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Resolution of Ambiguities in Zhdanov Notation: Actual Examples of Homometric Structures

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Very often, ambiguities arise in deciding if two similar-looking Zhdanov symbols represent the same structure or two different structures. Starting from the concept of congruence of two structures, the effect of various symmetry operations on the crystal structure has been systematically analysed and the corresponding changes in Zhdanov symbol examined. Practical criteria have been evolved to decide quickly the congruence of two polytypic structures represented by similar-looking Zhdanov symbols. Pairs of structures in MX_2-type and MX-type polytypic compounds have been identified which are fundamentally noncongruent but give the same set of X-ray intensities on calculation. These have been identified as first-found practical examples of homometric structures. Semi-empirical rules have been formulated to obtain theoretically an infinite number of such pairs.

Introduction

Of the known systems of notation for close-packed structures, the Zhdanov notation is found to be the most suitable as it is compact and yet very informative of the crystal structure. Therefore, it is commonly employed for designating these structures and, in particular, polytypes with close-packed structures. Prominent, known polytypic substances with close-packed structures, for some of which more than 100 polytypes have been discovered, mostly fall under two main categories, *viz* MX_2-type (CdI_2, SnS_2, *etc.*) and MX-type (SiC, ZnS, *etc.*). An account of the polytypic substances and various notations used to describe them is available in a recent review (Trigunayat & Verma, 1976).

A survey of crystallographic work on polytypism (*e.g.* Trigunayat & Chadha, 1971; Prager, 1975; Pandey & Krishna, 1975) shows that often there has been confusion in deciding the identicality of two polytypic structures represented by similar-looking Zhdanov notations; *e.g.* whether the sets of similar-looking hexagonal structures 2321, 2123 and 3212, or, say, the rhombohedral structures $(31)_3$ and $(13)_3$, represent the same or different crystal structures, is not readily understood. *Prima facie* such symbols appear to represent the same structure as they differ merely in their starting points, but in reality this is not always true. The formulation presented in the next section aims at resolving such ambiguities efficiently and quickly.

Two structures which can be brought into coincidence by the operation of translation, rotation, inversion (assuming Friedel's law holds) or any combination thereof yield the same X-ray diffraction pattern and are regarded as congruent structures. We shall study the changes brought about in the Zhdanov symbol by the application of these symmetry operations on a structure and then deduce practical rules for quick identification of the equality or nonequality of the structures. We shall later discover that there exist pairs of structures which are found to be noncongruent but still happen to give the same set of X-ray diffraction intensities on calculation. These structures have been identified as homometric structural pairs and are possibly the first actual examples of such pairs.

Effect of symmetry operations on Zhdanov notation

Any rotation through $\pm 60°$ of a close-packed structure about an axis passing through one of the *A*, *B* and *C* sites and parallel to **c** results in the interchange of the remaining two sites. Any shift of the origin from the *A* site to the *B* or *C* site causes the anticyclic $B \rightarrow A \rightarrow C \rightarrow B$ or the cyclic $A \rightarrow B \rightarrow C \rightarrow A$ change, respectively (conventionally, the origin is taken as located at an *A* site). Thus the interchange of any two sites or the cyclic or anticyclic change of the three sites essentially produces a congruent structure. Note that while the *ABC* sequences of two such structures look different, their Zhdanov symbol necessarily remains unaltered.

The translation of the origin along **c** needs a rather proper understanding. We shall denote two structures simply as translationally congruent (TC) if they can be brought into coincidence by any combination of translation and *c*-axis rotation. It can be seen that in close-packed polytypic compounds of the MX_2-type a shift of the starting position by an even number of X layers in the *ABC* notation of the unit cell of an extended structure merely implies a shift of the starting position through the same number in the corresponding Zhdanov symbol.

The converse of this, *viz* if two Zhdanov symbols can be brought into coincidence by shifting the starting point in one of them by Zhdanov numbers whose sum is even (to be referred to as 'even shift'), the structures represented by them are congruent, is evidently true. On the other hand, the operation of shifting the origin by an odd number of X layers in the *ABC* sequence brings us to the top of an MX_2 sandwich, thus putting us in an unconventional* starting position for the representation in terms of Zhdanov symbol. Therefore a shift of the origin through an odd number of X layers in the *ABC* sequence of an MX_2-type compound does not lead to a corresponding 'odd shift' in the Zhdanov notation. Conversely, it can be seen that two Zhdanov symbols differing by an 'odd shift' in their starting points will not give congruent structures. Therefore, the hexagonal structures 1232 and 2321 or the rhombohedral structures $(31)_3$ and $(13)_3$ are not TC. We are thus led to the general criterion for close-packed MX_2-type compounds that two Zhdanov symbols are TC only if one is obtainable from the other by an 'even shift' (including zero shift) of the starting point. We shall refer to this as the TC-criterion in the following.

