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Enumeration of polytypes MX and MX_2 through the use of the symmetry of the Zhdanov symbol

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The different close-packed polytypes MX and MX_2 have been enumerated for each of the possible space groups by counting the corresponding Zhdanov symbols for each space group and period of stacking, P, by the use of elementary combinatorial techniques. In special cases, simple closed formulae are obtained for these numbers as functions of P. The symmetry properties of the Zhdanov symbol have been investigated with the help of its cyclotomic representation and the two-color symmetry point group thereof. Zhdanov-like rules have been developed for MX_2 polytypes. The SiC cases have been generated to $P = 18$ under the '1-exclusion' rule and the possible diamond polytypes have been examined.

1. Introduction

Among the many families of polytypes [for a definition of the term 'polytype' see Guinier *et al.* (1984); for a survey of the phenomenon of polytypism, see Trigunayat (1991)], the so-called close-packed polytypes are those in which the several polymorphic variants result from different modes of stacking hexagonal layers, piled up in ways similar to those exhibited by the closest packings of equal spheres. In particular, it is all-important in this connection that the heaping of the layers on top of each other occurs in such a way that the projection of a layer parallel to the axis of stacking (be it normal to the layers or otherwise) occurs in one of three possible settings, labeled A, B and C, and such that no two consecutive layers have the same label. Of course, these conditions arise naturally when one stacks close-packed hexagonal layers of equal spheres (*i.e.* planar layers in which every sphere is surrounded by six other spheres, all in contact), with the aim of obtaining an optimal packing: every sphere of a layer must rest on three spheres of the layer directly below, and this can be done in two ways, labeled B and C, if we label the initial layer as A.

The close-packed polytypes generally are compounds of a large anion, atom X, and a smaller metal atom, atom M; the large atoms play the role of the spheres in the close packing and the smaller atoms can be looked on as interstitial atoms. However, the insertion of M atoms in the holes of a packing of spheres generally entails that these spheres are no longer in contact, so the name 'close packed' must not be taken too literally: the important feature is that the array of one of the two classes of atoms (normally the larger X atoms) follows the same rules as the stacking of closest-packed layers of spheres. This point of view is useful even in a case like that of diamond (see below), where C atoms fill a subset of the tetrahedral holes of a 'close packing' of C atoms, the resulting structure being a tetrahedral network where each sphere (C atom) only touches four equal spheres, a far cry from the 12 contacts (kissing number in dimension 3) present in any close packing of equal spheres.

The present paper deals with the enumeration and classification of the close-packed polytypes of formula MX and MX_2 in the possible space groups. The MX polytypes are tetrahedral frameworks of corner-linked tetrahedra, while the MX_2 polytypes are exclusively octahedral structures. We assume the stackings are periodic and that the structure (the stacking) is repeated by a vector, not necessarily normal to the layers, encompassing P layers; we try to find the number $N(P)$ of distinguishable structures that could possibly be constructed for each period P. This author solved the corresponding problem for equal spheres (Iglesias, 1981*a*) by simple combinatorial methods. Not long after this, McLarnan (1981) solved the same problem by the use of more advanced techniques (Pólya's theory of counting). McLarnan imposed the condition that the translation repeating the stacking be normal to the layers: this constraint is equivalent to defining a hexagonal triple cell for all rhombohedral structures, whereby their period is three times that corresponding to the rhombohedral primitive translation. The present author enumerated the stackings by counting the corresponding Zhdanov symbols (see definition below) and, hence, only primitive (hexagonal and rhombohedral) translations were allowed. The values in Table 1 of McLarnan (1981) can therefore be reconciled with those in Table 1 of Iglesias (1981*a*) by the equivalence $N_H(P) + N_R(P/3) = N_{\rm Mc}(P)$ when P is a multiple of 3 and $N_H(P) = N_{\rm Mc}(P)$ otherwise; the left-hand sides of these equalities represent values from Iglesias (1981*a*) (H stands for hexagonal, R for rhombohedral) and those on the right-hand side are from McLarnan's. The distribution of the packings of equal spheres among the possible space groups has been studied by McLarnan (1981) and Estevez-Rams *et al.* (2005) by counting Hägg symbols, and by the present author (Iglesias, 2006*a*) by counting Zhdanov symbols.

McLarnan (1981) also counted several kinds of polytypes, including those of formula MX and MX_2 which are the object of this paper, although these polytypes were not classified according to space group, which they are in this paper; still, the main purpose of this paper is to show that these counting problems can be solved by rather elementary methods that do not require of the reader the mastering of the most sophisticated techniques, albeit the elegance of these may be lost. Our method is based on simple combinatorial lore, in connection with a graphical interpretation of the Zhdanov symbol, which makes it extremely simple to detect equivalence among these symbols through the analysis of the two-color symmetry group of the graphical representation. We have used it successfully in the enumeration of the possible sphere stackings in bulk (Iglesias, 1981*a*) and by the space group (Iglesias, 2006*a*).

Each sphere close packing can be represented by its Zhdanov symbol (Zhdanov, 1945, 1965), which consists of an even number of nonzero (see exception below) integers, to be called 'components' in what follows, $n_1 n_2 n_3 \ldots n_{2k}$, such that $\Sigma n_i = P$. The symbol represents n_1 layers stacked $\ldots A \rightarrow B \rightarrow C \rightarrow A \ldots$, followed by n_2 layers stacked $\ldots A \rightarrow C \rightarrow B \rightarrow A \ldots$ and so on, when we move along, say, the positive direction of the stacking axis. If we define $n_1 + n_3 + n_5 + \ldots = p$ and $n_2 + n_4 + n_6 + \ldots = q$, then for $p - q \equiv 0 \,(\mathrm{mod}\, 3)$ the lattice of the stacking will be hexagonal, otherwise it will be rhombohedral. The Zhdanov symbol uniquely represents the structure but the reciprocal is not true: the same structure can be represented by different Zhdanov symbols, *i.e.* the mapping between structures and Zhdanov symbols is a one-to-many mapping. If one intends to count structures by counting possible Zhdanov symbols, the different ways in which a Zhdanov symbol may vary while the represented polytype structure remains invariant must be analyzed. Also, when enumerating all Zhdanov symbols corresponding to a given value of P, care must be exercised to eliminate those cases showing internal periodicities, which can be recognized because there is a run of an even number of components which repeats d times within the Zhdanov symbol: these components are really the Zhdanov symbol of a polytype of period P/d, and as such it must be counted. Thus, when one insists on counting all polytypes as hexagonal, as other authors do, truly rhombohedral polytypes show an internal period of $P/3$, *i.e.* a run of an even number of components appear thrice repeated in the Zhdanov symbol. This cumbersome notation is sometimes abbreviated by enclosing these components in parentheses, and adding the subindex 3 to the symbol; for instance, $((33)_5 34)_3$ is SiC polytype 111R (*i.e.* P = 111, rhombohedral lattice, which for us would be P = 37, since the structure repeats every 37 layers along the rhombohedral translation).

Since the Zhdanov symbol is meant to represent one-dimensional periodicity, it is natural to impose cyclic boundary conditions, of the kind of those (see, for instance, Kittel, 1967) used frequently in solid-state physics[1] and sometimes in one-dimensional problems in crystallography (Patterson, 1944; Iglesias, 1981*b*). The natural representation is to divide a circle into P equal arcs and place at the resulting points n_1 black dots, followed by n_2 white dots, followed by n_3 black dots *etc.* We call this the circular representation of the Zhdanov symbol, or CRZS for short. Rules for the identification of polytype symmetry elements in its Zhdanov symbol were found for sphere packings (Zhdanov, 1945, 1965), and were quoted in *International Tables for X-ray Crystallography* (Patterson & Kasper, 1959). These appear to be necessary conditions: when a symmetry element is present in the structure of the sphere stacking, then 'it shows up in the Zhdanov's symbol' (Patterson & Kasper, 1959) in a way prescribed by Zhdanov's rules. In fact, they are also sufficient conditions, *i.e.* the presence of certain symmetry in the Zhdanov symbol necessarily implies certain other symmetry elements in the structure of the stacking thus represented; a proof of this will be published elsewhere (Iglesias, 2006*b*). The symmetry properties of the structure can be easily studied by considering the two-color two-dimensional point group of the CRZS. One thing to note is that, since the minimal symmetry of a close-packed polytype is $P3m1$, and this group has mirror planes, no polytype can be an enantiomorph of a different (non-congruent) polytype: each polytype is its own enantiomorph, and two polytypes are either congruent or different.

2. Polytypes *MX*

2.1. Preliminary considerations

The generic name MX is frequently used to denote stackings of hexagonal layers of spheres (X atoms) placed with respect to each other with sphere closest packing, although contact between these spheres is often impossible because half of the tetrahedral holes, all tetrahedra having three vertices on a layer and the fourth one pointing up (*i.e.* in the positive direction of the normal to the layers), are filled with another (or the same, see below) kind of sphere (the M atom). This results in a tetrahedral coordination of the M atoms by the X atoms, and reciprocally, in such a way that each M sphere has three bonds to three X spheres lying in a layer, the bonds being inclined 19°28′ to the layers, and the fourth bond is perpendicular to the layers. Since all interlayer spaces between X spheres contain M spheres, one could equally well think of the structure as constituted by the packing, in a close-packed fashion, of hexagonal double layers, *i.e.* hexagonal planar lattices having at each node a dumb-bell constituted of one M and one X sphere, such that the dumb-bell handle is normal to the layer and the polarity of the dumb-bell is preserved throughout. These layers of dumb-bells can be stacked in the usual A, B, C configurations, the dumb-bell pairs now taking the place of the individual spheres in a closest packing of equal spheres. Since the point symmetry of an isolated dumb-bell is

[1] They are usually known as Born–von Kármán boundary conditions.

∞mm, which does not have a mirror plane normal to the dumb-bell handle, these polytypes cannot have such a plane of reflection parallel to the layers as an operation of symmetry; hence the possible space groups are drastically limited among the supergroups of $P3m1$ (Iglesias, 2006*a*) to $F\bar{4}3m$, $P6_3mc$, $P3m1$ and $R3m$. Space group $F\bar{4}3m$ corresponds to the exceptional Zhdanov symbol 10, the only Zhdanov symbol containing a zero, and is the only possible cubic space group; we may recall that for the full symmetry group of the sphere this stacking belongs to space group $Fm\bar{3}m$, with mirror planes normal to the cubic threefold axes, which are now lost. Polytypes of this kind are shown by SiC (see below), ZnS [Steinberg (1983) lists about 150 characterized polytypes], ZnSe, GaN, AlN, InN (Strite & Morkoç, 1992), BN (Huang & Zhu, 2000) *etc*.

