On the structure of ZnI_2

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The halides of cadmium, mercury and zinc form layered structures and hence their physical and structural study is of interest for material scientist, as is evident from the extensive studies made recently on these halides in thin film state by Tyagi *et al.* [1] and Rawat *et al.* [5]. In fact CdI_2 is known to crystallize in more than 200 different states [6], with each poly-state exhibiting different properties. While CdI_2 in its hexagonal state is most prevalent, HgI_2 is known to exist with a tetragonal structure. A survey of the literature shows that ZnI_2 has not attracted the same attention as CdI_2 and HgI_2. Only three structural studies have been done on ZnI_2 [7, 9], and they report two possible states that it can exist in. While Fourcroy *et al.* [9] assigns a large unit cell size ($a = b = 1.2284$ nm, $c = 2.3582$ nm) whose Miller indices are listed in ASTM 30-1479, the remaining studies have indexed ZnI_2 with $a = b = 0.4388$ nm and $c = 1.1788$ nm (ASTM 10–72). Even though majority of the peak positions listed in both the above mentioned ASTMs agree well (till the second place of decimal), the assigned unit cell dimensions differ remarkably. This is a direct consequence of the fact that ASTM 10-72 only reported peaks between $2\theta = 25^\circ$ and 80° while the more recent ASTM 30-1479 reports X-ray diffraction peaks between 10° to 60°. Peaks occurring at lower diffraction angles demand larger lattice parameters. These old studies have suggested ZnI_2 to exist either with the same crystal structure as HgI_2 or with a hexagonal structure similar to $CdCl_2$ (CdI_2). While HgI_2 has a tetragonal structure with two bases per unit cell, i.e. with body center cubic (bcc) arrangement, $CdCl_2$ has only one basis per its hexagonal unit cell. The relatively poor attention on ZnI_2 and the fact that Fourcroy assumed a rather large basis of Zn_4I_{10} chain motivated us to investigate whether a structure with I–Zn–I basis can exist.

The initial indexing was done using a computer program in Turbo-BASIC developed by us. However, the refinement of cell dimensions, $\delta 2\theta$, space group analysis etc., were performed using a software developed by Charles W. Burnham, Department of Earth and Planetary Sciences, Harvard University. The result of our indexing program is listed in Table I. The best indexing was obtained for tetragonal unit cell of dimensions $a = 1.3898$ nm and $c = 2.1362$ nm, the ratio c/a is equal to 1.537, and is comparable to those of layered compounds [7]. These computed lattice parameters are comparable with the lattice parameters attributed to ZnI_2 by Fourcroy, however are largely different from that reported in ASTM 10–72. As explained earlier, this is expected since ASTM 10-72 had missed out the small angle diffraction peaks. Table I compares the indexing of ASTM 30-1479 and the indexing done in the present study. The error is the difference in the ASTM listed ‘d’ spacing and the calculated value of ‘d’ using the h, k, l and unit cell dimensions. Consistently, the error in ‘d’ spacing of the present study is lower than the ASTM’s reported indexing. Even though our cell dimensions are similar to that of Fourcroy, whose structural analysis suggested ZnI_2 to exist with tetragonal structure having only single basis per unit cell, in light of the new Miller indexing we did we carried out structural analysis to investigate whether a structure with I–Zn–I basis can exist rather than Zn_4I_{10} chain as described by Fourcroy.

The crystal structure determination was done using trial and error method as outlined by Glasser in his book [10] after incoperating the usual corrections on the observed diffraction peak’s intensity for polarization and Lorentz factors. Table II list the corrected intensity (F_o) alongside with the measured intensity level, I_{rel}. Fig. 1a shows the proposed structure. The assumed basis has one Zn atom in bonding with two I atoms forming a “V” shape, with the angle between the two Zn–I bonds to be 151.1° (Fig. 1b). The structure gives ZnI_2 a Zn–I–I-Zn–I–I–Zn layered structure. This is readily understood from the projections shown in Fig. 2.

