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Determination of the Structures of Three New Cadmium Iodide Polytypes

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Abstract. The structures of three new polytypes, $16H_{12}$, $22H_{10}$ and $22H_{11}$, of cadmium iodide have been determined. The structures are $222112(11)_3$, $(22)_2 1122(11)_4$ and $2112(11)_8$ in Zhdanov notation, each with space group $P3m1$. The respective homometric counterparts of the above structures are $(11)_3 211222$, $(11)_4 2211(22)_2$ and $(11)_8 2112$.

Introduction. In the study of the phenomenon of polytypism cadmium iodide has emerged as one of the most extensively studied and richly polytypic compounds. So far, crystal structures of about 190 different polytypes of this compound have been determined by various workers. The three polytypes of which the crystal structures are reported in the present paper were discovered during a combined optical and X-ray diffraction study of the complete history of growth of CdI_2 crystals.

Even for the moderately sized unit cell of cadmium iodide, the number of possible structures runs into a few thousands, to start with. However, existence of specific regularities in the stacking of layers (see *e.g.* Srinivasan & Parthasarathi, 1973) and other considerations help to reduce the number of possibilities substantially. The methods of structure determination of MX_2-type compounds have been refined by Jain & Trigunayat (1978) and Wahab & Trigunayat (1980), permitting a drastic reduction in the number of initial possibilities. These refinements have been employed in the present structure determination.

Experimental. Crystals grown at room temperature in Petri dish by slow evaporation of aqueous solution of cadmium iodide; well developed crystals picked up for X-ray diffraction; *a*-axis 15° oscillation photographs, which record a large number of 10.*l* reflections, used for both identification and structure determination of polytypes. Usual method of comparison of calculated intensities of reflections with observed intensities employed for structure determination.

Discussion. The complete structures of the three polytypes are listed in Table 1.

Polytype $16H_{12}$. This polytype was found on one of the faces of a well developed crystal, the other face of which was found to be the polytype $16H_9$. Various Zhdanov sequences containing several 2's and pairs of 1's were tried. Of these, the sequence $222112(11)_3$ gave satisfactory agreement between the calculated and the observed intensities (Table 2). The oscillation photograph of the polytype is depicted in Fig. 1. According to Jain & Trigunayat (1977), the structural sequence $222112(11)_3$ possesses a homometric counterpart $(11)_3 211222$. There is no known way of distinguishing between two homometric structures. Hence the structure in the present case is not uniquely determinable and the actual structure may be either of the two sequences. Since eleven CdI_2 polytypes of 16 layers each have already been reported (Pałosz & Gierlotka, 1984), the present polytype has been denoted as $16H_{12}$.

Polytype $22H_{10}$. This polytype was found on one of the faces of a well developed crystal, the other face of which was found to be $16H_7$. The intensities of reflections on the X-ray photograph (Fig. 1) showed a similarity to $2H$ in that the positions of the strongest reflections coincided with those of the $2H$ reflections. Therefore, it was surmised that the crystal structure ought to contain a large number of (11) units. Further, a symmetric distribution of the intensities of spots suggested the presence of 2's and pairs of 1's alone in the Zhdanov symbol. A large number of arrangements containing 2's and (11) units were tried. Excellent agreement between the calculated and the observed values of the intensities was obtained for the structure $(22)_2 1122(11)_4$. The intensity values are listed in Table 3. Like the previous case, this structure has $(11)_4 2211(22)_2$ as its homometric counterpart. The actual structure may be either of these two. With nine polytypes of 22 layers each having already been reported (Pałosz & Gierlotka, 1984), the present one has been designated as $22H_{10}$.

Polytype $22H_{11}$. This polytype was detected on one of the faces of a thin crystal, the other face of which was detected to be a heavily disordered unidentified polytype. Initial examination of the intensity distribution of the reflections on the X-ray photograph (Fig. 1) showed that the most intense spots lay on or symmetrically around the diffraction spots of the smallest-period polytype $2H$. So a number of possibilities containing a majority of (11) units were tried, out of which the structure $2112(11)_8$ gave an excellent