In MX-type compounds, however, since there are alternate layers of the same kind of atoms, a shift of the origin by any number of one kind of layers leads to a corresponding shift in the Zhdanov symbol and *vice versa*. Therefore, in this category of compounds, if two Zhdanov symbols differ merely in their starting points, they are TC. The same conclusion applies to substances with close-packing of only one kind of atoms.

Two structures which are related to each other by a centre of symmetry are called enantiomorphs. In close-packed polytypic crystals an inversion about a point lying on any one of the *A*, *B* and *C* sites simply inverts the whole stack of layers, with the positions of the remaining two sites interchanged. An inversion plus a ±60° rotation, therefore, reverses the *ABC* sequence of the polytype. The reversal of the whole stack can also be achieved by rotation through 180° about an axis lying in the basal plane, coupled with a further suitable translation and *c*-axis rotation. Thus, these structures are their own enantiomorphs. Two non-TC structures which become TC by inverting the stack of layers of one of them will be termed as reversibly congruent (RC). In representing the Zhdanov sequence of the reversed stack in MX_2-type compounds one has to take care of maintaining the convention of starting from an X layer that is immediately followed by an M layer. Consequently, in the following example one finds that the reversed sequence for the structure 2211 turns out to be not 1122 but 1221:

$$\begin{array}{c} \longleftarrow 2211 \longrightarrow \\ \ldots (A\gamma B)|(A\gamma B)\,(C\alpha B)\,(A\gamma B)|(A\gamma B) \ldots \\ \longleftarrow 1221 \longrightarrow \end{array}$$

The structures 2211 and 1221 are thus RC. Since the reversed sequence 1221 as obtained by us is different from the sequence 1122 resulting from a literal reversal of the original Zhdanov symbol, we shall refer to the former as a 'truly reversed' sequence, to distinguish it from the latter. One may similarly note that the 'true reverse' of the rhombohedral structure $(31)_3$ is not $(13)_3$ but $(31)_3$ itself. Therefore, the structures $(31)_3$ and $(13)_3$ are not RC as they *prima facie* appear to be. It is readily concluded that the practical rule for obtaining the 'truly reversed' symbol is: 'first write the literally reversed sequence and then rewrite it after deleting the digits whose sum is odd'. The examples in Table 1 will illustrate the point.

Table 1. *Obtaining the 'truly revised' sequence by the practical rule*

Zhdanov sequence	Literally reversed sequence	Truly reversed sequence
2123	3212	2123
$(31)_3$	$(13)_3$	$(31)_3$
11123211	11232111	12321111
31231112	21113213	11321321

Unlike in MX_2-type compounds, in MX-type compounds the reversal of the stack does not bring about the reversal of the Zhdanov symbol, as for instance, illustrated for the polytype 2431 in Fig. 1(*a*) and (*b*), which depict the sequence of atomic planes in the direct and reverse order respectively. Note that here the M layers are not symmetrically situated between the X layers. The reversed stack cannot be represented by a Zhdanov symbol according to the accepted convention.† Thus, unlike the MX_2-type compounds, there does not exist a Zhdanov symbol for the reversed stack of an MX-type compound. Consequently, in the MX-type compounds the direct and the reversed Zhdanov sequences, in general, represent different structures. The fact that these still happen to give the same set of intensities does not mean that they necessarily represent the same structures, as discussed in detail later in this paper. However, in substances which have close-packing of only one kind of atom, it may be readily examined that the direct and the reverse Zhdanov symbols do represent the same structure.

Conclusion (working rules)

To find if two Zhdanov sequences represent the same or different structures, one has simply to examine if they are TC or RC. If they are so, the two structures are congruent; otherwise they are noncongruent.

For close-packed MX_2-type structures two Zhdanov symbols are TC if one is obtainable from the other by an 'even shift' of the starting point, *i.e.* a shift through Zhdanov digits whose sum is even. For MX-type structures, two Zhdanov symbols are TC if one is obtainable from the other by any shift of the starting point.