TABLE I The ‘d’ spacing (in Å) of ZnI_2 listed in ASTM card 30-1479 along with the orignal Miller indexing (*hkl*) and it’s error is compared with the Miller indexing done in present work. The improvement in indexing is evident from the decrease in error

d	ASTM 30-1479 *hkl*	|error|	Present study *hkl*	|error|
6.9542	112	0.050154	200	0.005146
6.3406	200	0.180550	103	0.003103
4.5210	213	0.011000	301	0.006467
3.6901	312	0.008817	133	0.049893
3.5099	224	0.007706	304	0.010346
3.0797	400	0.000325	421	0.004359
2.9553	008	0.010260	333	0.020717
2.7601	420	0.005242	431	0.003713
2.1729	440	0.005006	540	0.002380
2.1267	408	0.001878	542	0.000348
2.0439	444	0.001164	20(10)	0.001932
1.8442	624	0.005258	714	0.000342
1.7886	22(12)	0.001330	33(10)	0.000080
1.7497	448	0.001396	608	0.000076
1.6543	40(12)	0.001296	717	0.001856
1.5358	800	0.004212	26(10)	0.004041
Average error		0.01847		0.007220

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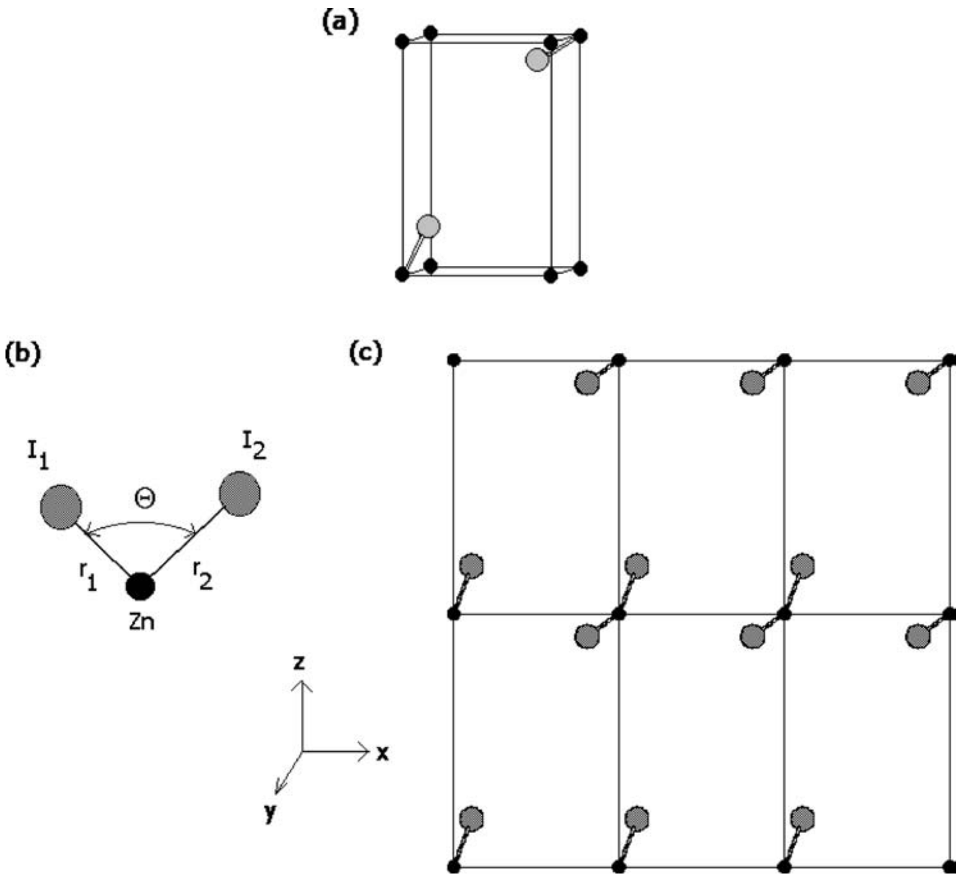

Figure 1 The (a) proposed structure of ZnI_2 with (b) the basis being the non-linear molecule of ZnI_2 and (c) the 'xz' plane of the lattice formed.