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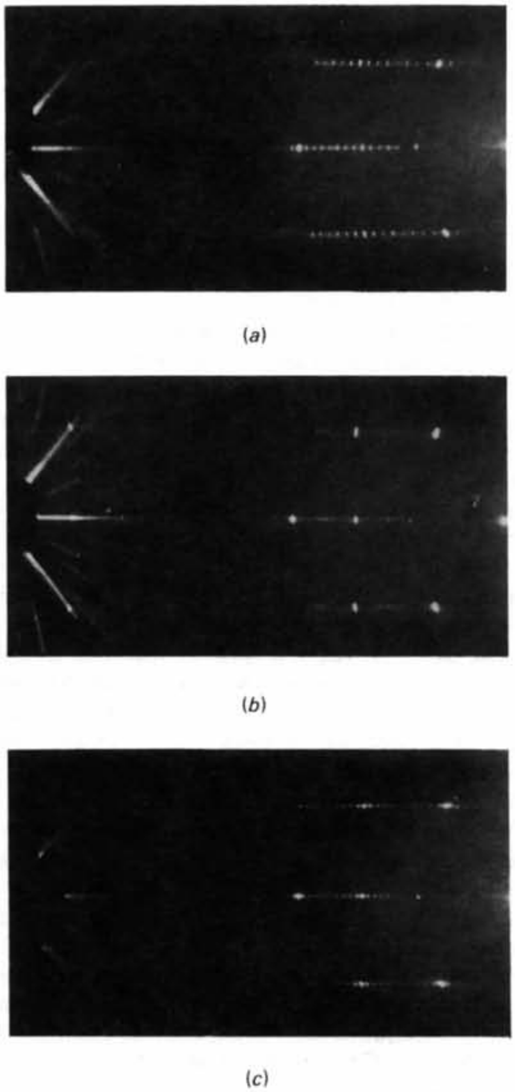
Table 1. *The detailed structural data of the polytypes* $16H_{12}$, $22H_{10}$ *and* $22H_{11}$

	$16H_{12}$	$22H_{10}$	$22H_{11}$
Cell dimensions (Å)	$a = b = 4{\cdot}24, c = 54{\cdot}68$	$a = b = 4{\cdot}24, c = 75{\cdot}19$	$a = b = 4{\cdot}24, c = 75{\cdot}19$
Zhdanov symbol	$222112(11)_3$	$(22)_2 1122(11)_4$	$2112(11)_8$
ABC sequence	$[(A\gamma B)(C\alpha B)]_2(C\alpha B)(A\gamma B)_3$	$[(A\gamma B)(C\alpha B)]_2(A\gamma B)_2(C\alpha B)(A\gamma B)_4$	$(A\gamma B)(C\alpha B)_2(A\gamma B)_8$
Atom coordinates	Iodine atoms at $00n_1/32, \frac{2}{3}\frac{1}{3}n_2/32, \frac{1}{3}\frac{2}{3}n_3/32$ $n_1 = 0,8,20,24,28$ $n_2 = 2,6,10,14,18,22,26,30$ $n_3 = 4,12,16$ Cadmium atoms at $00n_4/32, \frac{1}{3}\frac{2}{3}n_5/32$ $n_4 = 5, 13, 17$ $n_5 = 1,9,21,25,29$	Iodine atoms at $00n_1/44, \frac{2}{3}\frac{1}{3}n_2/44, \frac{1}{3}\frac{2}{3}n_3/44$ $n_1 = 0,8,16,20,28,32,36,40$ $n_2 = 2,6,10,14,18,22,26,30,34,38,42$ $n_3 = 4,12,24$ Cadmium atoms at $00n_4/44, \frac{1}{3}\frac{2}{3}n_5/44$ $n_4 = 5, 13, 25$ $n_5 = 1,9,17,21,29,33,37,41$	Iodine atoms at $00n_1/44, \frac{2}{3}\frac{1}{3}n_2/44, \frac{1}{3}\frac{2}{3}n_3/44$ $n_1 = 0,12,16,20,24,28,32,36,40$ $n_2 = 2,6,10,14,18,22,26,30,34,38,42$ $n_3 = 4,8$ Cadmium atoms at $00n_4/44, \frac{1}{3}\frac{2}{3}n_5/44$ $n_4 = 5, 9$ $n_5 = 1,13,17,21,25,29,33,37,41$
Space group	$P3m1$	$P3m1$	$P3m1$


(*a*)

(*b*)

(*c*)

Fig. 1. 15° *a*-axis oscillation photograph of the polytypes (*a*) $16H_{12}$, (*b*) $22H_{10}$ and (*c*) $22H_{11}$ (3 cm camera; Cu $K\alpha$ radiation). The first most intense spot from the centre on the zero layer has $l = 5n/2$ for all three *nH* polytypes.

Table 2. *Calculated and observed relative intensities for* 10.*l* *reflections of the polytype* $16H_{12}$

(*w*→weak, *m*→medium, *s*→strong.)

l	Calculated intensity	Observed intensity	*l*	Calculated intensity	Observed intensity
35	40	*vw*	44	86	*ms*
36	22	*vw*	45	267	*vs*
37	93	*w*	46	91	*s*
38	41	*ms*	47	273	*vs*
39	150	*vs*	48	570	*vvs*
40	1242	*vvs*	49	263	*vs*
41	203	*vs*	50	84	*s*
42	75	*s*	51	238	*vs*
43	243	*vs*	52	74	*ms*

Table 3. *Calculated and observed relative intensities for* 10.*l* *reflections of the polytypes* $22H_{10}$ *and* $22H_{11}$

