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**The crystal structure of  $\gamma$ -Cd(OH)<sub>2</sub>.** By P. M. DE WOLFF, *Laboratorium voor Technische Natuurkunde, Technische Hogeschool, Delft, The Netherlands*

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A new Cd(OH)<sub>2</sub> phase entirely different from the C6 type was discovered by Glemser, Hauschild & Richert (1957), who termed it  $\gamma$ -Cd(OH)<sub>2</sub>. It shows a very close similarity to the 'hydroxyfluoride II' Cd(OH)<sub>2-x</sub>F<sub>x</sub>,  $x=0.3$  to  $0.4$  (Feitknecht & Bucher, 1943), the powder pattern of which can be indexed (Oswald, 1959) on the basis of an *I*-centered unit cell:

$$a = 5.63, b = 10.18, c = 3.40 \text{ \AA}; \alpha = \beta = \gamma = 90^\circ$$

as compared with

$$a = 5.67, b = 10.25, c = 3.41 \text{ \AA}; \alpha = \gamma = 90^\circ; \beta = 91^\circ.4$$

for the pure  $\gamma$ -hydroxide. Moreover, the intensities of corresponding lines agree very closely.

Powder samples of both compounds were kindly submitted to us by Dr H. R. Oswald (Bern). The hydroxyfluoride was chosen for structure analysis because it produced sharper diffraction lines. Its structure can be regarded as essentially identical with that of  $\gamma$ -Cd(OH)<sub>2</sub>, apart from partial (and in this work unobservable) replacement of OH by F, which will be disregarded in what follows.

The integrated diffraction intensities were obtained from microphotometer records of patterns taken with a Guinier-type camera using the  $\alpha_1$  component of the Cu *K* doublet.

In view of the above data, the crystal was considered to be monoclinic, with *b* unique. A Patterson synthesis at once showed the metal positions, which were in accordance with the number *Z*=4 derived from Glemser's measured density value. Subsequently, a three-dimensional difference Fourier synthesis with coefficients  $F_{\text{obs}} - F_{\text{Cd}}$  (both *F*'s taken as real) was prepared and investigated for each of the space groups

*I2*, *I2/m* and *Im* allowed by the absence of special systematic extinctions. Due attention was given to the possible occurrence of false or distorted maxima through the use of real coefficients. The first two space groups soon led to contradictions with the formula and with possible distance ranges. In *Im*, however, a direct and unambiguous interpretation of the three main peaks in the difference synthesis (all at  $z=0$  and  $\frac{1}{2}$ ) was possible. The resulting positions were refined by changing the parameters (including the scale factor and an isotropic temperature factor) successively and in steps (Bhuiya & Stanley, 1963) until a minimum of  $\Sigma (I_{\text{obs}} - I_{\text{calc}})^2$  was reached, leaving out the strongest two lines. This program was written by Drs J. W. Visser (Delft), who adapted the method to the case of powder intensities with overlapping lines. The atomic scattering factors were derived from analytic expressions given by Moore (1963) for Cd and O<sup>-</sup>. The final value of the temperature factor was 1.8. The combined effects of absorption in the specimen, oblique incidence on the film and the correction for the Guinier camera geometry were accounted for by a factor  $1 + [0.8 \sec(2\theta - 30^\circ) - 1]$ . The polarization factor was  $1 + 0.45 \cos^2 2\theta$ . The final results are shown in Tables 1 and 2.

Table 2. *Coordinates of atoms in  $\gamma$ -Cd(OH)<sub>2</sub>, space group Im*

4Cd	in 0;	$\pm 0.1522$ ;	0	}	(+000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ )
2OH(1)	in 0.105;	0;	0.508		
2OH(2)	in 0.714;	0;	0.006		
4OH(3)	in 0.879;	$\pm 0.879$ ;	0.583		

Table 1. *Powder diffraction data for  $\gamma$ -Cd(OH)<sub>2</sub>*

<i>hkl</i>	$10^4/d^2$	$I_{\text{obs}}^*$	$I_{\text{calc}}^*$	<i>hkl</i>	$10^4/d^2$	$I_{\text{obs}}$	$I_{\text{calc}}$
020	386	52	59	321	4081	7	12
010	412	350	381†	251	4532	0	1
011	956	116	118	132	4623	56	60
101 } 130 }	1179	390	379†	161	4647	60	56
200	1260	106	110	202	4707	35	36
040	1544	20	22	260	4732	31	25
121	1561	50	49	042	5000	13	12
220	1649	45	39	400 } 170 }	5041	43	47
031	1728	160	160	222	5086	4	10
211	2217	55	56	341 } 350 }	5239	30	29
141 } 150 }	2720	142	137	420	5426	2	2
240	2804	52	50	071	5588	17	20
310	2932	28	27	411	5997	20	22
231	2988	153	148	152	6167	0	1
051	3272	3	1	080	6176	0	2
002	3440	43	42	242	6244	26	32
060	3472	25	22	312	6372	12	17
301 } 330 }	3700	117	115	440	6584	16	19
022	3826	4	6	431	6768	33	35
112	3852	30	36	271	6848	35	35
				062	6912	20	17

\* Total integrated intensity of *hkl* and  $\bar{h}\bar{k}l$  together.

