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# On Centrosymmetric Space Groups in Close-Packed $MX_2$-Type Structures

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Shortcomings in the conditions imposed on Zhdanov sequences for close-packed $MX_2$-type structures to be centrosymmetric have been pointed out and the correct conditions derived. Accordingly, the space groups of six $CdI_2$ and two $PbI_2$ polytypes, wrongly reported earlier, have been rectified.

A close packing of spheres can have one of the following eight space-group symmetries (Verma & Krishna, 1966): $P3m1$, $P\bar{3}m1$, $P\bar{6}m2$, $P6_3mc$, $P6_3/mmc$, $R3m$, $R\bar{3}m$, $F\bar{4}3m$. In close-packed $MX_2$-type structures, the presence of cation layers in between the alternate pairs of anion layers forbids the existence of a mirror plane perpendicular to **c** as well as the existence of cubic close packing. A close-packed $MX_2$-type structure can, therefore, belong to only one of the following five space groups: $P3m1$, $P\bar{3}m1$, $R3m$, $R\bar{3}m$, $P6_3mc$. Of these, the space groups $P\bar{3}m1$ and $R\bar{3}m$ are centrosymmetric. While one can distinguish between the space groups $P3m1$ and $P\bar{3}m1$ on one hand and the space group $P6_3mc$ on the other hand with the help of X-rays, identification of the centrosymmetric nature of the structure cannot be made with X-rays (assuming Friedel's law holds); but is made only after the complete crystal structure has been determined.

The space groups $P3m1$ or $R3m$ represent the minimum symmetry exhibited by a close packing of spheres depending on whether the lattice is hexagonal or rhombohedral. Higher symmetries than these arise from special kinds of packings of layers, which, in turn, imply imposition of certain conditions on the Zhdanov sequence of the given structure. The conditions have already been derived for the centrosymmetric space groups $P\bar{3}m1$ or $R\bar{3}m$ as well as for the hexagonal space group $P6_3mc$ in the case of $CdI_2$ polytypes (Srivastava, 1964). Subsequently the same conditions have been repeated by other workers (*e.g.* Chadha, 1967). However, the conditions for centrosymmetry are misleading and have presumably led to the wrong reports of the space groups of six $CdI_2$ and two $PbI_2$ polytypes by various workers, as discussed shortly by us.

The main conclusion drawn by the earlier workers has been that a $CdI_2$ structure should possess a centre of symmetry if its Zhdanov symbol consists of an odd set of numbers repeated twice but the number of layers in its unit cell is not a multiple of 4. The fallacy involved here is quickly exposed by considering a representative example, say the hypothetical $CdI_2$ structure $14H[(421)_2]$. This structure obeys both the conditions above but is not centrosymmetric, as one can verify by writing down its *ABC* sequence. On the other hand, the structure $12R[(13)_3]$, which does not conform to either of the two conditions, is indeed centrosymmetric, as will be seen later. The correct conditions for a close-packed $MX_2$ structure to be centrosymmetric can be derived as follows. If the centre of symmetry lies on an *A* site, it demands that (i) corresponding to every *A* layer on one side of the centre there should exist another *A* layer on the opposite side and at an equal distance from the centre; (ii) corresponding to each *B* or *C* layer on one side there should be a *C* or *B* layer on the opposite side and at an equal distance from the centre.

In cadmium iodide, since the cations do not lie between successive layers of anions but only between the alternate pairs of such layers, the centre of symmetry cannot lie on an anion; it can lie on a cation or at the centre of octahedral voids between two anion layers (the previous workers have considered the first possibility alone; possibly they have overlooked the fact that a space group is an array of symmetry elements that is consistent with an infinitely extended, regularly repeating pattern and it is not necessary that the unit cell should exhibit the space group symmetry). In any case it lies at the centre of two anion layers. The packing would, therefore, have to be of the type (Verma & Krishna, 1966):

$$\ldots A\,C\,B\,C\,A\overset{\downarrow}{}B\,C\,A\,C\,B\ldots$$

The arrow shows the position of centre of symmetry, which, in this case, lies at site *C*. The cation layers have not been shown; they may occupy one of the two possible sets of alternate positions between the anion layers. It may be easily examined that for such a symmetry the Zhdanov symbol consists of a symmetrical arrangement of numbers surrounding a single odd number. The converse of this is also true. Indeed, this constitutes a general necessary and sufficient condition