The Zhdanov symbol of a polytype *MX* can be defined to be the Zhdanov symbol of the stacking of the *X* layers (or *M* layers) or it can be thought of as the Zhdanov symbol of the stacking of the dumb-bell layers: both ways of thinking produce indistinguishable results. We shall think of the Zhdanov symbol as representing the stacking of layers of dumb-bells, with a polarity defined by the order *M*–*X* (say) in the positive sense of the axis of stacking, and a stipulated distance (say the length of the handle). Since we intend to count the possible polytypes by enumerating the corresponding Zhdanov symbols, we need to establish which transformations of the Zhdanov symbol will leave the polytype structure invariant. To begin with, we can change the starting point in the Zhdanov symbol by shifting it by any number of components. However, since the two spheres constituting the dumb-bell are, in general, unequal (see important exception below), it is quite clear that a reversal of the Zhdanov symbol will represent, if taken to be a new Zhdanov symbol, a polytype incongruent with the original one. To see this, we select the clockwise sense of describing the CRZS as corresponding to a description of the stacking in the positive sense of the stacking axis (normally the *c* axis) and take black to represent + Hägg signs [*i.e.* $\ldots A \rightarrow B \rightarrow C \rightarrow A \ldots$, see Verma & Krishna (1966)], white to symbolize $-$ Hägg signs (*i.e.* $\ldots A \rightarrow C \rightarrow B \rightarrow A \ldots$); we realize that for a general configuration there are four CRZS intimately related, constituting a quartet (see Fig. 1). They are related in pairs by a mirror line, and likewise by an anti-mirror line and anti-twofold rotation, in such a way that each term of the quartet is related to the other three terms by means of the three symmetry operations described. Two members of a quartet related by an anti-twofold rotation (for instance, in Figs. 1*a* and *d*) have exactly the same Zhdanov symbol, but every black dot is now white and, reciprocally; if we start from an *A* layer clockwise in both cases, in the run of three dots of the same color marked with a cross, we can see that the sequence[2] in Fig. 1(*a*) goes as *ABCACBCAC*..., while the sequence in Fig. 1(*d*) is *ACBABCBAB*...; in other words, the *A* layer remains invariant, and *B* and *C* are exchanged. But this is precisely (Jain & Trigunayat, 1977) the description of the original structure after rotation through 60° around an axis normal to the layers, and passing through the dumb-bells of the *A* layer: both CRZS represent the same polytype structure. The CRZS in Figs. 1(*a*) and (*b*) represent, in general, different polytypes (Jain & Trigunayat, 1977) but the duet will degenerate into a singlet whenever the CRZS possesses a line of mirror symmetry: the two CRZS in Fig. 2 represent, therefore, a unique polytype structure. The same result will be obtained when the CRZS possesses an anti-mirror line.

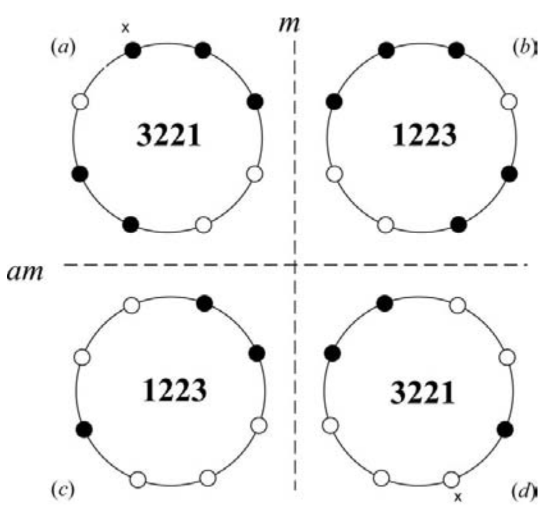

Figure 1
A quartet of CRZS for polytypes *MX*. There are only two different polytypes, that represented by (*a*) or (*d*) and that represented by (*b*) or (*c*).

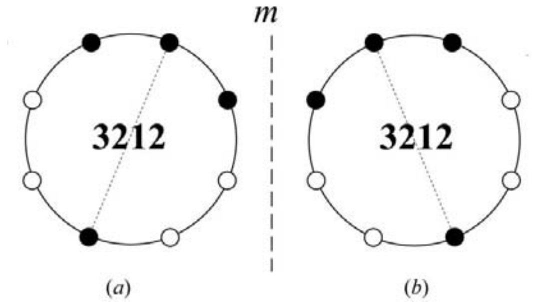

Figure 2
The duet of polytypes *MX* is degenerate because the CRZS possesses a mirror line of symmetry.

2.2. Enumerating *MX* polytypes

We are now ready to compute the number of distinguishable polytype structures of this *MX* family for a given repeat period *P*. To that end, we use the function (Iglesias, 1979, 1981*a*, 2006*a*)

$$a(p,q)=\frac{1}{p+q}\sum_{d|(p,q)}\mu(d)\frac{((p+q)/d)!}{(p/d)!(q/d)!}, \qquad (1)$$

[2] Notice that in this example $p-q=5-3\equiv 2\,(\mathrm{mod}\,3)$; the polytypes are rhombohedral and their *ABC* sequences repeat after three complete turns around the circle.

Table 1
Distribution of *MX* polytypes among the possible space groups.

P	$P6_3mc$	$P3m1$	$R3m$
2	1	0	0
3	0	0	1
4	1	0	1
5	0	1	2
6	1	1	3
7	0	3	6
8	2	4	10
9	0	9	19
10	3	15	33
11	0	31	62
12	5	53	112
13	0	105	210
14	9	189	387
15	0	363	728
16	16	672	1360
17	0	1285	2570
18	28	2407	4845
19	0	4599	9198
20	51	8704	17459
21	0	16641	33288
22	93	31713	63519
23	0	60787	121574
24	170	116390	232960
25	0	223696	447392
26	315	429975	860265
27	0	828495	1657009
28	585	1597440	3195465
29	0	3085465	6170930
30	1091	5964488	11930100
31	0	11545611	23091222
32	2048	22368256	44738560
33	0	43383477	86767016
34	3855	84212475	168428805
35	0	163617801	327235602
36	7280	318140816	636289024
37	0	619094385	1238188770
38	13797	1205595657	2411205111
39	0	2349383715	4698767640
40	26214	4581280972	9162588158
41	0	8939118925	17878237850
42	49929	17452532040	34905114396
43	0	34093383807	68186767614
44	95325	66637004800	133274104925
45	0	130312488852	260624978432
46	182361	254959096461	509918375283
47	0	499069107643	998138215286
48	349520	977343435440	1954687221760
49	0	1914795759936	3829591519872
50	671088	3752999242080	7505999155248
51	0	7358822919255	14717645841080
52	1290555	14434613329920	28869227950395
53	0	28324525958305	56649051916610
54	2485504	55599993740209	111199989970767
55	0	109178172784733	218356345569466
56	4793490	214457121917220	428914248627930
57	0	421389438813693	842778877636584
58	9256395	828248201161575	1656496411579545
59	0	1628420204246959	3256840408493918
60	17895679	3202559723079823	6405119464072784
61	0	6300117511512825	12600235023025650
62	34636833	12397005402788853	24794010840214539
63	0	24400455123937788	48800910247908864
64	67108864	48038395980546048	96076792028200960
65	0	94598687557484859	189197375114969718
66	130150493	186330748132489640	372661496395193292
67	0	367099384551433863	734198769102867726
68	252645135	723401728212336640	1446803456677318415
69	0	1425835290721450449	2851670581443022472
70	490853403	2810932429952315079	5621864860395483561
71	0	5542683665339959171	11085367330679918342
72	954437120	10931403894895178240	21862807790745026560

Table 1 (continued)

P	$P6_3mc$	$P3m1$	$R3m$
73	0	21563317273377375405	43126634546754750810
74	1857283155	42543842186776632975	85087684375410549105
75	0	83953181917682357808	167906363835365163008
76	3616814565	165697069571962306560	331394139147541427685
77	0	327090319159802265879	654180638319604531758
78	7048151355	645793707054397583640	1291587414115844178900
79	0	1275238206344545542939	2550476412689091085878
80	13743895344	2518595457521314850272	5037190915056373595888
81	0	4975003372899707709381	9950006745799417075771
82	26817356775	9828665200101058141875	19657330400228933640525
83	0	19420495094210910437047	38840990188421820874094
84	52357696365	38378597448048559135005	76757194896149479161840
85	0	75854169073859085471503	151708338147718170943006
86	102280151421	149944287704071865909121	299888575408246011969663
87	0	296441580288644698758195	592883160577289403687320
88	199911205050	586145851934232386326900	1172291703868664683858850
89	0	1159119886971329845411165	2318239773942659690822330
90	390937467284	2292481554231925063313852	4584963108464241076025088
91	0	4534578898481246428201905	9069157796962492856403810
92	764877654105	8970579994821086276485120	17941159989642937430624345
93	0	17748244290829824718190937	35496488581659649459473096
94	1497207322929	35118866362704825263178309	70237732725411147733679547
95	0	69498388170407313678546405	138996776340814627357092810
96	2932031006720	137548893253929186945751040	275097786507861305967247360
97	0	272261726853142053586061685	544523453706284107172123370
98	5744387279808	538967091933767174446194048	1077934183867540093279667904
99	0	1067045959788071886738353196	2134091919576143773563473408
100	11258999068416	2112751000380374829828457984	4225502000760760918655984384

where $\mu(n)$, the Möbius function (see, for instance, Hardy & Wright, 1979), is defined by

$$\mu(n) = \begin{cases} 1, & n = 1 \\ 0, & n \text{ contains a squared factor} \\ (-1)^k, & n \text{ has } k \text{ different prime factors.} \end{cases} \tag{2}$$

The function $a(p, q)$ counts the number of different CRZS of p black and q white dots, $P = p + q$. In this expression, sequences showing inner periodicity are properly assigned to period P/d, where $d|(p, q)$ is a divisor of (p, q), the greatest common divisor of p and q. From Figs. 1 and 2, it can be deduced that we just need to consider those cases for which $p \leq q$, since the cases for which $p > q$ are represented by CRZS′ where black and white are exchanged, and we have seen that all of them are equivalent to sequences for which $p < q$. The case $p = q$, as is usual (Iglesias, 1981*a*, 2006*a*), requires special care. In principle, we ought to halve $a(P/2, P/2)$ to get rid of the two configurations related by the anti-twofold rotation in Fig. 1, since we have reasoned above that configurations related by this kind of operation (those diagonally related in Fig. 1) represent exactly the same polytype structure and are counted as separate cases in the formula for $a(p, p)$. However, those CRZS having anti-twofold symmetry are related to themselves by this operation (Fig. 3). Hence, if we simply halve $a(P/2, P/2)$, we will be subtracting these cases twice. Taking all this into account, the number of different *MX* polytypes having periodicity P is

$$N^{MX}_{\text{total}}(P) = \sum_{\substack{p<q \\ p+q=P}} a(p, q) + \tfrac{1}{2} k(P)\{a(P/2, P/2) + \text{ATF}(P/2)\}, \tag{3}$$

where

$$k(n) = \begin{cases} 1 & n \text{ even} \\ 0 & n \text{ odd} \end{cases} \tag{4}$$

and ATF(p) is the number of CRZS having p black and p white dots showing at least an anti-twofold axis of symmetry. This number is (Iglesias, 1981*a*, 2006*a*)

$$\text{ATF}(p) = \frac{1}{p} \sum_{\text{od}|p} \mu(\text{od}) 2^{[(p/\text{od})-1]}, \tag{5}$$

where the summation runs over all odd divisors, od, of p.

