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**The crystal structure of CdAs<sub>2</sub>.** By L. ČERVINKA\* and A. HRUBÝ, *Institute of Solid State Physics, Czechoslovak Academy of Science, Prague, Czechoslovakia*

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CdAs<sub>2</sub> has a tetragonal structure with  $a=7.96$ ,  $c=4.67$  Å,  $c/a=0.59$ ; measured density  $5.8$  g.cm<sup>-3</sup>, four molecules of CdAs<sub>2</sub> in the elementary cell. The space group is  $D_4^{10}$ ,  $I4_122$ . Four Cd atoms are in the  $4(b)$  positions and eight As atoms in the  $8(f)$  positions, with  $x=0.06 \pm 0.01$ .

CdAs<sub>2</sub> was prepared by direct synthesis of stoichiometric quantities of the elements in an evacuated quartz ampoule. Cadmium, refined by multiple sublimation and by zonal melting, had a purity 6N; arsenic, from which oxygen and water were removed by heating to 300°C in a vacuum of  $10^{-5}$  mmHg, had a purity 5N. The synthesis itself was achieved by slow heating to ca. 700°C. After reaction had finished, the ampoule was taken out of the furnace and left to cool freely in air. The cooling rate is critical, for rapid cooling may cause metastable solidification with decomposition to Cd<sub>3</sub>As<sub>2</sub> and arsenic (Scheil & Kalkuhl, 1961; Hansen & Anderko, 1958).

No preliminary crystallographic information was available. According to a private communication by Senko & Stemple cited in a paper by Silvey, Lyons & Silvestri (1961), this compound should be tetragonal with parameters  $a=4.65$ ,  $c=7.93$  Å. Silvey *et al.* (1961) further pointed out that CdAs<sub>2</sub> should have properties similar to ZnAs<sub>2</sub>, another compound of the  $A^{II}B_2^V$  type. ZnAs<sub>2</sub> has been reported as orthorhombic with  $a=7.72$ ,  $b=7.99$ ,  $c=36.28$  Å (Stackelberg & Paulus, 1935) and as primitive monoclinic with  $a=9.28$ ,  $b=7.68$ ,  $c=8.03$  Å,  $\beta=102^\circ 19'$  (Senko, Dunn, Weidenborner & Cole, 1959). Furthermore, similarity might be expected with such other compounds of the  $A^{II}B_2^V$  group as ZnP<sub>2</sub> (tetragonal with  $a=5.07$ ,  $c=18.65$  Å,  $c/a=3.69$ ) or CdP<sub>2</sub> (tetragonal with  $a=5.28$ ,  $c=19.70$  Å,  $c/a=3.73$ ) (Stackelberg & Paulus, 1935).

Contrary to the above expectations, X-ray analysis of CdAs<sub>2</sub> powder samples (only polycrystalline material was available) using a Guinier camera with monochromatized Cu  $K\alpha$  ( $\lambda=1.5418$  Å) radiation showed that this compound has a tetragonal structure with lattice parameters  $a=7.956$ ,  $c=4.674$  Å and  $c/a=0.587$ .

Table 1 gives the observed intensities relative to the most intense line 211 and the calculated  $d$  values, which are in good agreement with the experimental values.

The density of CdAs<sub>2</sub> was found to be  $5.8$  g.cm<sup>-3</sup>, this value being in good agreement with the value  $5.88$  g.cm<sup>-3</sup> calculated on the basis of four molecules of CdAs<sub>2</sub> in the unit cell.

Further analysis of experimental data based on the absences and intensities of the first 39 lines of the powder pattern enabled the structure of this compound to be determined.

The space group is  $D_4^{10}$ ,  $I4_122$ , and the four Cd atoms are in the  $4(b)$  positions with coordinates  $(0, 0, \frac{1}{2})$ ;  $(0, \frac{1}{2}, \frac{3}{4})$ ; the eight As atoms are in the  $8(f)$  positions with coordinates  $(x, \frac{1}{2}, \frac{3}{4})$ ;  $(\bar{x}, \frac{1}{2}, \frac{3}{4})$ ;  $(\frac{1}{2}, x, \frac{3}{4})$ ;  $(\frac{1}{2}, \bar{x}, \frac{3}{4})$ ; coordinates of equivalent positions are  $(0, 0, 0)$ ;  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ .

$8(f)$  sites giving best agreement with experimental data was found to be  $x=0.06 \pm 0.01$ . In Fig. 1 the projection of the structure onto the  $xy$  and  $xz$  planes is illustrated with supposed bonds between atoms.

