average values 0·956 Å for the O—H length and 107·8° for the H—O—H angle. In the present study only the O(W)—H(2) bond of 0·931 Å deviates from the average water molecule.

There are only two possible O acceptor atoms (O···H < 2·4 Å) to the water H atoms: O(1) at 1·90 and O(W) at 2·26 Å. The corresponding O···O distances are 2·85 and 3·18 Å with O—H···O angles of 171 and 170°. Brown (1976) has, from a bond-valence analysis of the repulsion between the O atoms in an O—H···O bond, predicted a correlation between the O···H distance and the O—H···O angles. The angle 171° is somewhat larger than calculated from the O···H distance of 1·90 Å and for an acceptor distance of 2·26 Å a much more bent hydrogen bond is suggested than that found in the present structure. A weak hydrogen bond with a similar geometry is however found in $Na_2H_2SiO_4.5H_2O$ (Williams & Dent Glasser, 1971) with an O···O hydrogen bond of 3·13 Å, an acceptor distance of 2·24 Å and an O—H···O angle of 175°. The hydrogen bond of normal strength, O(W)···O(1), connects the $HgSO_4.H_2O$ molecules in chains running in the xz plane (Fig. 2), linked in the y direction by the very weak hydrogen bond O(W)··· O(W). The environment of the water molecule in $HgSO_4.H_2O$ is tetrahedral (Fig. 3), including the two hydrogen-bonded atoms O(1) and O(W) and, in the directions of the lone pairs, Hg and H(2). The hydrate thus belongs to class $2H$ according to Ferraris & Franchini-Angela (1972).

References

AURIVILLIUS, K. (1964). Ark. Kemi, 23, 205–211.
AURIVILLIUS, K. (1968). Ark. Kemi, 28, 279–288.
AURIVILLIUS, K. & STÅLHANDSKE, C. (1975). Z. Kristallogr. 142, 129–141.
AURIVILLIUS, K. & STÅLHANDSKE, C. (1976a). Z. Kristallogr. 144, 1–15.
AURIVILLIUS, K. & STÅLHANDSKE, C. (1976b). Acta Chem. Scand. Ser. A, 30, 735–739.
AURIVILLIUS, K. & STÅLHANDSKE, C. (1980). Z. Kristallogr. To be published.
BACON, G. E. (1972). Acta Cryst. A28, 357–358.
BONEFAČIĆ, A. (1961). Acta Cryst. 14, 116–119.
BRÉGEAULT, J.-M. & HERPIN, P. (1970). Bull. Soc. Fr. Minéral. Cristallogr. 93, 37–42.
BROWN, I. D. (1976). Acta Cryst. A32, 24–31.
CROMER, D. T. & LIBERMAN, D. (1970). J. Chem. Phys. 53, 1891–1898.
DOYLE, P. A. & TURNER, P. S. (1968). Acta Cryst. A24, 390–397.
FERRARIS, G. & FRANCHINI-ANGELA, M. (1972). Acta Cryst. B28, 3572–3583.
GRDENIĆ, D. (1965). Q. Rev. Chem. Soc. 19, 303–328.
KAMENAR, B. (1969). Acta Cryst. B25, 800–804.
KOKKOROS, P. A. & RENTZEPERIS, P. J. (1963). Z. Kristallogr. 119, 234–244.
SLEIGHT, A. W. & PREWITT, C. T. (1973). J. Solid State Chem. 6, 509–512.
STÅLHANDSKE, C. (1978). Acta Cryst. B34, 1408–1411.
STÅLHANDSKE, C. (1980). Acta Cryst. To be published.
TEMPLETON, L. T., TEMPLETON, D. H. & ZALKIN, A. (1964). Acta Cryst. 17, 933–936.
WILLIAMS, P. P. & DENT GLASSER, L. S. (1971). Acta Cryst. B27, 2269–2275.
ZACHARIASEN, W. H. (1967). Acta Cryst. 23, 556–564.

The Crystal Structure of a New Polytype 12R of Cadmium Bromide

By S. D. Sharma and G. L. Sharma*

Department of Physics, Indian Institute of Technology, New Delhi 110029, India

and V. K. Agrawal

Department of Physics, Motilal Nehru College (University of Delhi), New Delhi 110021, India

Abstract

The crystal structure of a new rhombohedral polytype, 12R, of cadmium bromide, $CdBr_2$, has been determined. It is found to be $(13)_3$ in the Zhdanov notation with space group $R\bar{3}m1$. Its formation has been explained by a layer-transformation mechanism.

Introduction

Only two reports (Mitchell, 1962; Agrawal & Trigunayat, 1970) are available on polytypism in $CdBr_2$

---

* On leave from Department of Physics, Government Science College, Gwalior, India.

crystals grown at room temperature. Most of the crystals were found to have a $6R$ twinned structure or were coalesced with $4H$ or were disordered. However, crystals grown in the vapour phase under stabilized conditions were found to be only $6R$ type (Mitchell, 1962; Mehrotra, 1978). In the present study, an attempt was made to grow the crystals from solution in a furnace at a constant temperature of 313 K. One of the crystals has been found to be $12R$ mixed with $4H$ and $6R$. Earlier, Mitchell (1962) had also reported a 12-layered polytype coalesced with $4H$ and twinned $6R$ but did not determine its stacking sequence because the presence of superposed twinned $6R$ and $4H$ reflexions made a choice between $12H$ and $12R$ impossible. However, in the present case, the polytype could be easily identified as $12R$ by taking oscillation photographs in different ranges.