Hexagonal and rhombohedral cases can be separately counted by restricting the above sum to the cases $p - q \equiv 0 \,(\text{mod}\, 3)$ (hexagonal cases):

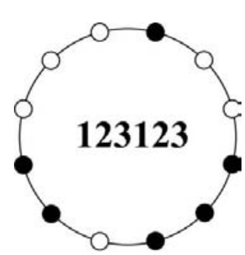

Figure 3
A polytype *MX* for which the CRZS shows a twofold, two-color symmetry rotor.

$$N_H^{MX}(P) = \sum_{\substack{p<q \\ p+q=P \\ 3|(p-q)}} a(p,q) + \tfrac{1}{2}k(P)\{a(P/2, P/2) + \mathrm{ATF}(P/2)\} \quad (6)$$

or $p - q \equiv \pm 1 \,(\mathrm{mod}\, 3)$ (rhombohedral cases):

$$N_R^{MX}(P) = \sum_{\substack{p<q \\ p+q=P \\ 3\nmid(p-q)}} a(p,q). \quad (7)$$

The above formulae simplify notably for prime P; thus, equation (3) reduces to[3]

$$N_{\mathrm{total}}^{MX}(P) = \frac{2^{P-1}-1}{P}, \quad P \text{ a prime } \geq 3, \quad (8)$$

which turns out to coincide with ATF(P), the number of CRZS having at least an anti-twofold axis, for period $2P$, P prime (Iglesias, 1981*a*, 2006*a*, Table 1). One can get, after some manipulation,[4]

$$N_H^{MX}(P) = \frac{2^{P-1}-1}{3P}, \quad P \text{ a prime} > 3. \quad (9)$$

In other words, for P a prime > 3 exactly one third[5] of the polytypes are hexagonal:

$$N_H^{MX}(P) = \frac{N_{\mathrm{total}}^{MX}(P)}{3}, \quad P \text{ a prime} > 3. \quad (10)$$

It is tedious, but not difficult, to find that, for $k > 0$,

$$N_H^{MX}(P) = \begin{cases} \dfrac{2^P - 2^{P/n}}{6P}, & P = n^k,\ n \text{ a prime} > 3 \\ \dfrac{2^P - 3 \times 2^{P/3} - 2}{6P}, & P = 3^k \end{cases} \quad (11)$$

$$\left.\begin{aligned} N_H^{MX}(P) &= \frac{2^{P-1}+2^{P/2}}{3P}, \\ N_{\mathrm{total}}^{MX}(P) &= \frac{2^{P-1}}{P}, \end{aligned}\right\} \quad P = 2^k,\ k \geq 2. \quad (12)$$

The values we find for the number of MX polytypes match those published by McLarnan (1981) for ZnS polytypes, once the different nature of the objects being counted is allowed for:

$$N_{\mathrm{Mc}}^{MX}(P) = N_H^{MX}(P) + m(P)N_R^{MX}(P/3), \quad (13)$$

where $m(P) = 1(0)$, $P \equiv 0 \,(\mathrm{mod}\, 3)$ (otherwise), and the left-hand side denotes values by McLarnan; the right-hand side values are from Table 1 in this paper, where our values are presented up to $P = 100$, distributed among the three possible space groups. In that connection, we realize that those Zhdanov symbols ascribed to space group $P6_3/mmc$ when they represent close packings of spheres (Iglesias, 2006*a*) now have to be lumped together with those belonging to $P6_3mc$ in order to get the MX polytypes whose symmetry group is $P6_3mc$. In other words, the polytypes belonging to space group $P6_3mc$ are all those whose CRZS exhibits an anti-twofold axis, *i.e.* they belong to the two-color two-dimensional point groups $2'$ or $2'mm'$. Their number is ATF(P/2), defined in (5) above. The number of polytypes MX belonging to space group $P3m1$ is obtained by difference. Finally, all rhombohedral MX polytypes belong to space group $R3m$. Then,

$$\begin{aligned} N_{P6_3mc}^{MX}(P) &= k(P)\mathrm{ATF}(P/2) \\ N_{P3m1}^{MX}(P) &= N_H^{MX}(P) - k(P)\mathrm{ATF}(P/2) \\ N_{R3m}^{MX}(P) &= N_R^{MX}(P) \end{aligned} \quad (14)$$

with $k(n)$ as defined in (4).

Closed formulae for ATF(p) for $p = r^k$, $k > 0$, r an odd prime, and for $p = 2^k$, $k > 0$ can be found in Iglesias (2006*a*).

2.3. SiC polytypes

The polytypes of SiC were among the first to be noticed and studied. The *Encyclopaedia Britannica* attributes its discovery to Acheson (1893), although others claim the compound was first prepared by Berzelius in 1824 (Jepps & Page, 1983). SiC was found subsequently by Moissan (1905) in meteoritic material and was widely employed thenceforth in sandpaper, grinding wheels and cutting tools under the commercial name of Carborundum®. Recently (materials advertised as 4H and 6H), it has been put to use as a high-temperature semiconductor and it stands among the candidates to take the place of silicon in selected electronic applications, including power transistors, microwave devices and others. Since the energy gap varies between 2.4 and 3.3 eV depending on the polytype, control of polytype formation is important for application to semiconductors, especially blue-light-emitting diodes (Kanaya *et al.*, 1991). The material is also currently marketed, under its mineral name moissanite, in the form of (almost) colorless macroscopic single crystals for jewelry uses, as a substitute for diamond, which it surpasses in every desirable jewel property (brilliance, refractive index, dispersive power, toughness, temperature resistance) except in hardness, in which it is second to diamond. Recently, SiC has attracted the interest of cosmochemists because of its occurrence in chondritic meteorite material thought to predate the solar system (presolar dust) and its polytypic composition has become of interest since it is known to be sensitive to growth conditions. Also, its spectral signature has apparently been detected in the dust envelopes of carbon stars and *supernovae ejecta* (Daulton *et al.*, 2003, and references therein).

The possible polytypes of SiC coincide, in principle, with the MX polytypes enumerated above. However, since the initial studies of Zhdanov, an empirical rule was found that the SiC polytypes, for unknown reasons, did not show a '1' in their Zhdanov symbol (see, for instance, Pandey & Krishna, 1983, who list 55 known polytypes). Eventually, the polytype 2H with the wurtzite structure (Zhdanov symbol 11) was found, and the rational designation of the well known cubic variety with the zincblende (sphalerite) structure is 10 (not ∞0, which would make it appear non-periodic), so it is clear that the rule

[3] Fermat's theorem (Hardy & Wright, 1979, Theorem 71) guarantees that P divides $2^{P-1} - 1$, P a prime number.
[4] The expression $\sum_{k\equiv 0\,(\mathrm{mod}\,3)}[N!/k!(N-k)!] = \frac{1}{3}\{2^N + 2\cos(N\pi/3)\}$ (Gradshteyn & Ryzhik, 1965, p. 3, formula 0.152.1) was used in the derivation.
[5] To prove that 3 divides $2^{P-1} - 1$, for prime P, put $2^k = (3-1)^k$ and use the binomial theorem.

Table 2
Polytypes of SiC.

P	$P6_3mc$	$P3m1$	$R3m$
4	22		
5			32
6	33		42
7		52	43
8	44		62, 53
9		63	72, 54, 3222
10	55	82, 3322	73, 64, 4222
11		74, 4232, 5222	92, 83, 65, 3332, 4322, 4223
12	66	93, 4224, 4323	(10)2, 84, 5232, 6222, 75, 4332, 4233, 5322, 5223
13		(11)2, 85, 4342, 6322, 6223, 5233, 5332	(10)3, 94, 5242, 7222, 6232, 76, 4333, 5323, 5422, 5224, 4234, 4432, 322222
14	77, 232232	(10)4, 6242, 8222, 7232; 4433, 5423, 5324, 5225, 332222	(12)2, (11)3; 95; 5342, 5243, 7322, 7223, 6332, 6233; 86, 4442, 5234, 5432, 6323, 6422, 6224, 5333, 323222, 422222
15		(12)3, 96, 5343, 7323, 6333, 5442, 5244, 7422, 7224, 6432, 6234, 222252, 423222, 422232	(13)2, (11)4, 6252, 9222, 8232, 7242; (10)5, 5352, 8322, 8233,7332, 7233, 6342, 6243; 87, 4443, 6423, 6324, 5433, 5334, 5235, 5325,4542, 6522, 6225, 333222, 432222, 234222, 232242, 323322, 323223
16	88, 323323, 422422	(14)2; (11)5, 6352, 6253, 9322, 9223, 8332, 8233, 7342, 7243, 5335, 6424, 5434, 6523, 6622, 5632, 333322, 432322, 232342, 234322, 422224	(13)3; (12)4, 7252; (10)222, 9232, 8242; (10)6, 6244, 8323, 7333, 6343, 5452, 8422, 8224, 7432, 7234, 6442, 423232, 222262, 325222, 424222, 523222, 97, 5443, 5344, 7423, 7324, 6433, 6334, 5542, 5245, 7522, 7225, 6532, 6235, 333232, 433222,432232, 234232, 233242, 332242, 334222, 532222, 235222, 232252
17		(13)4, 7262; (11)222; (10)232, 9242, 8252; (10)7, 5453, 5552, 6542, 6245, 8423, 8324, 7433, 7334, 6443, 6344, 8522, 8225, 7532, 7235, 433232, 334232, 533222, 532232, 333242, 434222, 235232, 233252, 332252, 335222, 632222, 236222, 232262, 424322, 424223	(15)2; (14)3; (12)5, 6362, 9332, 9233, 8342, 8243, 7352, 7253; (10)223; (10)322; (11)6, 6353, 9323, 8333, 7343, 6452, 6254, 9422, 9224, 8432, 8234, 7442, 7244, 424232, 523232, 222272, 326222, 226232, 6236, 5543, 5345, 7523, 7325, 6533, 6335, 333332, 433322, 233342, 432332, 332342, 234332, 334322, 532322, 232352, 235322, 222254, 524222, 522242; 98, 5444, 7424, 6434, 5642, 5246, 7622, 7226, 6632, 222245, 224234, 422432, 522422, 322244, 223442, 244232, 442232, 343232, 32222222
18	99, 522522, 342342, 243243	(15)3; (12)6; (10)323, 9333, 8343, 7353, 6462, 7254, 7452; (10)422; (10)224, 9432, 9234, 8442, 8244, 228222, 623232, 525222, 426222, 422262, 327222, 227232, 524232, 523242, 5544, 6336, 7722, 7425, 7524, 6534, 6435, 7623, 6732, 532323, 342243, 442332, 222255, 443223, 433323, 432333, 324225, 224235, 223245, 423225, 322245, 223542, 443322, 442233, 33222222, 23222232	(16)2; (14)4, 8262; (12)222; (11)232; (10)242, 9252; (13)5, 7362, 7263; (11)322; (11)223; (10)332; (10)233, 9342, 9243, 8352, 8253; (11)7, 6453, 6354, 9423, 9324, 8433, 8334, 7443, 7344, 6552, 6255, 9522, 9225, 8532, 8235, 7542, 7245, 434232, 333252, 232272, 533232, 335232, 534222, 435222, 532242, 235242, 234252, 432252, 633222, 336222, 632232, 236232, 233262, 332262, 732222, 237222, 424332, 424233; (10)8, 8424, 7434, 6444, 5652, 5553, 6345, 6543, 8622, 8226, 7632, 7236, 6642, 6246, 7335, 7533, 8523, 8325, 334332, 236322, 423432, 242262, 444222, 424323, 433332, 333342, 434322, 434223, 533322, 233352, 532332, 332352, 235332, 335322, 632322, 232362, 622224, 222264, 322254, 345222, 323244, 423234, 325422, 523224, 225234, 522432, 424422, 424224, 32322222, 22222242