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* The Zhdanov symbol of an MX_2-type structure is conventionally started with an X layer that is immediately followed by an M layer. The rationality of the convention is borne out by the fact that the representation of the structure is physically meaningful only when made in this manner, otherwise one has to start with an isolated X layer.

† Here the convention is to start with an M (or X) layer followed by an X (or M) layer situated at a fixed specified distance and having atoms at the same site (*A*, *B* or *C*) as the M (or X) layer.

For MX_2-type structures two Zhdanov symbols are RC if one is obtainable from the other by literally reversing the sequence plus rewriting it after an 'odd shift' of the starting point. For MX-type structures no two Zhdanov symbols are RC.

The total number of distinct structures for a polytype

In deriving the total number of possible structures for a given polytype, mistakes can be detected in the work reported by earlier investigators. Mitchell (1956) has listed just six possibilities for the CdI_2-polytype 8*H*, omitting two additional possible sequences 17 and 71. For a 10*H* polytype, he has listed only 15 possibilities, while actually the total number should be 22. Similarly the total number for a 12*H* polytype should be 66 while he has put it as 45.

Using the foregoing practical rules one can, in principle, figure out all the distinct possibilities for a given polytype. Indeed the rules can be used to carry out a computer program for obtaining the required information.*

Practical examples of homometric structures

Structures which are not congruent in the sense of being related by a rotation, a translation or an inversion or some combination of these, but give the same diffraction effects are called homometric structures. Attention was first drawn towards the possibility of non-unique determination of crystal structures by X-ray diffraction by the work of Pauling & Shappell (1930) on the mineral bixbyite. They arrived at two noncongruent structures by assigning the values $+u$ and $-u$ to the parameter governing the positions of atoms in the unit cell. The difficulty was overcome by discarding one of the arrangements which did not fit into a reasonable stereochemical configuration. Subsequently, Patterson (1944) has cited many theoretical examples of one-dimensional homometric sets and has extended them to two and three dimensions. Recently, Franklin (1974) has given a mathematical construction for many distinct arbitrary crystal structures all of which would give the same diffraction pattern. However, no practical example of homometric structures is known to date and it has been a common belief (*e.g.* Lipson & Cochran, 1966; Stout & Jensen, 1968) that the occurrence of homometric structures is extremely unlikely in actual practice. In contradiction to this belief we have identified several (theoretically, infinite) possible instances of homometric pairs in polytypic crystals.

We have already evolved the criteria for determining the congruence of two structures directly from their Zhdanov symbols. Let us apply them to the MX_2 structures 1121111222 and 2221111211. The two structures are, obviously, not TC. Further, the 'truly reversed' Zhdanov symbol of 2221111211 is 1211112221 which is not TC to 1121111222. Thus in no way are the two structures mutually congruent. However, the calculated intensities for the 10.*l* row of reflexions (which are sufficient for a complete structure analysis) for two CdI_2 structures represented by these symbols have been found to be the same. The same has been found to be the case with two corresponding PbI_2 structures. The two structures are, therefore, homometric. Many more noncongruent pairs, *e.g.* 22211221111211 and 11211112211222, 211112222211 and 112222211112, 4268 and 8624, 246224 and 422642, *etc.* have been verified to yield the same X-ray diffraction intensities. We have computed intensities for a large number of such structural pairs, whence we can conclude that there exist an infinite number of such pairs. Based on these computations, the following two empirical rules have been evolved for constructing such pairs.

A Zhdanov symbol consisting of only even digits and its literally reversed sequence would be either TC (which happens when the arrangement of Zhdanov numbers is symmetrical about one of the even digits or about the space between two successive digits) or else homometric. The structures 82 and 28, for example, are simply TC. The structure 82 has a symmetrical arrangement of numbers about both 2 and 8. On the other hand, the 'literal reverse' of 4268 is 8624. The latter is in no way congruent to 4268. Consequently, the structures 4268 and 8624 are homometric. The pairs 448866 and 668844, $(2246)_3$ and $(6422)_3$ and many more are further examples of homometric pairs of this category which have been verified by us as yielding the same values of X-ray intensities separately for cadmium iodide and lead iodide. It is obvious that an infinite number of such pairs can be postulated. Secondly, if the Zhdanov symbol of a structure consists of only 2's and pairs of 1's, then this structure and its literally reversed sequence are either TC (which again happens when the Zhdanov numbers are symmetrical as before) or else homometric. The pairs of structures 112221111112 and 211111122211, 112222111122 and 221111222211, *etc.* are the homometric pairs of this category which have been verified by us for the actual substances CdI_2 and PbI_2. But the symmetrical structures 2211 and 1122 are simply TC. Again, it is evident that an infinite number of homometric pairs can be postulated for this category, too.