† Left out of refinement.

In this structure (Fig. 1) the cadmium ions have roughly octahedral coordination. The octahedra occur in pairs, each pair sharing the face which lies in the mirror plane. All octahedra share edges with both neighbours in the *c* direc-

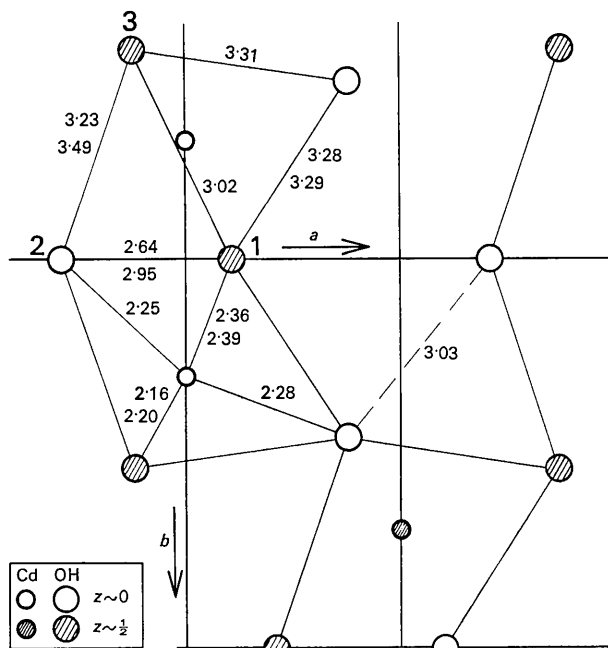


Fig. 1. Bond lengths (Å).

tion. Finally, the infinite double strings thus formed share corners with 4 neighbouring strings. Hydroxyl groups (1), (2) and (3) are bonded to 4, 2 and 3 cadmium ions respectively. The bond distances are given in Fig. 1.

The r.m.s. errors in the positions are estimated to be 0.04 Å for the oxygen atoms and 0.01 Å for cadmium. The deviations of *z* from 0 or ½ are insignificant except for OH(2). This deviation was already apparent as an elongation of the corresponding maximum in the difference Fourier synthesis. It is the only structural aspect preventing the symmetry from becoming orthorhombic (*I2mm*); its cause may be a constraint resulting from the - unknown - proton configuration.

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**Uncertainties in crystal size computed from the standard deviation of the X-ray line breadth.** By CHESTER R. BERRY, *Research Laboratories, Eastman Kodak Company, Rochester, New York 14650, U.S.A.*

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The breadths of X-ray diffraction lines which are used in the Scherrer equation for computing the sizes of small crystals are usually either the half-breadth or the integral breadth. Recently, it was proposed by Pitts & Willets (1961, 1965) that the standard deviation be used. They defined the breadth as twice the standard deviation,  $2\sigma$ , which is obtained from the variance,  $\sigma^2$ . The variance is defined by the equation:

$$\sigma^2 = \frac{\int_{-\infty}^{\infty} y^2 I(y) dy}{\int_{-\infty}^{\infty} I(y) dy},$$

in which *I* is the X-ray intensity and *y* is twice the Bragg angle. Since the theoretical diffraction functions for small crystals have asymptotic values of  $(1/y^2)$  at large values of *y* (Wilson, 1962), the variance and standard deviation do not have finite values. If the range of integration is restricted to a finite value, then this difficulty can be avoided. Using this approach, Tournarie (1956) discussed some theoretical aspects of the use of the variance as a measure of line

breadth. He required that the breadth be expressed in terms of  $\sigma^2/L$ , where the integration was restricted between the specific limits  $-L$  and  $+L$ . Langford & Wilson (1963) used a variance measurement of line breadth for specific ranges of integration for a few reflections from metal powders. Their preliminary measurements on line profiles at small Bragg angles indicated that the variance function could be made linear as a function of the range of integration over a considerable change in the range of integration but only by properly choosing the background level. It is evident that the approach taken by Langford & Wilson is workable, but it is not clear that the added effort leads to more reliable results than are obtained by using the simpler half-breadth or integral breadth.

The approach used by Pitts & Willets to achieve finite, reproducible values of standard deviation was simply to set subjectively a baseline (for zero intensity). Since no theoretical values of the Scherrer coefficient were available for this procedure, they deduced an empirical value of 1.44 for small monodisperse cubes whose size was known from electron-microscopic measurements. The amount of error which can enter this subjective type of measurement will