of 'exclusion of 1' is, at best, an approximation; nevertheless, it seems to be a useful one and, when attempts are made at solving the structure of new SiC polytypes, only the possible cases including no 'ones' in the Zhdanov symbol are tried. The number of possible SiC polytypes under this 'exclusion of 1' assumption was calculated first by McLarnan (1981); a previous attempt by Mogami *et al.* (1978) was criticized, and the corresponding data superseded, by the results of McLarnan. Shortly thereafter, Inoue (1982) published a table of possible SiC polytypes, classified by the number of layers in the period, which was obtained by exhaustive generation under the '1-exclusion' rule. Since the number of cases found by Inoue did not match the numbers published by McLarnan, we carried out an exhaustive generation anew, excluding the sequences containing '1' in their Zhdanov symbol, which is presented in Table 2. The number of cases we get coincides with McLarnan's enumeration, once the oft-repeated transformation [see equation (13)] is applied to the data, to reflect the fact that McLarnan counted all cases as hexagonal, while the counting scheme by which we (and Inoue) enumerate Zhdanov symbols produces separate countings for hexagonal and rhombohedral cases. A first look at Inoue's data shows that the numbers this author gets are, for sufficiently large P, always less than the expected values. Thus, Inoue gets $NI_H^{\rm SiC}(11) = 3$, $NI_R^{\rm SiC}(11) = 5$ (the I after the N stands for Inoue); our Table 2 disagrees in that $N_R^{\rm SiC}(11) = 6$, the difference coming from the fact that Inoue only lists 4322 out of the pair (4322, 4223) of mirror-related CRZS. For P = 12, Inoue gets the same number of hexagonal cases as we get (4), but the number of rhombohedral cases is 7 in Inoue's table and 9 in ours. Again, the reason is that this author lists only one member of each of the pairs (4332, 4233) and (5322, 5223). Notice that, up to P = 12, and since $N_R^{\rm SiC}(4) = 0$ (see Table 2), there is no apparent disagreement between the values in Inoue's Table IV and those in McLarnan's Table 6, but there are differences between Inoue's values and ours, since we both count the same kind of objects (Zhdanov symbols). Starting from P = 13, the numbers from Inoue's paper deviate from McLarnan's, and keep deviating from ours. Thus, Inoue lists 5 hexagonal cases where McLarnan expects 7, the number of cases we list in Table 2. The reason is, once more, that Inoue fails to list 6223 and 5233 while listing their reverses. Among the rhombohedral cases, the disagreement is similar: Inoue lists 11 cases where there are 13, as he fails to list 5224 and

4234. For $P = 14$, Inoue fails to find 5324 among the hexagonal cases, while listing the remaining 10 sequences; and lists 14 rhombohedral sequences, missing 5243, 7223, 6233, 5234 and 6224, although the corresponding reversed sequences are listed. For $P = 15$, Inoue's table misses 4 hexagonal and 9 rhombohedral cases; for $P = 16$, 6 hexagonal and 14 rhombohedral sequences are not listed; for $P = 17$, 24 hexagonal cases are listed out of 36, and only 45 rhombohedral cases out of the possible 69.

It appears that the main reason for Inoue missing so many cases is always this author's failure to include the reversed sequences of those listed not having a mirror line in their CRZS, but it would be tedious and error-prone to check this exhaustively in Table IV of Inoue's paper. It is also difficult to locate the origin of these errors in the explanations offered in justification of Inoue's generation algorithm, but the only rational explanation of so large a deviation from the correct results must be some intrinsic flaw in the design of that algorithm.

Perhaps we should mention at this point the work of Bojin & Hoffmann (2003*a*,*b*). They deal with layered polymorphs of so-called REME phases. These are complex phases where RE = rare earth, actinide, or metals from groups 1 to 4 in the Periodic Table (alkali and alkaline-earths and the Sc and Ti groups), M = transition metal from groups 8 to 12, and E = elements from groups 13–15 (groups of B, C and N). Their two consecutive papers constitute a long (60-odd printed pages) exposition of stacking principles among these phases, of which about 1000 are known. The second paper is of a predictive nature, and the authors try to forecast possible polymorphs with different stacking sequences. Since one of their unit layers is a 'diamond layer', many of the stackings they describe must coincide with those tabulated by Inoue and in this paper. However, for the structures they deal with, there appear to be restriction rules limiting the initial theoretical possibilities, so it turns out to be a difficult task to compare their complex tabulated results and those of SiC, or of the general MX case. Nevertheless, one must take exception to the comment they print on page 1706 of the second paper: 'It seems that studies on SiC are typically concerned with describing the structures experimentally observed; there appears to be little consideration of the full range of potential structures'. They may have a point, but they refer with little or no comment to McLarnan's paper, which deals precisely with potential structures, which this author flawlessly enumerated, and they ignore the work of Inoue, which is perhaps incomplete, but not wrong, in those SiC polytype structures this author lists.

2.4. Diamond polytypes

Since the normal cubic structure of diamond is a tetrahedral linkage entirely similar to that of cubic SiC (sphalerite-type structure), it is only natural to expect that polytypes of a geometrical nature akin to that of the SiC polytypes might be found in pure carbon crystals. We shall refer to them, albeit perpetrating abuse of language, as 'diamond polytypes', since 'carbon polytypes' may be taken to carry the connotation of graphite having a part in this business; however, we must be aware of the fact that 'diamond' is a mineral name referring to pure carbon in a particular crystal structure.

In addition to diamond *sensu stricto* several other polytypes of tetrahedral carbon are known. The two-layer polytype was described as a mineral by Frondel & Marvin (1967) who found it in meteoritic materials and christened it lonsdaleite. Its structure can be described as a wurtzite-type structure, with all atoms of the same species. The so-called 6H polytype (Frenklach *et al.*, 1989; Spears *et al.*, 1990), obtained by nucleation in low-pressure mixtures of dichloromethane and oxygen passing through a high-power microwave generator, appears to be well characterized as 33 in Zhdanov notation (space group $P6_3/mmc$), although it is not altogether clear how the other possibility for a 6H structure, 2112 (space group $P\bar{6}m2$), was excluded. The remaining polytypes frequently referred to in the literature, 4H, 8H, 10H, 15R and 21R (see, for instance, Ownby *et al.*, 1992), appear to be postulated structures, whose diffraction and spectroscopic signatures are computed in the hope of recognizing the real thing whenever it comes across. Certain reports claim to have identified some of them in meteoritic material (Phelps, 1999).

There is an important difference between SiC polytypes and diamond polytypes: since the symmetry of a C—C dumb-bell is ∞/mmm, rather than ∞mm, the symmetry of the C—Si dumb-bell, the space-group symmetry of the diamond polytypes is expected to be higher than that of the equivalent SiC polytypes, although they must still be restricted to the supergroups of $P3m1$ (Iglesias, 2006*a*). In particular, they can be centrosymmetric, since the C—C dumb-bell has an inversion center midway between the two C atoms. In fact, with the sole exception of the normal cubic diamond structure (Zhdanov symbol 10), which belongs to space group $Fd\bar{3}m$, reflecting the fact that the point-symmetry group of the C—C dumb-bell is intermediate between the full symmetry group of the sphere (10 stacking belongs to $Fm\bar{3}m$) and that of the C—Si dumb-bell (10 stacking belongs to $F\bar{4}3m$), every other diamond polytype must belong to one of the seven space groups permissible for stackings of equal spheres: $P3m1$, $P\bar{3}m1$, $P\bar{6}m2$, $P6_3mc$, $P6_3/mmc$, $R3m$ and $R\bar{3}m$. This has been pointed out by Phelps *et al.* (1993). When the stacking has S-type centers of symmetry, these always lie at the central point of C—C dumb-bells, which take the place of the spheres of a sphere packing; O-type inversion centers are midway between C atoms belonging to different vertical (normal to the hexagonal layers being packed) dumb-bells. One could say that O-type centers are at the center of oblique C—C dumb-bells (inclined 19°28′ to the plane of the layers), since every C atom is covalently bonded to another C atom directly on top of it (the two make one vertical dumb-bell) and to three other atoms, lying on the layer below the given atom, and belonging to different vertical dumb-bells. The drawing exercise Phelps *et al.* (1993) embark upon, apparently to locate the inversion centers for known or postulated structures of diamond polytypes, can be entirely dispensed with once the Zhdanov symbol is known (or postulated), by strict application of Zhdanov's rules, after taking a look at the two-color symmetry point group of the cyclotomic representation (Iglesias, 2006*a*). Thus, the six $8H(a–f)$ postulated polytypes drawn in Fig. 4 of Phelps *et al.* (1993) have Zhdanov symbols 44, 71, 221111, 211211, 3212 and 3113; and, from the CRZS of these, one gets by inspection the following space groups: $P6_3/mmc$, $P\bar{3}m1$, $P\bar{6}m2$, $P6_3/mmc$, $P\bar{3}m1$ and $P\bar{6}m2$. Since half the period is even, both instances of $P6_3/mmc$ will have S-type inversion centers; and, since both 71 and 3212 have *TT*-type mirror lines (Iglesias, 2006*a*), the two cases belonging to $P\bar{3}m1$ will have exclusively O-type inversion centers.

3. Polytypes MX_2

3.1. Introductory remarks

This family includes CdI_2, $CdBr_2$, PbI_2, SnS_2, $SnSe_2$, TaS_2 and $TaSe_2$ (Trigunayat, 1991). According to Trigunayat, about 200 polytype structures are known for CdI_2; but the reference he gives (Krishna & Verma, 1966) only mentions 64, and the book by the same authors (Verma & Krishna, 1966) only considers the structure to be settled for 14 out of 68 polytypes. However, in a later paper (Wahab & Trigunayat, 1980), which is not referred to in Trigunayat (1991), about 90 CdI_2 polytypes are listed, and their stacking sequences reported. The number of known polytypes for the other listed compositions is much smaller.

The MX_2 polytypes are built by close-packed frameworks of large X atoms (iodine in the prototype CdI_2 family) with one half of the octahedral voids filled with M atoms, in such a way that the M atoms fill complete layers of octahedral voids alternating with empty octahedral layers. A necessary consequence of this is that the number of layers within a full period must be an even integer. For an alternative description of the structure, one can start with 'molecular' sandwiches of composition MX_2, made of two close-packed layers of X atoms with all the octahedral holes filled with M atoms, and stack them in a pile in a close-packed way. Since the centers of the octahedral holes of a sphere packing themselves constitute a hexagonal layer, a representation of the polytype can be given as a sequence of sandwiches $(A\gamma B)(C\alpha B)(C\beta A)\ldots$ *etc.*, where the Greek letters represent the M atoms, and an α, β, γ position corresponds with the usual A, B, C positions. If we agree on the convention that the first interlayer of a symbol is always filled, then we can entirely dispense with the Greek letters, and the polytype can be represented by the Zhdanov symbol of the stacked X atoms. If we represent the Zhdanov symbol by a CRZS, each dot symbolizes (see above) the interlayer between two X-atom layers; again, we paint black those dots representing the passage $\ldots A \to B \to C \to A \ldots$, whereas white-painted dots represent $\ldots A \to C \to B \to A \ldots$; we take the clockwise motion on the CRZS to represent the stacking of layers in the positive direction of the c axis. Since we have eliminated the Greek letters from the symbol but need to start the symbol at a metal-filled layer, we need an additional mark to flag those sandwiches containing M atoms. We use asterisks for that purpose (see, for example, Fig. 4) and only alternate dots can be thus marked.