Experimental

The crystals grown from aqueous solution (Mitchell, 1962) were thick hexagonal platelets ranging from 1 to 7 mm in length and from 0·01 to 1·4 mm in thickness. X-ray a-axis oscillation photographs were taken in the ranges 25–40°/33–48°, the angles which the c axis made with the incident X-ray beam, to record a large number of $01.l/10.l$ reflexions on the zero/first layer lines. Figs. 1 and 2 are the oscillation photographs of a CdBr$_2$ crystal in the ranges 25–40° and 33–48°, respectively.

Fig. 1. X-ray a axis 15° oscillation photograph of polytype $12R$; the angle between the incident beam and c varies between 25 and 40°; Cu $K\alpha$ radiation, camera radius 30 mm. The arrow indicates the l value of a $01.l$ reflexion.
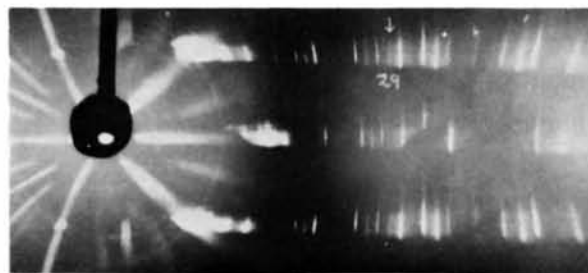

Fig. 2. As Fig. 1 but the angle between the incident beam and c varies between 33 and 48°. The arrow indicates the l value of a $10.l$ reflexion.

Structure determination

There are only two possible structures for $12R$: (a) $(31)_3$ and (b) $(13)_3$. The intensity calculations were made for $01.l$ and $10.l$ reflexions, l varying from 0 to 48 for these structures, with standard formulae (Jain & Trigunayat, 1978) and compared with observed intensities. Since the spots for $l = 0$ to 24 are obtained in transmission, and some of them are not visible due to absorption, the comparison was made for the reflexions 10.24 to 10.48 and 01.24 to 01.48. Calculated and observed intensities listed in Table 1 were found to be in good agreement with each other for structure (b). The polytype $12R$ was found to be coalesced with $4H$ and $6R$; the spots of $4H$ do not interfere with the positions of $12R$; however, the spots of $6R$ overlap on alternate spots of $12R$, marked by asterisks in Table 1. Therefore, the actual comparison of intensities could be made only for reflexions with $l = 25, 29, 31, 35, 37$. Since the calculated intensities for these l values differed widely for the structures (a) and (b), there was no ambiguity in identifying the present structure as $(13)_3$. The detailed structure of $12R$ is as follows:

Space group $R\bar{3}m1$; Zhdanov symbol 131313; ABC sequence: $(A\gamma B)(A\beta C)(B\alpha C)(B\gamma A)(C\beta A)(C\alpha B)$; $a = b = 3.985$, $c = 37.682$ Å (hexagonal indexing).

Atomic coordinates

Iodine atoms at $00n_1Z$, $\frac{12}{33}n_2Z$, $\frac{21}{33}n_3Z$; $n_1 = 0, 4, 14, 18$; $n_2 = 2, 8, 12, 22$; $n_3 = 6, 10, 16, 20$.

Cadmium atoms at $00n_4Z$, $\frac{12}{33}n_5Z$, $\frac{21}{33}n_6Z$; $n_4 = 9, 21$; $n_5 = 5, 17$; $n_6 = 1, 13$, where $Z = 1/24$.
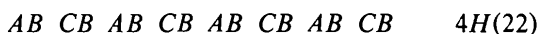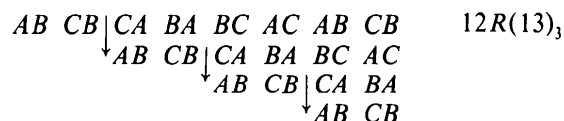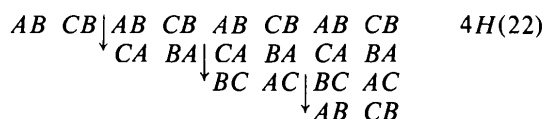
Discussion

Since the crystals of CdBr$_2$ were generally found to consist of a mixture of polytypes in syntactic coalescence with each other, the oscillation photographs were separately recorded from opposite basal

Table 1. *Calculated and observed relative intensities for the structure $12R$*

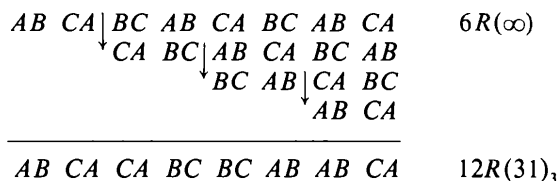| $(01.l)$	I_{calc} $(31)_3$	I_{obs} $(13)_3$	
25	46	11	a
28*	61	95	ms
31	303	133	ms
34*	90	353	s
37	129	10	a
$(10.l)$			
26*	0	65	s
29	0	165	ms
32*	9	313	vs
35	214	11	a
38*	185	483	s