	$22H_{10}$		$22H_{11}$	
l	Calculated intensity	Observed intensity	Calculated intensity	Observed intensity
48	6	*vw*	9	*vvw*
49	6	*w*	1	*vvw*
50	9	*w*	2	*vvw*
51	21	*w*	22	*w*
52	3	*vvw*	66	*ms*
53	9	*w*	130	*ms*
54	12	*vvw*	194	*s*
55	276	*vvs*	1373	*vvs*
56	17	*w*	241	*vs*
57	17	*w*	201	*s*
58	7	*vw*	131	*ms*
59	75	*s*	56	*w*
60	47	*ms*	7	*vvw*
61	50	*ms*	7	*vvw*
62	89	*s*	62	*w*
63	10	*vw*	155	*s*
64	26	*w*	258	*vs*
65	30	*w*	334	*vs*
66	304	*vvs*	2010	*vvs*
67	30	*w*	326	*vs*
68	26	*w*	244	*vs*
69	10	*vw*	143	*s*
70	91	*s*	55	*w*
71	52	*ms*	6	*vvw*
72	49	*ms*	6	*vvw*
73	79	*s*	46	*w*

match between the observed and the calculated intensities. The intensity data are given in Table 3. Once again, this structure has a homometric counterpart $(11)_8$-2112. Hence the actual structure is either of the two. Since the previous 22-layered polytype was represented as $22H_{10}$, the present one has been designated as $22H_{11}$.

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Structure du Sulfure de Gallium et de Potassium, $KGaS_2$

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Abstract. $M_r = 172{\cdot}95$, monoclinic, Aa, $a = 14{\cdot}791$ (5), $b = 10{\cdot}425$ (3), $c = 10{\cdot}424$ (2) Å, $\gamma = 100{\cdot}16$ (2)°, $V = 1582{\cdot}15$ (77) Å^3, $Z = 16$, D_m(293 K) $= 2{\cdot}8$ (1), $D_x = 2{\cdot}90$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 90{\cdot}9$ mm^{-1}, $F(000) = 1312$, 293 K, $R = 0{\cdot}039$ for 1293 independent reflections. The compound crystallizes in a layer structure; each layer is made up of tetrahedral Ga_4S_{10} polyanions, with two anion layers perpendicular to **a*** in the unit cell. Two adjacent layers are held together by K^+ ions. The Ga—S and K—S bond lengths are normal and the structure is typical of tetrahedral MX_2 structures.

Introduction. $KGaS_2$ a été préparé dans le cadre de l'étude de chalcogénures mixtes du gallium et d'éléments monovalents (Na,K). Il est obtenu par action de H_2S sur un mélange de GaO(OH) et K_2CO_3, en proportions stoechiométriques, à 1070 K. Les cristaux se sont formés au cours du chauffage de ce composé avec dix parties de KBr, vers 1270 K.

Partie expérimentale. Monocristal de couleur orange, parallélépipède de dimensions: 150 × 160 × 240 µm, masse volumique mesurée par pycnométrie à 293 K; 15 réflexions utilisées pour affiner les paramètres de la maille, θ variant de 5,91 à 26,81°; 1509 réflexions indépendantes, $\sin\theta \leq 0{,}65$, h −20 à 0, k −15 à 15, l 0 à 15; diffractomètre automatique à quatre cercles Syntex, balayage ω–2θ, angles $-0{,}7° + 2\theta_1$ à $0{,}7° + 2\theta_2$, θ_1 et θ_2 étant les angles de diffraction correspondant respectivement aux longueurs d'onde $K\alpha_1$ et $K\alpha_2$ du molybdène; 1293 réflexions telles que $I > 3\sigma(I)$ conservées; l'écart-type $\sigma(I)$ sur la mesure de l'intensité I est déduit de l'écart-type σ_c sur le taux de comptage et de l'écart-type relatif σ_i sur la variation des réflexions de référence par la relation: $\sigma(I) = (\sigma_c^2 + \sigma_i^2 I^2)^{1/2}$; l'écart-type relatif sur l'instabilité égal à 0,015 déterminé avec l'intensité des réflexions de référence $\bar{1}44$ et $1\bar{4}4$ et vérifiées toutes les 50 mesures; les I corrigées des facteurs de Lorentz–polarisation et mises à l'échelle absolue par la méthode statistique de Wilson; correction d'absorption réalisée au moyen du programme de J. A. Ibers d'après la méthode analytique décrite par de Meulenaer & Tompa (1965), max. et min. facteur de transmission 0,55 et 0,38; résolution de la structure effectuée en deux étapes: localisation des atomes de gallium par les méthodes directes, puis recherche de la position des atomes de potassium et de soufre par analyse des densités électroniques tridimensionnelles; facteurs de structure normalisés E calculés pour toutes les réflexions en prenant comme facteur d'agitation thermique celui obtenu par la méthode statistique de Wilson, soit $B = 0{,}71$ Å^2; la distribution statistique des E est acentrique ce que confirme la noncentrosymétrie de la structure; les 150 valeurs de $E > 1{,}53$ introduites dans *MULTAN* de Germain, Main & Woolfson (1971); un calcul de cartes de Fourier des E à partir de la solution ayant la figure de mérite la plus élevée fait apparaître dans l'unité asymétrique quatre pics de même poids que l'on attribue au gallium; plusieurs autres séries de Fourier des différences effectuées à partir des phases calculées avec ces atomes

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