We know that the Zhdanov symbol of a stack of close-packed layers of equal spheres can be cycled through its components, in any sense of rotation on the circle, and we always get different representations of the same stacking; for instance, Zhdanov symbols 5317, 3175, 1753, 7531, 7135, 5713, 3571 and 1357 all represent the same sphere stacking. The first four amount to simple changes of origin layer in descriptions of the structure reporting the stacking as we move in the positive direction of the axis of stacking; the remaining four are the reversal of the first four. In the CRZS, the second set of representations is supposed to be described counterclockwise, and the colors black and white are exchanged. Notice that giving the order of stacking as we move in the negative direction of the piling axis requires color reversal if the layers have to keep their A, B, C description, so by moving counterclockwise we keep our convention, but we have to exchange colors if we want to describe the same structure. The situation is not so simple in the MX_2 polytypes, because the fact that only alternating interlayers are filled with M atoms reduces the number of equivalent representations. It can be seen that two symbols related by cyclical permutation do represent the same structure if the two Zhdanov symbols differ by an even shift, *i.e.* the origins are shifted by an even number of layers, since the new origin satisfies the above-mentioned convention of always starting with a filled interlayer. This means that polytype 5317 is the same as 1753 (see Fig. 4*a*), but the reversed symbol 7135 represents in general a different structure, which happens to be the same as that represented by 3571, since both Zhdanov symbols differ by an even shift. In Fig. 4(*a*), we can see that the polytype represented can be described by the Zhdanov symbol 5317 (starting clockwise at *a*), or 1753 (starting clockwise at *b*). But the same polytype is obtained if we describe it by 1357 (starting counterclockwise at *b*) or 5713 (starting counterclockwise at *c*). In these last two cases, the colors had to be exchanged, but we can train ourselves to do these operations without actually changing colors, which saves us the work of repeating the drawing. In other words, 5317, 1753, 5713 and 1357 all represent exactly the same structure. The last two can be seen to derive from the first two by reversal of the Zhdanov symbol,

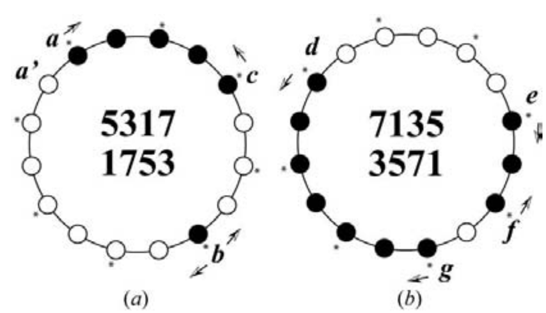

Figure 4
Relations among CRZS for MX_2 polytypes. (*a*) A unique polytype is represented by the sequences starting: clockwise at *a*, 5317; clockwise at *b*, 1753; counterclockwise at *b*, 1357, and at *c*, 5713. (*b*) A unique polytype is represented by the sequences starting: counterclockwise at *d*, 7135, and *f*, 3571, and clockwise at *e*, 3175, and at *g*, 7531.

followed by an odd shift (Jain & Trigunayat, 1977). Reversal followed by an odd shift always produces a (in general) different description of the same structure (see Appendix *A* for the commuting properties of the shift and reverse operators). Assume in Fig. 4(*a*) that we want to reverse the description 5317; we exchange colors (but omit) and start rotating counterclockwise in Fig. 4(*a*) at point a': it is clear that we need to advance an odd number of layers to point *b* to reach an admissible starting position.

In Fig. 4(*b*), we can see the same configuration of black and white dots as in Fig. 4(*a*). The asterisks are now placed in such a way that the reversal of 5317 [clockwise in Fig. 4(*a*) from *a*], which is 7135 [counterclockwise from *d* in Fig. 4(*b*)] now has a meaning as an admissible symbol for a polytype; it is clear that it will be a polytype different from that depicted in Fig. 4(*a*). In Fig. 4(*b*), it is obvious that this second polytype could be equally well represented by the symbols 3571 (counterclockwise at *f*) or 3175 (clockwise at *e*) or 7531 (clockwise at *g*). For this second polytype, we have obtained, therefore, the four different representations 7135, 3571, 3175 and 7531. Again, the first two (and the last pair) are related by an even shift, while the first and third are related by reversal followed by an odd shift, and the same relation holds for the second and the fourth.

Hence, given any Zhdanov symbol *Z* representing a polytype, we can represent the same polytype by ES(*Z*), or by OS(Rev(*Z*)), where ES/OS represents an operator that shifts the origin by an even/odd number of layers, and Rev is an operator that literally reverses the symbol. However, *Z* and Rev(*Z*) represent, in general, two different polytypes. In this connection we prove the following.

Proposition 1. Given any Zhdanov symbol of an MX_2 polytype, the operations of reversing and shifting by any number of layers will produce symbols representing no more than two different polytypes in all.

Proof. Let Zhdanov symbol *Z* represent polytype Poly1

$$Z = r_1 r_2 r_3 \ldots r_{k-1} r_k r_{k+1} \ldots r_{2n-1} r_{2n} \prec\!\succ \text{Poly1}, \qquad (15)$$

where the symbol $\prec\!\succ$ will be taken to mean 'represents'. We know that

$$\text{Rev}(Z) = r_{2n} r_{2n-1} \ldots r_{k+1} r_k r_{k-1} \ldots r_3 r_2 r_1 \prec\!\succ \text{Poly2} \qquad (16)$$

and that, in general, Poly1 $\neq$ Poly2. Now, since obviously

$$\text{Rev}(\text{Rev}(Z)) = Z \qquad (17)$$

$$\text{Poly3} \prec\!\succ \text{OS}(Z) = \text{OS}(\text{Rev}(\text{Rev}(Z))) = \text{Rev}(Z) \prec\!\succ \text{Poly2}. \qquad (18)$$

The conclusion is that, for any given Zhdanov symbol, reversal and shifting that symbol by any amount can produce representations for, at most, two distinct polytypes: ES(*Z*) and OS(Rev(*Z*)) produce several distinct representations all equivalent to *Z*, and OS(*Z*) and Rev(*Z*), represent a new polytype, Rev(*Z*), which we call the 'conjugate' of the initial one, *Z*. We also say that the polytypes represented by *Z* and Rev(*Z*) are a pair of conjugates. When both conjugates are congruent, the conjugate pair is degenerate.

3.2. Effect of the symmetry of the CRZS

We now investigate the consequences of having some symmetry in the CRZS. The first thing to notice is that the period of repetition being necessarily even implies (Iglesias, 2006*a*) that there can only be *BB*-type and *TT*-type mirror lines. We recall that a *BB*-type mirror line goes through the midpoint of the arc between dots at its two ends, while a *TT*-type mirror line intercepts a dot at both its extremities (Iglesias, 2006*a*). In addition to these, we can have anti-mirror line, anti-twofold rotor and combinations thereof: $2'mm'$, where $m = BB$ (*TT*) for *P*/2 even (*P*/2 odd). We now prove the following.

Proposition 2. Whenever the Zhdanov symbol of an MX_2 polytype has a *BB*-type mirror line in its CRZS, the polytype thus represented and that represented by the reversed symbol are one and the same.

Proof. We assume that the CRZS has a *BB*-type mirror line of symmetry and prove that the Zhdanov symbols *Z* and Rev(*Z*) represent the same polytype. Since a *BB* line intercepts no dot, it is clear that between a given dot and its symmetric mate by the operation of the *BB* mirror line there must be an even number of dots. This guarantees that in every pair of mirror-related mates only one can be marked with an asterisk. Consider now, in Fig. 5(*a*), the Zhdanov symbol *Z* starting clockwise at position *a*. The reversed sequence Rev(*Z*) would start at *b*, running counterclockwise. However, the sequence starting at *b* is not a valid one since it lacks an asterisk, although the sequence starting clockwise at *c*, the mate of point *b* by the operation of the *BB* mirror line, is a valid one, since there is necessarily an asterisk at that dot. Moreover, it is identical with that starting counterclockwise at *b*. Hence the

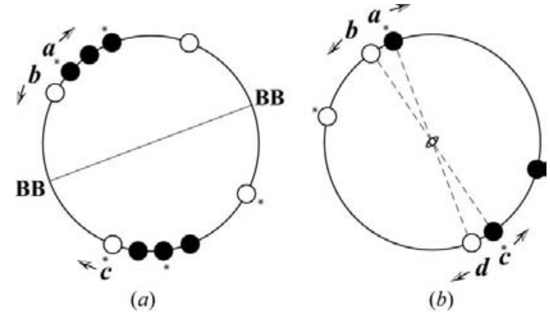

Figure 5
(*a*) CRZS of an MX_2 polytype possessing a *BB*-type mirror line. The sequence starting clockwise at *c* coincides with the reverse of that starting clockwise at *a*. (*b*) CRZS of an MX_2 having an anti-twofold rotor. The sequence starting at *c* counterclockwise is identical to that starting at *b* in the same sense of rotation and will be a valid sequence if *P*/2 is odd.

Zhdanov symbol Z and the reversed symbol Rev(Z) represent exactly the same polytype structure. (*q.e.d.*)

The TT-type mirror line does not have a similar property. To prove that the presence of a TT-type mirror line does not make equivalent Z and Rev(Z), it suffices to give a counter-example, such as that shown in Fig. 6, where it can be seen that 2321 $\prec\!\succ$ 3212 represents a different polytype to that represented by 1232 = Rev(2321) $\prec\!\succ$ 2123. The significance of the TT-type mirror line will be appreciated below.

Proposition 3. If the CRZS has a $2'$ rotation axis, *i.e.* it is invariant under rotation of 180° followed by color exchange, then the MX_2 polytype represented by any valid Zhdanov symbol and that represented by the reversed symbol will be the same, provided that $P/2$ is odd.

Proof. We refer to Fig. 5(b) and suppose that $P/2$ is odd. The sequence Z starting clockwise at a has as its reverse that sequence starting counterclockwise at b, but this is not a valid starting point for a Zhdanov symbol; however, the two-color twofold rotation ensures that an identical sequence, Rev(Z), will start counterclockwise at c and, since $P/2$ is odd, it will be a valid starting point for the Zhdanov symbol of a polytype MX_2. But this is the reverse of that sequence going clockwise from d, which coincides with Z. Hence, $Z \prec\!\succ$ Rev(Z). Notice that this would be impossible if $P/2$ happens to be even, in which case Z and Rev(Z) represent different polytypes.

Proposition 4. If the CRZS of an MX_2 polytype has a two-color mirror line, *i.e.* it is invariant under reflection on a line followed by color exchange, then the polytype represented by any Zhdanov symbol and that represented by the reversed symbol will coincide.

Proof. The argument is almost identical with that given for the BB-type mirror line above, and will be easily reconstructed by the interested reader. Both BB-line and anti-mirror line pass

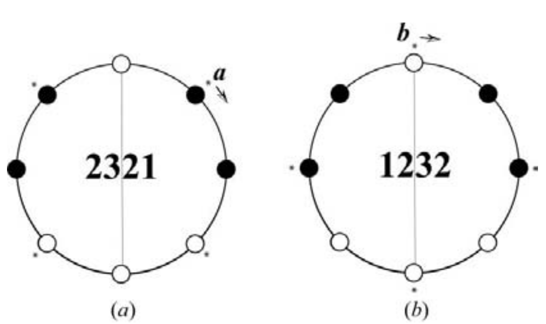

Figure 6
The presence of a TT-type mirror line in the CRZS does not make the sequence 2321 represent the same polytype as its reverse, 1232.

between dots and have the same effect as far as asterisk marks are concerned; they differ in that the anti-mirror switches colors and the BB-line does not.

The converse to *Propositions* 2, 3 and 4 can be written as the following proposition.

Proposition 5. If Z and Rev(Z) represent the same MX_2 polytype, then the CRZS has at least one of the following: a BB-type mirror line, an anti-mirror line or, if $P/2$ is odd, an anti-twofold rotor.