* As mentioned in the text, these reflexions overlap with $6R$ positions.

faces of the crystal. In the present case, one basal face of the crystal exhibited the reflexions of 4H, 12R and 6R (Figs. 1, 2) whereas the opposite one showed the spots of 4H, 12R and twinned 6R. The shape and size of the spots of twinned 6R were different from those of 4H and 12R; the spots of only 4H and 12R were found to be joined to each other by streaks. Also, when different regions of the basal face of the crystal were irradiated only one of the twinned 6R was found in coexistence with 4H and 12R. Therefore, it is plausible to assume that the type 12R coalesced with 4H occurred as a result of transformation of 4H or *vice versa*. This transformation can easily take place by introducing periodic slip in either of the polytypes 4H or 12R, as explained below.

$$
\begin{array}{llllllll}
AB & CB| AB & CB & AB & CB & AB & CB & \quad 4H(22) \\
& {}^{\downarrow}CA & BA| CA & BA & CA & BA \\
& & {}^{\downarrow}BC & AC| BC & AC \\
& & & & {}^{\downarrow}AB & CB
\end{array}
$$

$$
\begin{array}{llllllll}
AB & CB| CA & BA & BC & AC & AB & CB & \quad 12R(13)_3 \\
& {}^{\downarrow}AB & CB| CA & BA & BC & AC \\
& & {}^{\downarrow}AB & CB| CA & BA \\
& & & & {}^{\downarrow}AB & CB
\end{array}
$$

$$
\begin{array}{llllllll}
AB & CB & AB & CB & AB & CB & AB & CB & \quad 4H(22)
\end{array}
$$

Although there are two possible structures of 12R, only the one with Zhdanov symbol $(13)_3$ has been observed in CdBr₂ as well as in the isostructural CdI₂ and PbI₂ (Agrawal & Trigunayat, 1968; Mitchell, 1959). Recently, Agrawal (1979) has explained the non-occurrence of the other structure in CdI₂ and PbI₂ by a change in hexagonality (defined as the ratio of the number of anion layers in h.c.p. orientation to the total number of anion layers in the unit cell) of the transformed structure and through the orientation of the top and bottom layers of two successive sandwiches around the boundary of rotation coming into the same orientation after transformation. Similar argu-

ments can be given for transformation of 4H into 12R in CdBr₂. However, the most common polytype of CdBr₂ is reported to be 6R and if the periodic slip is introduced in 6R at the same interval as in 4H/12R, the other structure $(31)_3$ would be formed, as explained below.

$$
\begin{array}{llllllll}
AB & CA| BC & AB & CA & BC & AB & CA & \quad 6R(\infty) \\
& {}^{\downarrow}CA & BC| AB & CA & BC & AB \\
& & {}^{\downarrow}BC & AB| CA & BC \\
& & & & {}^{\downarrow}AB & CA
\end{array}
$$

$$
\begin{array}{lllllllll}
AB & CA & CA & BC & BC & AB & AB & CA & \quad 12R(31)_3
\end{array}
$$

Therefore, the occurrence of 12R $(31)_3$ as a result of a transformation of 6R is quite probable in CdBr₂. However, in this process, the hexagonality of a transformed structure is increased from 0 to 0·5 and also the top and bottom layers of two successive sandwiches around the boundary of rotation occur in different orientations whereas in 6R they are in the same orientation. For these reasons, stable polytypes may not be formed in CdBr₂ and disordered structures are observed in abundance.

References

AGRAWAL, V. K. (1979). To be published.
AGRAWAL, V. K. & TRIGUNAYAT, G. C. (1968). *Acta Cryst.* B24, 971–972.
AGRAWAL, V. K. & TRIGUNAYAT, G. C. (1970). *Acta Cryst.* A26, 426–429.
JAIN, P. C. & TRIGUNAYAT, G. C. (1978). *Acta Cryst.* B34, 2677–2684.
MEHROTRA, K. (1978). *J. Cryst. Growth*, 44, 45–49.
MITCHELL, R. S. (1959). *Z. Kristallogr.* 111, 372–384.
MITCHELL, R. S. (1962). *Z. Kristallogr.* 117, 309–318.

The Structure of KNiCl₃ at Room Temperature

BY D. VISSER, G. C. VERSCHOOR AND D. J. W. IJDO

Gorlaeus Laboratories, University of Leiden, PO Box 9502, 2300 *RA Leiden, The Netherlands*

Abstract

The crystal structure of KNiCl₃ at room temperature has been determined by single-crystal X-ray techniques.

The crystals are hexagonal, $P6_3cm$, with the cell dimensions $a = 11·795$ (1) and $c = 5·926$ (1) Å, and $Z = 6$. Full-matrix least-squares refinement of 323 observed reflexions gave a conventional index R_w of