A new structure for ZnI$_2$ is proposed which it exists in tetragonal state. In this structure the ZnI$_2$ molecule exists in a nonlinear array and forms the basis of the tetragonal unit cell with one basis per unit cell. The structural analysis based on the reflections listed in ASTM 30-1479 shows that the proposed structure is correct.

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I. INTRODUCTION

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 Pankaj Tyagi et al.\textsuperscript{1} and Rawat et al.\textsuperscript{5}. In fact CdI$_2$ is known to crystallize in more than 200 different states, with each poly-state exhibiting different properties. While CdI$_2$ in it’s 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$_2$\textsuperscript{7,9}, and they report two possible states that it can exist in. While Fourcroy et al\textsuperscript{9} assigns a large unit cell size (a=b=1.2284nm, c=2.3582nm) whose Miller indices are listed in ASTM 30-1479, the remaining studies have indexed ZnI$_2$ with a=b=0.4388nm and c=1.1788nm (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° 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 it’s hexagonal unit cell. The relatively poor attention on ZnI$_2$ and the fact that Fourcroy assumed a rather large basis of Zn$_4$I$_{10}$ chain motivated us to investigate whether a structure with I-Zn-I basis can exist.

II. RESULTS

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
The 'd' spacing (in Å) of ZnI₂ listed in ASTM card 30-1479 along with the original Miller indexing (hkl) and its error is compared with the Miller indexing done in present work. The improvement in indexing is evident from the decrease in error.

| ASTM 30-1479 | Present Study |
|--------------|--------------|
| d            | hkl          | error        | 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          | 0.003250     | 421          | 0.004359     |
| 2.9553       | 008          | 0.010260     | 333          | 0.020717     |
| 2.7601       | 420          | 0.005242     | 431          | 0.003713     |
| 2.1729       | 440          | 0.005066     | 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 vs. 0.007220

The best indexing was obtained for tetragonal unit cell of dimensions a=1.3898nm and c=2.1362nm, the ratio c/a is equal to 1.537, and is comparable to those of layered compounds. These computed lattice parameters are comparable with the lattice parameters attributed to ZnI₂ 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 ZnI₂ 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 Zn₄I₁₀ chain as described by Fourcroy.

The crystal structure determination was done using trial and error method as outlined by Glasser in his book after incorporating the usual corrections on the observed diffraction peak’s intensity for polarization.
FIG. 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.

and Lorentz factors. Table II list the corrected intensity ($F_o$) alongside with the measured intensity level, $I_{rel}$. Figure(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° (figure 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 figure(2).

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 inter-atomic distances ($r_1$ and $r_2$ of fig) is easily computed from these position co-ordinates. The two bond lengths Zn – I$_1$ and Zn – I$_2$ works out to be 5.827Å and 7.303Å respectively. Both bond lengths are greater then the sum of zinc and iodine atom’s ionic radii 3.4Å (1.34+2.06Å)\textsuperscript{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 2.6Å. The result, hence, in that study leads to the conclusion that zinc and iodide atoms are held together by ionic bonds.

| S.No | d   | $I_{rel}$(%) | $\sqrt{I_{corr}}$ | $|F_o|$ | $|F_c|$ |
|------|-----|-------------|-------------------|-------|-------|
| 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 |

Table II: Details of the diffraction data

Table IIIa: The position of Iodine atoms.

| S.No | x      | y      | z      |
|------|--------|--------|--------|
| 1.   | 0.11   | 0.28   | 0.19   |
| 2.   | 0.81   | 0.53   | 0.91   |
Table IIIb: Position of Zinc atoms

| S.No. | x   | y   | z   |
|-------|-----|-----|-----|
| 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   |

FIG. 2: Projection of ZnI₂ in 'xz' (010) and 'xy' (001) plane respectively.

Conclusion

In conclusion, the proposed crystal structure is a possible state in which ZnI₂ can exist. The large ratio 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 necessary due to the new peaks detected at low diffraction angles. In the present study, the indexing and lattice parameter’s of ASTM 30-1479 have been refined allowing for a proposing simpler structure for ZnI₂ based on a simpler basis selection as compared to Fourcroy’s chain of Zn₄I₁₀ basis.

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