Proof. We refer again to Fig. 5(a) and forget momentarily about the drawn BB line. We assume that the sequence starting clockwise at a and that running counterclockwise from b represent the same structure. Since b is not a valid starting point, there must be a valid starting point differing from a by an even number of layers from which the sequence is the same as that running counterclockwise from b. Assume the point is c, a dot with asterisk, for which we ignore both its color and the adequate sense of rotation. Let the color be white and the sense clockwise: this implies a BB-type line as drawn. We now suppose the dot is black and the sense is clockwise: between b and c there must be an anti-mirror line. We now assume the sense to be counterclockwise. First we assume the color of c is white: but this is impossible, because then the CRZS would contain subperiods, and we are assuming that these have been excluded by our counting scheme [and are reckoned among the set of period P/d, $d|(p,q)$]. Now we assume the color is black; the only way to have two equal sequences in the same sense of rotation, one starting white and the other black is having the operation of a $2'$ rotation in the CRZS, and having c exactly opposite to b. Moreover, one of the sequences lacks an asterisk and the other must have one, and this requires $P/2$ to be odd. (*q.e.d.*)

3.3. Enumeration of MX_2 polytypes

Propositions 1–5 give us working rules to count polytypes by counting Zhdanov symbols. For every distribution of p black dots and q white dots in the circle, there is a pair of conjugate polytypes, which is the same conjugate pair if we exchange the colors (*i.e.* if we consider the arrangements of q black dots and p white dots as well); then the number of different polytypes would be $\sum_{p\leq q} a(p,q)$, with $a(p,q)$ as given above, but we have to correct this value by properly taking care of degenerate pairs of conjugates. It is convenient to distinguish two cases.

(a) For $p \neq q$, we recall that $a(p,q)$ counts separately the two members of each pair of mirror-related CRZS, and counts singly those arrangements having a mirror line. However, we have seen (Proposition 2) that only BB-type mirror lines produce degenerate pairs of conjugates, while TT mirror lines do not introduce any degeneracy. We therefore must correct $a(p,q)$ by increasing its value by $\mathrm{tt}(p,q)$, the number of configurations having a TT-type mirror line, where $\mathrm{tt}(p,q) = b(p,q) - \mathrm{bb}(p,q)$; $b(p,q)$ is the number of arrangements showing at least a mirror line of any kind (Iglesias, 1979, 1981*a*, 2006*a*); and $\mathrm{bb}(p,q)$ is the number of arrangements whose CRZS contains at least a BB line (Iglesias, 2006*a*).

There is an additional difficulty derived from the fact that only an even period P can occur among these polytypes: half-order subperiods having an odd sum must be added in, because such subperiods cannot represent a polytype of half periodicity, but have been nevertheless subtracted in the computation of $a(p,q)$. Thus a Zhdanov symbol such as 5252 should be considered as having $P = 7$ if it represents a stacking of spheres, and the proper symbol would be 52. But if we are dealing with MX_2 polytypes, 52 is not a valid symbol, but 5252 is, and properly belongs in the set for which $P = 14$. This means that $a(p,q)$ should be corrected by adding these cases, which in principle would be counted by $a(p/2, q/2)$, for $(p+q)/2$ odd. But some of these cyclic configurations could have mirror lines themselves, hence the real correction term should be $[a(p/2, q/2) + b(p/2, q/2)]/2$. Since these mirror lines are necessarily of the BT type (Iglesias, 2006*a*) because the period is odd, and these give, upon repetition, some BB-type lines (see Fig. 2 in Iglesias, 2006*a*), no more corrections are needed. Finally,

$$N^{MX_2}(p,q) = c(p,q) + \tfrac{1}{2} l(p,q) d(p/2, q/2), \qquad (19)$$

where

$$\left.\begin{array}{l} c(p,q) = a(p,q) + \mathrm{tt}(p,q) \\ d(p,q) = a(p,q) + bt(p,q) \end{array}\right\} \qquad (20)$$

and

$$l(p,q) = \begin{cases} 1 & p \text{ even and } 4 \nmid (p+q) \\ 0 & \text{otherwise} \end{cases} \qquad (21)$$

and $\mathrm{bt}(p,q) = b(p,q)(0)$, $p+q$ odd (otherwise).

A definition of $b(p,q)$ is in equation (32).

(*b*) For $p = q$, the number $a(p,p)$ contains pairs of color conjugates, representing a unique polytype; dividing by 2 would take care of this redundancy. But we must remember that those configurations having a mirror or anti-mirror line appear only once in the counting, while, out of these, those for which the mirror line is of the TT type produce two different polytypes; also, we have to correct for the fact that those having a two-color twofold rotor produce also two different polytypes if p is even, and only one if p is odd (Proposition 3). However, it can be seen that the correction (half-order subperiod of odd sum) introduced in equation (19) is not needed here; to see that, we prove the following.

Proposition 6. When $p = q$ there can be no Zhdanov symbol for an MX_2 polytype having a one-half subperiod of odd sum.

Proof. Let

$$Z = r_1 r_2 r_3 \ldots r_{n-1} r_n r_{n+1} \ldots r_{2n-1} r_{2n}, \quad n \text{ even}, \qquad (22)$$

where $\sum_{j \text{ odd}} r_j = \sum_{k \text{ even}} r_k$, *i.e.* $p = q$. [We need n even in (22) in order for the hypothetical subperiod $Z' = r_1 r_2 r_3 \ldots r_{n-1} r_n$ to be a legitimate MX_2 Zhdanov symbol by itself.]

Since $r_i = r_{i+n}$, $i = 1$ to n,

$$p = \sum_{\substack{i=1 \\ i \text{ odd}}}^{2n-1} r_i = (r_1 + r_{n+1}) + (r_3 + r_{n+3}) + \ldots + (r_{n-1} + r_{2n-1})$$

$$= 2 \sum_{\substack{i=1 \\ i \text{ odd}}}^{n-1} r_i \qquad (23)$$

and, similarly,

$$q = \sum_{\substack{j=2 \\ j \text{ even}}}^{2n} r_j = (r_2 + r_{n+2}) + (r_4 + r_{n+4}) + \ldots + (r_n + r_{2n})$$

$$= 2 \sum_{\substack{j=2 \\ j \text{ even}}}^{n} r_j, \qquad (24)$$

which would require both p and q to be even; and moreover, since $p = q$,

$$\sum_{\substack{i=1 \\ i \text{ odd}}}^{n-1} r_i = \sum_{\substack{j=2 \\ j \text{ even}}}^{n} r_j. \qquad (25)$$

Hence Z' cannot have an odd sum. (*q. e. d.*)

Taking all this into account, we can write

$$N^{MX_2}(p,p) = \left\{\begin{array}{ll} \tfrac{1}{2}\{a(p,p) + \mathrm{tt}(p,p) + \mathrm{ATF}(p)\}, & p \text{ even} \\ \tfrac{1}{2}\{a(p,p) + b(p,p)\}, & p \text{ odd} \end{array}\right\}, \qquad (26)$$

where use has been made of the fact that $b(p,p) = \mathrm{tt}(p,p)$ if p is odd (Iglesias, 2006*a*).

The two equations (26) can be combined with (19) to give the total number of hexagonal polytypes MX_2 for period P:

$$N_H^{MX_2}(P) = \sum_{\substack{p<q \\ p+q=P \\ 3|(p-q)}} c(p,q) + \tfrac{1}{2} l(p,q) d(p/2, q/2)$$
$$+ \tfrac{1}{2}\delta_q^p \{c(p,q) + k(p)\mathrm{ATF}(p)\}, \qquad (27)$$

where $k(n) = 1$ (0) for n even (odd) is defined in (4), δ_q^p is the Kronecker delta,[6] and $c(p,q)$, $d(p,q)$ and $l(p,q)$ have the meanings defined in (20) and (21). The rhombohedral cases would be counted by a similar expression:

$$N_R^{MX_2}(P) = \sum_{\substack{p<q \\ p+q=P \\ 3\nmid(p-q)}} c(p,q) + \tfrac{1}{2} l(p,q) d(p/2, q/2). \qquad (28)$$

These values are presented up to $P = 100$ in Table 3. Our values agree with those published by McLarnan (1981) to $P = 50$, with the equivalence

[6] $\delta_q^p = 1(0)$, $p = q$ (otherwise).

Table 3
Distribution of MX_2 polytypes among the possible space groups.

P	$P6_3mc$	$P\bar{3}m1$	$P3m1$	$R\bar{3}m$	$R3m$	Total hexagonal	Total rhombohedral
2	0	1	0	0	0	1	0
4	1	0	0	2	0	1	2
6	0	1	1	5	1	2	6
8	2	4	2	8	6	8	14
10	0	10	12	20	24	22	44
12	5	16	45	38	93	66	131
14	0	42	174	84	348	216	432
16	16	80	632	160	1280	728	1440
18	0	163	2344	341	4684	2507	5025
20	51	330	8539	660	17129	8920	17789
22	0	682	31434	1364	62868	32116	64232
24	170	1332	115724	2688	231616	117226	234304
26	0	2730	428820	5460	857640	431550	863100
28	585	5418	1594731	10836	3190047	1600734	3200883
30	0	10890	5959770	21840	11919544	5970660	11941384
32	2048	21760	22357376	43520	44716800	22381184	44760320
34	0	43690	84193200	87380	168386400	84236890	168473780
36	7280	87154	318097239	174422	636201813	318191673	636376235
38	0	174762	1205517474	349524	2411034948	1205692236	2411384472
40	26214	349180	4581106382	698360	9162238978	4581481776	9162937338
42	0	698922	17452215864	1398096	34904431992	17452914786	34905830088
44	95325	1397418	66636306091	2794836	133272707507	66637798834	133275502343
46	0	2796202	254957819934	5592404	509915639868	254960616136	509921232272
48	349520	5590800	977340640040	11182080	1954681630720	977346580360	1954692812800
50	0	11184800	3752994097072	22369600	7505988194144	3753005281872	7506010563744
52	1290555	22366890	14434602146475	44733780	28869205583505	14434625803920	28869250317285
54	0	44738731	55599973027843	89478485	111199946060029	55600017766574	111200035538514
56	4793490	89473020	214457077180710	178946040	428914159154910	214457171447220	428914338100950
58	0	178956970	828248117854020	357913940	1656496235708040	828248296810990	1656496593621980
60	17895679	357902010	3202559544128818	715806000	6405119106169784	3202559919926507	6405119821975784
62	0	715827882	12397005067966134	1431655764	24794010135932268	12397005783794016	24794011567588032
64	67108864	1431633920	48038395264729088	2863267840	96076790596567040	48038396763471872	96076793459834880
66	0	2863309482	186330746787601884	5726623056	372661493575265272	186330749650911366	372661499301888328
68	252645135	5726579370	723401725349046955	11453158740	1446803450950739045	723401731328271460	1446803462403897785
70	0	11453246070	2810932424552927646	22906492140	5621864849105855292	2810932436006173716	5621864872012347432
72	954437120	22906400832	10931403883441977824	45812809728	21862807767838621696	10931403907302815776	21862807813651431424
74	0	45812984490	42543842165108329500	91625968980	85087684330216659000	42543842210921313990	85087684421842627980
76	3616814565	91625794218	165697069526149409451	183251588436	331394139055915633467	165697069621392018234	331394139239167221903
78	0	183251929770	645793706967470386290	366503875920	1291587413934941624760	645793707150722316060	1291587414301445500680
80	13743895344	366503526320	2518595457338063087112	733007052640	5037190914689870069568	2518595457718310508776	5037190915422877122208
82	0	733007751850	9828665199752432503800	1466015503700	19657330399504865007600	9828665200485440255650	19657330400970880511300
84	52357696365	1466014788378	38378597447315551740816	2932029609264	76757194894683464357208	38378597448833924225559	76757194897615493966472
86	0	2932031007402	149944287702674037173034	5864062014804	299888575405348074346068	149944287705606068180436	299888575411212136360872
88	199911205050	5864060616700	586145851931300356018550	11728121233400	1172291703862800623242150	586145851937364327840300	1172291703874528744475550
90	0	11728123996680	2292481554226321626293580	23456248058880	4584963108452643264484864	2292481554238049750290260	4584963108476099512543744
92	764877654105	23456245263018	8970579994809358153853611	46912490526036	17941159989619481185361327	8970579994833579276770734	17941159989666393675887363
94	0	46912496118442	35118866362682367153334374	93824992236884	70237732725364734306668748	35118866362729279649452816	70237732725458559298905632
96	2932031006720	93824986579200	137548893253882274452461440	187649973288960	275097786507767480980602880	137548893253979031470047360	275097786507955130953891840
98	0	187649984473728	538967091933677179045477056	375299968947456	1077934183867354358090954112	538967091933864829029950784	1077934183867729658059901568
100	11258999068416	375299957762400	2112751000380187179849576784	750599915524800	4225502000760385618698221984	2112751000380573738806407600	4225502000761136218613746784

