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The crystal structure of cadmium indate.*

By M. Skribljak, Sharda Dasgupta and A. B. Biswas,
National Chemical Laboratory, Poona–8, India

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In the course of our studies on the physical and crystallographic properties of oxidic semi-conductors, we synthesized $CdIn_2O_4$ and investigated its structure. The earlier report about its structure was made by Passerini (1930), who found the structure to be tetragonal with lattice parameters

$$a = 8{\cdot}65,\ c = 9{\cdot}87\ \text{Å};\ c/a = 1{\cdot}14,\ d_x = 7{\cdot}30\ \text{g.cm.}^{-3}.$$

Assuming the distribution of cations as 'normal', Goodenough & Loeb (1955) suggested this tetragonal distortion from the ideal cubic symmetry of spinel as due to square, coplanar (dsp^2) bond formation by In^{3+} at the octahedral sites.

$CdIn_2O_4$ prepared by us shows, however, the cubic symmetry, and is more likely to have 'inverse' distribution of cations. Powdered samples were obtained by heating intimately mixed, equimolecular proportions of CdO (A.R. quality) and In_2O_3 (obtained from the pure metal dissolved in acid, precipitated as hydroxide and finally ignited in air) at 800 °C. in air for 24 hours. The heated product was quenched in air, while in another experiment the product was slowly cooled (1°/min.), to room temperature. These were then examined in a 14 cm. Debye–Scherrer camera using Mo $K\alpha$ radiation filtered through Zr foil. Both the quenched and annealed products gave the same cubic pattern. The reaction was found to be complete, as lines due to unreacted Cd- and In-oxides were not observed. The observed spacings are set out in Table 1.

Table 1. *Observed and calculated X-ray data*

hkl	d_o	d_c	I_o	I_c
111	5·309	5·263	13	13
220	3·232	3·222	38	38
311	2·757	2·749	100	132
222	2·620	2·631	30	28
400	2·287	2·279	27	17
331	1·973	2·091	3	< 1
422	1·863	1·861	25	15
511 333	1·755	1·754 1·754	50	56
440	1·609	1·611	50	61
531	1·536	1·541	3	3
442	—	1·519	< 1	< 1
620	1·438	1·441	5	7
533 622	1·381	1·390 1·374	45	51
444	1·318	1·316	9	3
711 551	1·275	1·276 1·276	5	1
642	1·216	1·218	12	9
731 553	1·186	1·187 1·187	44	29
800	1·136	1·139	15	9
733	—	1·113	< 1	< 1
644	—	1·106	< 1	< 1
822	1·071	1·074	5	4
751 555 662	1·050	1·052 1·052 1·046	35	24
840	1·024	1·019	6	4
911	—	1·000	< 1	< 1
753	—	1·000	< 1	< 1
842	—	0·994	< 1	< 1
664	—	0·972	< 1	< 1
931	0·953	0·955	17	11
844	0·931	0·930	22	16

All the reflexions could be indexed on the basis of a cubic unit cell with $a = 9{\cdot}11_5 \pm 0{\cdot}01$ Å, and the corresponding spacings are given in column 3. The extinctions suggest the structure to be of the spinel type, consistent with the space group O_h^7–$Fd3m$. With $Z = 8$ and $V = 756$ Å³, the calculated density 7·52 g.cm.$^{-3}$ compares satisfactorily with the experimental value of 7·13 g.cm.$^{-3}$, determined by pycnometric measurement. The atomic coordinates assuming 'inverse' distribution are:

$$\left.\begin{array}{l}
\qquad\qquad 8\,\mathrm{In}^{3+}\ \text{at}\ 000,\ \tfrac{1}{4}\tfrac{1}{4}\tfrac{1}{4} \\
8\,\mathrm{Cd}^{2+}\ \text{and}\ 8\,\mathrm{In}^{3+}\ \text{at}\ \tfrac{5}{8}\,\tfrac{5}{8}\,\tfrac{5}{8},\ \tfrac{5}{8}\,\tfrac{7}{8}\,\tfrac{7}{8}, \\
\qquad\qquad\qquad\qquad\quad \tfrac{7}{8}\,\tfrac{5}{8}\,\tfrac{7}{8},\ \tfrac{7}{8}\,\tfrac{7}{8}\,\tfrac{7}{8} \\
\text{and} \\
32\,\mathrm{O}^{2-}\ \text{at}\ uuu,\ u\bar{u}\bar{u},\ \bar{u}u\bar{u},\ \bar{u}\bar{u}u, \\
\qquad \tfrac{1}{4}-u\ \tfrac{1}{4}-u\ \tfrac{1}{4}-u,\ \tfrac{1}{4}-u\ \tfrac{1}{4}-u\ \tfrac{1}{4}+u \\
\qquad \tfrac{1}{4}+u\ \tfrac{1}{4}-u\ \tfrac{1}{4}+u,\ \tfrac{1}{4}+u\ \tfrac{1}{4}+u\ \tfrac{1}{4}-u
\end{array}\right\} + \text{f.c.c.}$$