Table 1. $CdI_2$ *and* $PbI_2$ *polytypes reported to belong to centrosymmetric space groups*

| Polytype | Zhdanov sombol | Reference |
|---|---|---|
| $2H(CdI_2)$ | 11 | Bozorth (1922) |
| $2H(PbI_2)$ | 11 | Terpstra & Westenbrink (1926) |
| $6H_2(CdI_2)$ | 33 | Pinsker (1941) |
| $6R(PbI_2)$ | $\infty$ | Pinsker, Tatarinova & Novikova (1943) |
| $10H_2(CdI_2)$ | 221221 | Jain & Trigunayat (1975) |
| $12R_1(PbI_2)$ | $(13)_3$ | Mitchell (1959) |

for the close-packed $MX_2$-type structures to be centrosymmetric in character. For example, the structure 132122322123 has symmetrical arrangement of numbers about the underlined odd digits and therefore it is centrosymmetric.

Until now only the three cadmium iodide polytypes and three lead iodide polytypes in Table 1 have been reported as belonging to the centrosymmetric space groups. In addition, there are six more $CdI_2$ polytypes and two $PbI_2$ polytypes which actually belong to the centrosymmetric space groups $P\bar{3}m1$ or $R\bar{3}m$, but have been earlier reported as belonging to the non-centrosymmetric space groups $P3m1$ or $R3m$ (Table 2).

Table 2. $CdI_2$ *and* $PbI_2$ *polytypes previously reported to belong to non-centrosymmetric space groups*

The digits around which the Zhdanov numbers in a symbol are symmetrically arranged, have been underlined.

| Polytype | Zhdanov symbol | Reference |
|---|---|---|
| $12R_1(CdI_2)$ | $(13)_3$ | Agrawal & Trigunayat (1968) |
| $12H_5(CdI_2)$ | 11123211 | Agrawal, Chadha & Trigunayat (1971) |
| $8H_3(CdI_2)$ | 1232 | Lal, Chadha & Trigunayat (1971*a*) |
| $18H_3(CdI_2)$ | 122232211 | Lal *et al.* (1971*b*) |
| $12H_6(CdI_2)$ | 221122 1 | Chadha (1974) |
| $16H_4(CdI_2)$ | 12223222 | Chadha (1974) |
| $18R_1(PbI_2)$ | $(1311)_3$ | Chand & Trigunayat (1975) |
| $18R_2(PbI_2)$ | $(2121)_3$ | Chand & Trigunayat (1975) |

The centrosymmetric character of the structures in Table 2 can be verified by examining their *ABC* sequences, *e.g.* for $12R_1$:

$$(A\gamma B)\,(A\beta C)\,(B\alpha C)\,(B\gamma A)\,(C\beta A)\,(C\alpha B).$$
$$\uparrow \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow$$

The arrows indicate the positions of the centres of symmetry.

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## References


AGRAWAL, V. K., CHADHA, G. K. & TRIGUNAYAT, G. C. (1971). *Z. Kristallogr.* **134**, 161–165.

AGRAWAL, V. K. & TRIGUNAYAT, G. C. (1968). *Acta Cryst.* B**24**, 971–972.

BOZORTH, R. M. (1922). *J. Amer. Chem. Soc.* **44**, 2232–2236.

CHADHA, G. K. (1967). Ph.D. Thesis, Delhi Univ.

CHADHA, G. K. (1974). *Z. Kristallogr.* **139**, 147–152.

CHAND, M. & TRIGUNAYAT, G. C. (1975). *Acta Cryst.* B**31**, 1222–1223.

JAIN, P. C. & TRIGUNAYAT, G. C. (1975). *Z. Kristallogr.* **141**, 458–464.

LAL, G., CHADHA, G. K. & TRIGUNAYAT, G. C. (1971*a*). *Acta Cryst.* B**27**, 2293–2298.

LAL, G., CHADHA, G. K. & TRIGUNAYAT, G. C. (1971*b*). *Z. Kristallogr.* **134**, 91–96.

MITCHELL, R. S. (1959). *Z. Kristallogr.* **111**, 372–384.

PINSKER, Z. G. (1941). *Acta Physiochim. URSS*, **14**, 503–530.

PINSKER, Z. G., TATARINOVA, L. & NOVIKOVA, V. (1943). *Acta Physiochim. URSS*, **18**, 378–386.

SRIVASTAVA, O. N. (1964). Ph.D. Thesis, Banaras Hindu Univ.

TERPSTRA, P. & WESTENBRINK, H. G. K. (1926). *Koninki. Ned. Akad. Wetenschap Proc.* **29**, 431–442.

VERMA, A. R. & KRISHNA, P. (1966). *Polymorphism and Polytypism in Crystals.* New York: John Wiley.