$$N_{\rm Mc}^{MX_2}(P) = N_H^{MX_2}(P) + m(P)N_R^{MX_2}(P/3), \qquad (29)$$

where $m(P) = 1\,(0)$, $P \equiv 0\,(\mathrm{mod}\,3)$ (otherwise); on the left-hand side of the equality are McLarnan's values, and on the right-hand side are ours, with subindices indicating hexagonal and rhombohedral cases. There is only one discrepancy between our results and McLarnan's: for $P = 6$ this author reports three polytypes, while we only get two hexagonal polytypes, 33 ($P\bar{3}m1$, see below) and 2211 ($P3m1$), Table 3. We also get 0 rhombohedral polytypes for $P = 2$, so the two values cannot be reconciled. Given the by now customary agreement between McLarnan's counting and ours, we have to surmise that there is a misprint in McLarnan's Table 5.

3.4. Distribution of polytypes MX_2 among the permissible space groups

A consequence of the structure of these polytypes is that there can be no centers of symmetry located at the centers of the X atoms, since such centers would relate empty to M-occupied octahedral positions. Since we are using essentially the Zhdanov symbol of the X-atom substructure to describe the structures of these polytypes, this means that BB-

type symmetry lines in the CRZS do not (as they did for sphere stackings) imply that the polytype has an S center, which we know is impossible. This is reflected in the fact that the set of asterisks does not obey the symmetry operation of the *BB* line (Proposition 2, Fig. 5). Moreover, there can be no mirror planes normal to the stacking axis, since there is no way of having such mirrors passing through octahedral holes (two successive *X* layers cannot be so related) and these mirror planes cannot pass through *X*-atom layers that systematically separate empty and filled octahedral holes. Hence, among the possible space groups of a stacking of equal spheres (Iglesias, 2006*a*), we have to strike out $P6_3/mmc$ and $P\bar{6}m2$; since $P \geq 2$, no cubic space group is possible either. Hence we are limited to $P6_3mc$, $P3m1$, $P\bar{3}m1$, $R3m$ and $R\bar{3}m$.

We are still at a loss to recognize in the Zhdanov symbol a centrosymmetric polytype. We deal with this in the following Proposition.

Proposition 7. The CRZS of an MX_2 polytype has a *TT*-type mirror line of symmetry if and only if the polytype is centrosymmetric.

Proof. (*A*) Assume first that the polytype has inversion centers placed at a subset of the octahedral centers of the *X*-atom stacking. This necessarily entails these *X* atoms being distributed centrosymmetrically, and this 'shows up in the Zhdanov symbol' (Patterson & Kasper, 1959) in the form of a *TT* mirror line in its CRZS. The asterisks conform to this symmetry (see Fig. 6).

(*B*) Assume now that a *TT* line of symmetry exists in the CRZS. We have proved (Iglesias, 2006*b*) that this implies that the arrangement of the *X* atoms is centrosymmetric, with $\bar{1}(O)$ inversion centers.

(*a*) Let *P*/2 be even. Since the CRZS has a *TT* line of symmetry, the number of dots of any color at each side of the *TT* line is $(P-2)/2$, an odd number (Fig. 7*a*). We place an *M* layer at the interlayer represented by the central dot of a run of *n* dots of the same color on which the *TT* line is incident (*i.e.* we place an asterisk on this dot). Since alternate interlayers must be *M*-filled, the dot at the opposite end of the *TT* line will carry an asterisk as well. If $(n-1)/2$ is even (which is the case in Fig. 7*a*), each end of the run of *n* dots can be the starting point of a valid Zhdanov symbol. If $(n-1)/2$ is odd, the start of a valid Zhdanov symbol will be at the beginning of the next run of dots of opposite color. In both cases, the configuration of asterisks satisfies the mirror line, *i.e.* the center of symmetry relates *M*-filled sandwiches with *M*-filled sandwiches. It remains to be seen that these *M*-layers are in the correct orientation. Suppose, for instance, that the uppermost black dot in Fig. 7(*a*) represents a $(A\gamma B)$ sandwich, and consider any pair of asterisk-bearing dots of any color, symmetrically placed with respect to the mirror line. We have proved (Iglesias, 2006*b*) that if the dot on the left represents, when described clockwise, sandwiches of the type $(A\gamma B)$, $(B\gamma A)$, $(A\beta C)$, $(C\beta A)$, $(B\alpha C)$ or $(C\alpha B)$, the corresponding sandwich on the right-hand side will be, respectively, of the type $(A\gamma B)$, $(B\gamma A)$, $(C\alpha B)$, $(B\alpha C)$, $(C\beta A)$ or $(A\beta C)$; hence the *M* atoms are centrosymmetrically distributed as well, since the rule $\gamma \rightleftharpoons \gamma$, $\alpha \rightleftharpoons \beta$ is satisfied throughout. It is easy to see that we will get the same result (*i.e.* asterisks symmetrically ordered with respect to the *TT* line and *M* layers correctly oriented) if we place the *M* layer not at the central dot but at the dot next to it, and that the dot at the other end of the *TT* line should be empty (asterisk-free). It should be clear that the two configurations represent different polytypes, but both are centrosymmetric.

(*b*) Let *P*/2 be odd. We place an asterisk at the central dot of a run of *n* dots of the same color, as in (*a*) above. Now the dot at the opposite end of the *TT* line will be asterisk-free. Again, if $(n-1)/2$ is even, the *n* run will be a valid start for a Zhdanov symbol and, if $(n-1)/2$ is odd (which happens in Fig. 7*b*), the next run of dots at any side will be a valid Zhdanov symbol. The asterisks conform, in any case, with the *TT* mirror line, and it can be verified that the *M* layers will have the correct orientation as well. The same result is obtained if the initial asterisk is placed at the dot next to the central one in the initial *n* run.

(*q.e.d.*)

Incidentally, we have proved for those CRZS having a *TT* line the following.

(*a*) If *P*/2 is even, both centers of inversion in a unit cell are filled with *M* atoms, or else both are empty. If a given Zhdanov symbol corresponds to a polytype in which both centers correspond to *M*-filled positions, the conjugate polytype (represented, for instance, by the reversed Zhdanov symbol) will have both inversion centers at empty octahedral holes.

(*b*) If *P*/2 is odd, half the inversion centers are at *M*-filled octahedra and the other half are at empty octahedra; the same occurs with the conjugate polytype.

For instance, polytype 512121 has both sets of inversion centers at metal-filled octahedral holes, at the mid dot of the first (5) and fourth (1) components. The conjugate polytype 151212 has both sets of inversion centers at empty octahedral voids, those corresponding to the mid dot of the second (5)

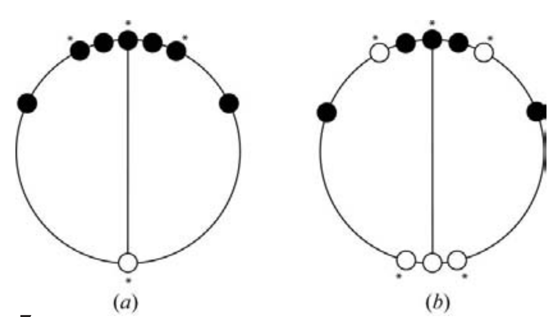

Figure 7
In an MX_2 polytype showing a *TT*-type mirror line in its CRZS, the distribution of asterisks (see text) satisfies the mirror-line operation. (*a*) When *P*/2 is even, both extremities of the *TT* line are filled positions or else they are empty. (*b*) If *P*/2 is odd, one of these extremities is filled and the other is empty.

and fifth (1) components. For those who only believe in the A, B, C way of thought, this will not be difficult to check. For the conjugate pair 71 and 17, the inversion centers are respectively at empty and filled octahedral holes. In general, it helps if the CRZS be drawn and the position of the TT line ascertained: it always goes through the central dot of two opposite odd runs. Let these odd runs contain r and s dots, respectively. If the Zhdanov symbol begins with r, the parity of $(r-1)/2$ will determine which inversion centers are at filled octahedra and which at empty ones: if the parity is even, the inversion centers are at filled octahedra, if it is odd, at empty ones.

Another example: polytype 221221 has a TT line passing through the two 'ones' in the Zhdanov symbol. We can transform it by an even shift into 122122. Since $P/2$ is odd and $(1-1)/2 = 0$ is even, the inversion center at the first octahedral hole is at a metal-filled position (we know that, anyway, because otherwise the Zhdanov symbol would be illegal), but the other inversion center is at an empty position. The conjugate polytype is, in this case, itself (because the CRZS has $2'$ symmetry, and $P/2$ is odd, see Proposition 3). The conjugate pair 9212 and 1292 are, however, different: both have inversion centers at filled positions at the mid dot of the first component (9 and 1, respectively) and inversion centers at empty octahedra (central dot of 1 and 9, respectively).

Now we study the conditions under which a polytype MX_2 will show a 6_3 screw axis. The first thing to notice is that a molecular sandwich MX_2 must generate, through the operation of the screw, another sandwich MX_2 displaced 1/2 along the stacking axis. This implies that the number of sandwiches in the first half of the unit cell must be an integer, and hence that the number of X layers in that half of the cell must be even, *i.e.* $P/2$ is necessarily even. We prove the following.

Proposition 8. An MX_2 polytype will have a 6_3 screw axis if and only if its CRZS shows an anti-twofold rotor, and $P/2$ is even.

Proof. (*a*) Assume first the structure has a 6_3 screw, hence $P/2$ must be even. Moreover, the subset constituted by the X atoms must conform to the 6_3 symmetry, hence (Zhdanov, 1945, 1965; Patterson & Kasper, 1959; Krishna & Verma, 1966; Iglesias, 2006*b*) the CRZS will have a $2'$ rotor.