The I_{hkl} values were calculated for all non-zero reflexions up to $h^2+k^2+l^2 = 96$ from the expression $I_c \alpha (1+\cos^2 2\theta)/(\sin^2\theta\cos\theta).p.F^2_{hkl}$ for values of u ranging from 0·380 to 0·400 at intervals of 0·005. The scale factor (K) was initially adjusted by making ΣI_o and ΣI_c equal and finally the Debye thermal parameter ($B = 0{\cdot}21$ Å²) and K were determined from the equation

$$I_c \exp\left[-2B(\sin\theta/\lambda)^2\right] = K I_o$$

by the method of least squares. Since the intensities are rather insensitive to the oxygen parameter, the u value cannot be reduced to a narrow limit. However, comparing reflexions such as 111, 400 and 422, which are relatively more sensitive to changes in u, and using the function

$$R = \Sigma(|\sqrt{I_c}| - |\sqrt{I_o}|)/\Sigma|\sqrt{I_o}|\ \text{as a criterion},$$

the best agreement appears to be for $u = 0{\cdot}385$ and $R = 0{\cdot}14$. The cation–oxygen distance is 2·13 Å at the tetrahedral site and 2·19 Å at the octahedral site, the former representing the In–O distance, which is in accordance with the size consideration that the ionic radius of In^{3+} (0·92 Å) is smaller than that of Cd^{2+} (1·03 Å).

The X-ray scattering factors for Cd^{2+} and In^{3+} are identical and therefore the cation distribution as either 'normal' or 'inverse' cannot be determined by this technique. However, the observed cubic symmetry suggests the structure to be inverse, and is consistent with the bonding properties of the cations. Both In^{3+} and Cd^{2+}

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have the $4d^{10}$ configuration in the ground state and have a preference for the tetrahedral sites. The dsp^2 hybridization for In^{3+}, suggested by Goodenough & Loeb (1955), does not appear feasible on energy considerations. Recently Miller (1959) has calculated site preference energy in spinels for different cations, and accordingly it can be concluded that the 'inverse' structure is more stable than the 'normal' by about 11 kcal./g.mol. and hence the structure should be almost completely 'inverse' at room temperature.

Further discussion of the structure along with the infrared absorption analysis results will be published elsewhere.

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Tetrahedral structures in amorphous carbons.

By SABRI ERGUN* and VICTOR H. TIENSUU,* *Special Coal Research Section, Branch of Bituminous Coal, Division of Solid Fuels Technology, Bureau of Mines, Region V, Pittsburgh* 13, *Pa., U.S.A.*

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The two well-known crystalline forms of carbon are graphite and diamond (face-centered cubic). X-ray diagrams of amorphous carbon contain three or more diffuse bands. Heretofore emphasis has been placed on the fact that the angular positions of these bands correspond approximately to the positions of the (002), (100), (110), etc., reflections of graphite.

Strong peaks at the angular positions of the (00*l*) reflections of graphite lattice tend to support the presence of graphite-like layers (turbostratic) in carbons (Warren, 1941; Biscoe & Warren, 1942). However, some non-graphitizing (Franklin, 1951) carbons have weak peaks at these angular positions and qualitative and quantitative deductions regarding their structure are based on profile analyses of the scattering intensities in terms of the (*hk*) reflections of graphite-like layers and Fourier transforms of the scattering intensities (Franklin, 1950). The hardness, density and non-graphitizability of some carbons do not appear to be entirely compatible with a graphite-like structure. Therefore, theoretical work on the scattering intensities of tetrahedrally-bonded structures of carbon appeared desirable. Preliminary results are presented here, and full details will be published later.

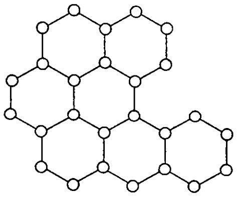
A graphite-like layer containing 26 carbon atoms (Fig. 1, Model No. 20) was first considered. The intensity $J(s)$ in atomic units, scattered at any angle 2θ, was computed by the Debye formula (Debye, 1915):

$$J(s) = \sum_r (n(r)/N) \sin 2\pi rs/(2\pi rs)$$

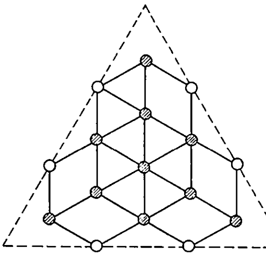
where $s = 2 \sin \theta/\lambda$, $n(r)$ is the number of interatomic distances of length r within the molecule, irrespective of direction, and N is the total number of atoms in the molecules. All carbon bonds were taken to be of equal length, 1·4174 Å (cf. Diamond, 1957) and all interbond angles to be 120°. After determining the interatomic distances and their number, intensity data were computed numerically on the Univac 120. The results are shown in Fig. 2 (solid line).

A molecule containing 26 carbon atoms arranged in a diamond type lattice shown in Fig. 1 (Model No. 12) was next considered. The molecule formed a tetrahedron. All carbon bonds were taken to be 1·5420 Å in length and all interbond angles 109° 28·4′, the tetrahedral bond angle. The computed curve is shown in Fig. 2 (dashed line).

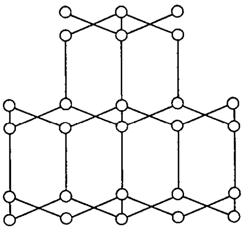
In a diamond lattice carbon atoms form cross-linked buckled layers composed of six-membered rings (chair type). Cross-linking is in such a manner that it yields a face centered cubic lattice, i.e., the projections on the (111) planes of the adjacent buckled layers do not superimpose. If the projections do superimpose a hexagonal



Model No. 20. Graphite-like layer



Model No. 12. Projection of tetrahedron on (111) plane of diamond lattice. Shaded circles show superimposed atoms.



Model No. 19. Projection of hexagonal lattice on (100) plane.

Fig. 1. Diagrams of models considered.

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* Special Coal Research Section, Bureau of Mines, Region V, U.S. Department of the Interior, Pittsburgh, Pa., U.S.A.