The initial discrepancy factor obtained was $R = 0.44$ or 44%. On further refinement of the atomic positions (Iodine atoms positions) we obtained $R = 0.098$ or 9.8%. This discrepancy factor may be further reduced by including anisotropic temperature factors which accounts for the thermal vibrations of the atoms. However, the discrepancy is low enough to consider the proposed crystal structure to be correct. The atomic position of all the Zn and I atoms are given in Table III. The interatomic distances (r_1 and r_2 of figure) is easily computed from these position co-ordinates. The two bond lengths $Zn-I_1$ and $Zn-I_2$ works out to be 5.827 and 7.303 Å, respectively. Both bond lengths are greater then the sum of zinc and iodine atom's ionic radii 3.4 Å(1.34 + 2.06 Å) [11], suggesting that the molecules are formed by covalent bonding. The bond lengths worked out in the present study is far greater than those reported by Fourcroy, where the average Zn–I bond length was only 2.6 Å. The result, hence, in that study leads to the conclusion that zinc and iodide atoms are held together by ionic bonds.

TABLE II Details of the diffraction data

S. No.	d	$I_{\text{rel}}(\%)$	$\sqrt{I_{\text{corr}}}$	$\lvert F_o \rvert$	$\lvert F_c \rvert$
1.	6.9542	6	0.96	22.22	23.83
2.	6.3406	6	0.75	17.26	19.51
3.	4.5210	8	1.23	28.26	27.71
4.	3.6901	7	1.0	23.14	27.86
5.	3.5099	100	5.68	130.52	122
6.	3.0797	30	2.53	58.22	66.11
7.	2.9553	7	1.81	41.6	34.61
8.	2.7601	5	1.16	26.81	10.06
9.	2.1729	2	1.37	31.49	29.74
10.	2.1267	45	4.71	108.33	108.61
11.	2.0439	3	1.8	41.45	49.93
12.	1.8442	10	2.63	60.54	60.54
13.	1.7886	7	3.23	74.36	87.34
14.	1.7497	6	3.08	70.72	64.55
15.	1.6543	3	1.65	37.88	38.01
16.	1.5358	6	2.55	58.72	61.15

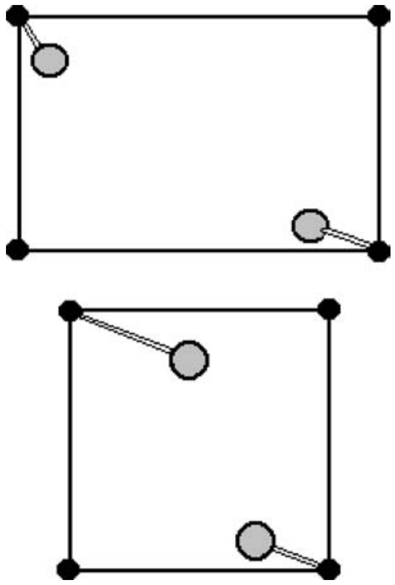

Figure 2 Projection of ZnI_2 in 'xz' (010) and 'xy' (001) plane respectively.

In conclusion, the proposed crystal structure is a possible state is which ZnI_2 can exist. The large ratio

TABLE III The position of Iodine and Zinc atoms

S. no	x	y	z
Iodine atoms			
1.	0.11	0.28	0.19
2.	0.81	0.53	0.91
Zinc atoms			
1.	0	0	0
2.	0	1	0
3.	1	0	0
4.	1	1	0
5.	0	0	1
6.	0	1	1
7.	1	0	1
8.	1	1	1

of lattice parameter (c/a) along with the larger bond lengths suggest covalent bond formation between the atoms of the molecule. Fourcroy's structure was more of a correction of the previous structure based on ASTM 10-72. The correction made necesscary due to the new peaks detected at low diffraction angles. In the present study, the indexing and lattice parmaeter's of ASTM 30-1479 have been refined allowing for a proposing simpler structure for ZnI_2 based on a simpler basis selection as compared to Fourcroy's chain of Zn_4I_{10} basis.

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