(*b*) We now assume that the CRZS has an anti-twofold rotor, and that $P/2$ is even. The symmetry of the CRZS implies that the X atoms are distributed in compliance with the operation of a 6_3 screw (Iglesias, 2006*b*). Moreover, since $P/2$ is even, the sandwiches (metal-filled pairs of X-atom layers) also conform as such to the operation of the 6_3 screw. It only remains to see that two symmetry-related sandwiches have their metal layers in the correct orientation. We take the origin at the layer on whose spheres the 6_3 screw is incident and choose the positive direction of the c axis so that this A layer is the first constituent of a metal-filled sandwich (we remember that this is the conventional way of symbolizing these polytypes, see §3.1). We can see (Iglesias, 2006*b*; Krishna & Verma, 1966) that, with these conditions, the sandwiches $(A\gamma B)$, $(B\gamma A)$, $(A\beta C)$, $(C\beta A)$, $(B\alpha C)$ and $(C\alpha B)$ will generate symmetry-related sandwiches $(A\beta C)$, $(C\beta A)$, $(A\gamma B)$, $(B\gamma A)$, $(C\alpha B)$ and $(B\alpha C)$, displaced by 1/2 along the c axis. Hence the metal layers follow the rule $\beta \rightleftharpoons \gamma$, $\alpha \rightleftharpoons \alpha$, which means they also obey the operation of the screw axis. Finally, as can be seen in Fig. 8, the asterisks follow the anti-twofold rotor.

This completes the proof.

3.4.1. Space-group $P6_3mc$. If the polytype belongs to this space group, then the X atoms taken alone must be compliant with the operations of the group, hence the CRZS must have at least an anti-twofold rotation (Patterson & Kasper, 1959; Iglesias, 2006*b*). However, if $P/2$ is odd, there is no way the M atoms could satisfy the operation of the 6_3 screw axis. Therefore (*cf.* Proposition 8),

$$N^{MX_2}_{P6_3mc}(P) = \begin{cases} 0, & P/2 \text{ odd} \\ \mathrm{ATF}(P/2), & P/2 \text{ even} \end{cases} \tag{30}$$

with $\mathrm{ATF}(P/2)$ as defined in equation (5). This function adequately counts as different polytypes Z and $\mathrm{Rev}(Z)$, except in those configurations belonging to point group $2'mm'$, where there is necessarily a BB-type mirror line (see Propositions 2–5), and the pair is degenerate (see §3.1).

As an example, for $P = 16$ there are 16 MX_2 polytypes belonging to space group $P6_3mc$:

88, 323323, 161161, 422422, 1411114111, 2121221212, 2112221122 & 21111112111111, which are all self-conjugate, and (413413, 431431), (251251, 152152), (1231112311, 1132111321) & (3112131121, 1121311213), which are pairs of conjugates.

3.4.2. Space groups $P\bar{3}m1$ and $R\bar{3}m$. We have seen (*cf.* Proposition 7) that centrosymmetric MX_2 polytypes exhibit a TT mirror line in their CRZS, and reciprocally. Hence we need to count those CRZS having a TT line of symmetry. For sphere stackings, that number is (Iglesias, 2006*a*)

$$\mathrm{tt}(p,q) = b(p,q) - \mathrm{bb}(p,q), \tag{31}$$

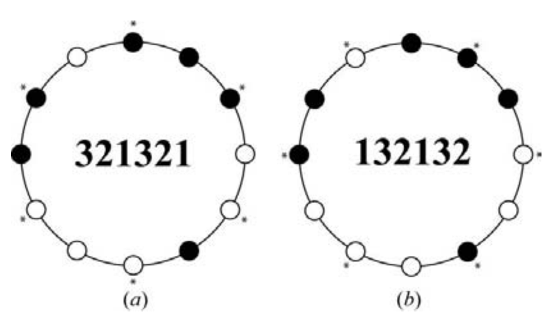

Figure 8
In an MX_2 polytype showing a $2'$ rotation in its CRZS and having $P/2$ even, the distribution of asterisks satisfies the operation of the anti-twofold rotor. Moreover, if this is the only symmetry of the CRZS, the polytypes corresponding to Zhdanov symbols Z and $\mathrm{Rev}(Z)$ are different. (Note that 132132 is the reverse of 321321; *cf.* Proposition 1.) If the symmetry group of the CRZS is $2'mm'$, the presence of m' guarantees that both Z and $\mathrm{Rev}(Z)$ will represent the same polytype, by virtue of Proposition 4.

where

$$b(p,q)=\sum_{d|(p,q)}\mu(d)\frac{([p/2d]+[q/2d])!}{[p/2d]![q/2d]!} \qquad (32)$$

and $[x]$ = integer part of x; $\mathrm{bb}(p,q)$ is the number of CRZS having at least a BB-type mirror line (Iglesias, 2006*a*).

When $p \neq q$, every CRZS having a TT line represents two different polytypes, corresponding to the direct and the reversed sequences; remember that reversing the sequence is equivalent to inverting the color (exchanging p and q) and shifting the asterisks by one dot. This means that one of the polytypes is counted when computing $\mathrm{tt}(p,q)$, and the conjugate when computing $\mathrm{tt}(q,p)$. Half-order subperiods of odd sum must be added (see above); but these configurations give, when repeated, symmetry $2mm$, with one of the mirror lines of the BB type and the other of the TT type, and hence only one distinguishable polytype is generated in each case, by virtue of Proposition 2. When $p = q$, the term $\mathrm{tt}(p,p)$ contains all cases, since color inversion is built-in. Putting all this together,

$$N^{MX_2}_{P\bar{3}m1}=\sum_{\substack{i=1\\3|(i-P/2)}}^{P-1}\mathrm{tt}(i,P-i)+(1-k(P/2))H_m(P/2), \qquad (33)$$

where,[7] again, $k(n)$ is as defined in (4) and $H_m(N)$ is the total number of hexagonal stackings of spheres for period N (Iglesias, 1981*a*) having a mirror line in the CRZS. Similarly, the rhombohedral centrosymmetric cases are

$$N^{MX_2}_{R\bar{3}m}=\sum_{\substack{i=1\\3\nmid(i-P/2)}}^{P-1}\mathrm{tt}(i,P-i)+(1-k(P/2))R_m(P/2) \qquad (34)$$

and the total number of rhombohedral stackings of spheres, having a mirror line in the CRZS, $R_m(P)$, can be found in Iglesias (1981*a*).

3.4.3. Space groups *P*3*m*1 and *R*3*m*. The number for the MX_2 polytypes belonging to these noncentrosymmetric space groups are obtained by difference:

$$N^{MX_2}_{P3m1}(P)=N^{MX_2}_{H}(P)-N^{MX_2}_{P6_3mc}(P)-N^{MX_2}_{P\bar{3}m1}(P) \qquad (35)$$

$$N^{MX_2}_{R3m}(P)=N^{MX_2}_{R}(P)-N^{MX_2}_{R\bar{3}m}(P). \qquad (36)$$

The results are tabulated to P = 100 in Table 3.

As a matter of example, the MX_2 polytypes for P = 8 are (enclosed in parentheses are conjugate pairs):

$P6_3mc$: 44 & 211211;

$P\bar{3}m1$: (71, 17) & (3212, 2123);

$R\bar{3}m$: (5111, 1115), (35, 53), (212111, 111212) & (311111, 111113);

$P3m1$: 3311 & 221111;

$R3m$: 62, 4121, (4211, 1124) & (3221, 1223).

And, for P = 10:

$P\bar{3}m1$: (7111, 1117), (5131, 1315), 4141, 55, 131131, 212212 & (232111, 111232);

$R\bar{3}m$: (91, 19), (73, 37), (511111, 111115), (212131, 213121), (313111, 111313), (3331, 1333), 3232, (5212, 2125), 11211121, (31111111, 11111113) & (21211111, 21111121);

$P3m1$: 82, 6121, (3421, 4213), 3223, 4411, 331111, 222211, (121132, 113212), 22111111 & 21121111;

$R3m$: (6211, 6112), (5221, 1225), (4231, 4132), (412111, 411121), 64, (5311, 1135), (4321, 4123), 4222, (421111, 411112), 212122, 121141, (322111, 211132), (321121, 123121) & (122131, 213112).

[7] The hexagonal cases require a sum over $i-(P-i)=2i-P\equiv 0\,(\mathrm{mod}\,P)\Rightarrow i\equiv P/2\,(\mathrm{mod}\,3)$, since $(2,3)=1$.

4. Concluding remarks

While trying to compute the numbers of different kinds of polytypes, we have needed to prove a few theorems, relating the symmetry group of the polytype with the two-color planar point group of the cyclotomic representation of the Zhdanov symbol (see Propositions 1–8 above). For these properties, we have found the extensive experimental literature on these materials to be quite incomplete, sometimes ambiguous and mostly inconclusive. For instance, we could find nothing on the symmetry of the Zhdanov symbol necessary to ensure that a conjugate pair is degenerate (Propositions 2–5), except, perhaps, the statement in Jain & Trigunayat (1977) that the structures represented by the direct and reverse sequences cannot be congruent unless 'the Zhdanov symbol has a symmetric arrangement of numbers'; but these authors do not bother to specify which kind of symmetric arrangement will work out (see Proposition 5). However, it must be said that this paper (Jain & Trigunayat, 1977) is the most important precedent the present author has found on the equivalence between the different representations (Zhdanov symbols) of a polytype, and it contains the all-important rules Z ⇎ ES(Z) and Z ⇎ OS(Rev(Z)). To aid in the comparison of that and the present paper, it must be said that these authors denote as 'literal reverse' of Z what we call Rev(Z), and by 'truly reversed' they mean what we denote by OS(Rev(Z)).

Finally, a comment on the numerical results of the enumeration is in order. The distribution of possible polytypes among the possible space groups has not been published before. The bulk numbers for both kinds of polytypes are, however, in McLarnan (1981), although in a different form, and obtained by application of a more sophisticated (and elegant) technique. It is then reassuring that two such different methods of counting should give the same results. The importance of so-called 'double counting' in combinatorial problems has been stressed by Cameron (1994). We believe our method will be of some interest for those people who do not intend to delve into the general theory devised by Pólya (1937; Pólya & Read, 1987) for counting sets in which there are elements equivalent under a permutation group. These people may appreciate the fact that this particular problem can be solved in an elementary way, which, being of a graphic nature, could presumably also be of help in the understanding of other related crystallographic problems. The interest in solving a problem by different methods is summarized in a sentence attributed to Pólya: 'It is better to solve a problem several ways, than solving several problems the same way'.

APPENDIX *A*

To find the commuting properties of the operators defined above, consider a Zhdanov symbol

$$Z = r_1 r_2 r_3 \ldots r_{k-1} r_k r_{k+1} \ldots r_{2n-1} r_{2n} \quad (37)$$

and apply successively the operators Rev and OS:

$$\mathrm{OS}[\mathrm{Rev}[Z]] = r_{k-1} \ldots r_3 r_2 r_1 r_{2n} r_{2n-1} \ldots r_{k+1} r_k, \quad (38)$$

where we are assuming that $\sum_{i=k}^{2n} r_i$ is an odd integer. We now apply the operators in reverse order:

$$\begin{aligned}\mathrm{Rev}[\mathrm{OS}[Z]] &= \mathrm{Rev}[r_k r_{k+1} \ldots r_{2n-1} r_{2n} r_1 r_2 r_3 \ldots r_{k-1}] \\ &= r_{k-1} \ldots r_3 r_2 r_1 r_{2n} r_{2n-1} \ldots r_{k+1} r_k \quad (39)\end{aligned}$$

since $\sum_{i=1}^{k-1} r_i$ can be seen to be also odd when we recall that the total number of layers in MX_2 polytypes must be even. Hence, OS and Rev are commuting operators, in the sense that, if there is an odd shift at all, OS_1, there can always be found an $\mathrm{OS}_2 = P - \mathrm{OS}_1$ such that

$$\mathrm{Rev}[\mathrm{OS}_1[Z]] = \mathrm{OS}_2[\mathrm{Rev}[Z]]. \quad (40)$$

With a similar argument, we can conclude that ES also commutes with Rev.

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