad\qquad\qquad\qquad\qquad
\end{array}$$

* This characteristic of $12R[13]_3$ had been pointed out by Agrawal & Trigunayat (1968).

† The Zhdanov numbers are rearranged from those reported in order to show a correspondence between R and H polytypes.

* The $8H$ is generated from $4H$ by the slip:

$$\begin{array}{c}
(AC) \qquad\qquad\qquad\qquad (AC) \\
\uparrow \qquad\qquad\qquad\qquad\quad \uparrow \\
\ldots (AB)\,(CB)\,(AB)\,(CB)\,(AB)\,(CB)\,(AB)\,(CB) \ldots.
\end{array}$$

† The $24R$ cannot be generated from $8H(111122)$ (Mitchell, 1956) because of the above assumption that the slip occurs only between two neighbouring I layers with no intervening Cd layer.

‡ The $36R$ can not be generated from $12H(22121121)$ (Mitchell, 1956) because of the previous assumption for the slip.

The case of $p=4$ stands for a generation of $60R$ from $4H$ and that of $p=5$ stands for a generation of $72R$ from $4H$. In these cases the large block $[4H]_p$ obeys the s.s.p. and, furthermore, incidental slips of the small blocks (AB) and (CB) occur.

Agrawal & Trigunayat (1968) reported that $12R$ was coalesced with $4H$. In the present study $18R$ was coalesced with $6H$ (Fig. 1). The layer sequences characteristic of R polytypes shown above are easily understood if, on the basis of these facts of coalescence, a hypothesis is built up that the s.s.p. with a slip unit of integral multiples of the period of an H polytype occurs in the H polytype, $4H$, $6H$, $8H$, $10H$ or $14H$, and an R polytype is formed.

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Coherent Nuclear Scattering Amplitudes of Germanium, Copper and Oxygen for Thermal Neutrons

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The forward nuclear scattering amplitudes of Ge, Cu and O for thermal neutrons have been determined from the refractive bending by pure single-crystal right prisms of germanium, copper, and quartz. The results are $b_{Ge}=8{\cdot}1929$ (17) fm and $b_{Cu}=7{\cdot}689$ (6) fm which are in good agreement with previous less accurate determinations by other methods and $b_O=5{\cdot}830$ (2) fm which disagrees with an independent accurate determination by four standard deviations.

Introduction

Both Pendellösung and prism refraction offer effects from which neutron structure factors or scattering amplitudes can be determined with a precision of one part in 5000 (Shull & Shaw, 1973; Schneider, 1973). Small-angle scattering (Koester & Knopf, 1971) from powders immersed in liquids of differing refractive indexes and mirror reflection (Donaldson, Passel, Bartolini & Graves, 1965) can lead to scattering amplitudes with precisions of one part in 1000. Since the small neutron–electron Foldy (1951) interaction disappears in the forward scattering direction, prism refraction, mirror reflection and small-angle scattering experiments on non-magnetic materials yield direct values for the nuclear-force scattering amplitude. Comparison of the prism and Pendellösung results can yield information on the Foldy scattering amplitude, $b_{\rm Atom}=b_{\rm Nucleus}+b_{\rm Foldy}$ where $b_{\rm Foldy}=+0{\cdot}00131\,(1-f)Z$ fm where Z is the number of nuclear protons and f is the electron form factor, if the Debye–Waller temperature factor is known with sufficient precision. The excellent work of Batterman & Chipman (1962) provides the Debye temperature $\theta_{Ge}=290$ (5) K with just less than sufficient precision to draw significant conclusions here. The discrepancy between the theoretical (Foldy, 1951) and experimental (Krohn & Ringo, 1966, 1973) values for the neutron–electron interaction must then be resolved by other means.

The purpose of this work is rather to improve the basic knowledge of thermal neutron scattering amplitudes for several common elements: Ge, Cu, and O. The need for scattering amplitudes is not only to extend our knowledge of the neutron interactions with atoms, but also to allow more detailed studies of materials' structures where diffracted intensities depend upon structure and scattering amplitudes.

The prism technique used here extracts the scattering