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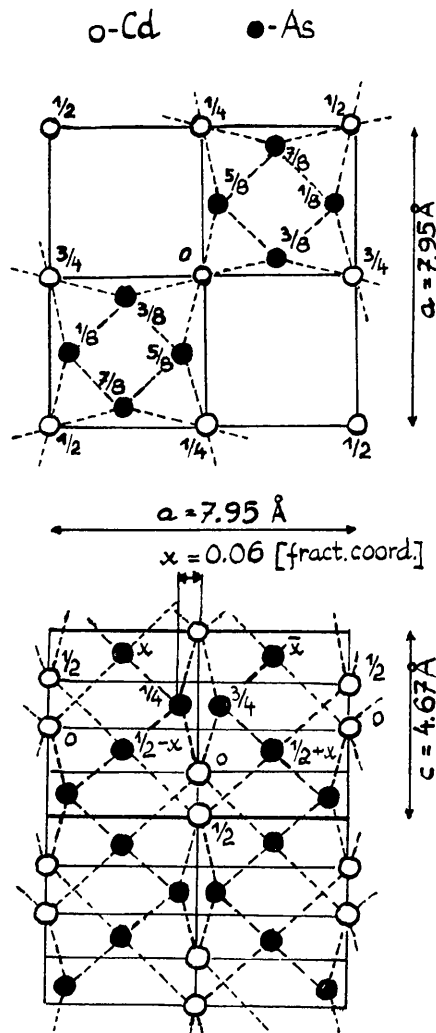


Fig. 1. Projection of the CdAs<sub>2</sub> structure on to the  $xy$  and  $xz$  planes together with the supposed bonds between atoms (dashed lines).

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Table 1. *Interplanar distances* ( $\text{\AA}$ ) (*calculated and observed*) and *relative intensities* in  $\text{CdAs}_2$ 

<i>hkl</i>	<i>d</i> <sub>calc</sub>	<i>d</i> <sub>obs</sub>	<i>I</i>	<i>hkl</i>	<i>d</i> <sub>calc</sub>	<i>d</i> <sub>obs</sub>	<i>I</i>
110	5.625	5.62 <sub>3</sub>	44	103	1.529	1.53 <sub>1</sub>	15
101	4.030	4.01 <sub>1</sub>	4	402	1.515	1.51 <sub>5</sub>	2
200	3.977	3.97 <sub>6</sub>	46	431 } 501 }	1.506	1.50 <sub>8</sub>	9
211	2.831	2.82 <sub>3</sub>	100	332	1.462	1.46 <sub>5</sub>	6
310	2.516	2.51 <sub>5</sub>	4	213	1.427	1.42 <sub>9</sub>	3
301	2.306	2.30 <sub>6</sub>	6	422	1.415	1.41 <sub>7</sub>	4
112	2.158	2.16 <sub>1</sub>	26	521	1.409	1.40 <sub>7</sub>	4
202	2.015	2.01 <sub>6</sub>	29	440	1.406	1.40 <sub>6</sub>	3
321	1.995 } 400 }	1.99 <sub>3</sub>	35	303	1.343	1.34 <sub>5</sub>	7
330	1.875 } 411 }	1.87 <sub>5</sub>	11	512	1.298	1.29 <sub>9</sub>	8
411	1.783 } 420 }	1.78 <sub>2</sub>	12	323	1.273	1.27 <sub>4</sub>	4
420	1.779 } 312 }	1.71 <sub>3</sub>	20	611	1.259 } 620 }	1.25 <sub>9</sub>	13
312	1.712 } 510 }	1.71 <sub>3</sub>	34	620	1.258 } 413 }	1.21 <sub>3</sub>	13
510	1.560 } 510 }	1.55 <sub>9</sub>	3	413	1.212	1.20 <sub>1</sub>	6
				541	1.201	1.20 <sub>1</sub>	6
				532	1.178	1.17 <sub>9</sub>	11

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#### References

- HANSEN, M. & ANDERKO, K. (1958). *Constitution of Binary Alloys*. New York: McGraw Hill.
- SENKO, M. E., DUNN, H. M., WEIDENBÖRNER, J. & COLE, H. (1959). *Acta Cryst.* **12**, 76.
- SCHEIL, E. & KALKUHL, A. (1961). *Z. Metallk.* **52**, 557.
- SILVEY, G. A., LYONS, V. J. & SILVESTRI, V. J. (1961). *Trans. Electrochem. Soc.* **108**, 653.
- STACKELBERG, M. VON & PAULUS, R. (1935). *Z. Phys. Chem.* **B28**, 427.