In the light of the above discussion, it is easy to see that six of the known polytypic structures of CdI_2, reported to be uniquely determined, are actually not so, and each of them possesses an alternative structure. These structures are tabulated in Table 2. The last column gives the alternative possible structure corresponding to the structure in the preceding column. There exist, however, no homometric mates amongst the known PbI_2 polytypes.

Next we consider the MX-type compounds. For a SiC crystal, which may be taken as a representative example of this category, the intensities for 10.*l* re-

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* The tables of total numbers of distinct possibilities for polytypes up to 12*H* and 36*R* for close-packed MX_2-type structures can be obtained from the authors.

Table 2. *List of homometric structures for known polytypes of cadmium iodide*

No.	Polytype	Reported structure (Zhdanov symbol)	Alternative possible structure (Zhdanov symbol)
1	$20H_2$	$22(11)_2(2112)_2$	$(2112)_2(11)_2 22$
2	$26H_3$	$(222211)_2 2112$	$2112(112222)_2$
3	$30H_1$	$(2211)_4 1122$	$2211(1122)_4$
4	$30H_2$	$(22)_2(211)_2(22)_3 11$	$11(22)_3(112)_2(22)_2$
5	$30H_4$	$(22)_4 211222(11)_2$	$(11)_2 222112(22)_4$
6	$36H_1$	$(22)_2(22221111)_2(11)_2$	$(11)_2(11112222)_2(22)_2$

Table 3. *List of homometric structures for known polytypes of silicon carbide*

No.	Polytype	Reported structure (Zhdanov symbol)	Alternative possible structure (Zhdanov symbol)
1	$33H$	3333353334	4333533333
2	$69R_2$	$(43332233)_3$	$(33223334)_3$
3	$75R$	$[(32)_3(23)_2]_3$	$[(32)_2(23)_3]_3$
4	$90R$	$[(23)_4 3322]_3$	$[2233(32)_4]_3$
5	$120R_1$	$[32(22)_5 322233]_3$	$[332223(22)_5 23]_3$
6	$174R$	$[(33)_3 6(33)_5 4]_3$	$[4(33)_5 6(33)_3]_3$

flexions are given by (Verma & Krishna, 1966),

$$I_{10.l} \propto |F_{10.l}|^2 = (f^2_{\rm Si} + f^2_{\rm C} + 2 f_{\rm Si} f_{\rm C} \cos 2\pi l p)\,(A^2_{\rm Si} + B^2_{\rm Si})\,, \tag{1}$$

where $p=3/(4n)$ for a polytype nH or nR. Note that the above expression remains unchanged if the positions of carbon and silicon atoms are interchanged. Fig. 1(*c*) shows the sequence of atomic planes obtained after effecting such an interchange in Fig. 1(*b*). It may be emphasized here that although the structures shown in Fig. 1(*b*) and (*c*) give the same X-ray diffraction intensities according to (1) above, they cannot be brought into coincidence; therefore they are noncongruent. Further, since Fig. 1(*a*) and (*b*) represent congruent structures, the structures of Fig. 1(*a*) and (*c*) are also necessarily noncongruent, although they yield the same diffraction intensities. The Zhdanov sequence for Fig. 1(*c*) obviously has to be the reverse of Fig. 1(*a*). The same arguments hold for other close-packed MX-type compounds. The pairs of direct and the reverse sequences in such compounds thus generally represent pairs of homometric structures. Note that unlike the MX_2-type compounds, this conclusion here is not empirical but perfectly general.

Sometimes it has been concluded (Verma & Krishna, 1966, p. 168) that the direct and the reverse Zhdanov symbols in MX-type compounds represent the same structure because of Friedel's law. Actually, as we have seen above the structures represented by the direct and the reverse sequences cannot be brought into coincidence by any combination of translation, rotation and inversion unless, of course, the Zhdanov symbol has a symmetrical arrangement of numbers, so that the reverse sequence is simply TC to the direct sequence. The equality of intensity values for the direct and the reverse structures essentially results from the symmetrical form of (1). If Friedel's law were operative here, the two structures should have turned out as congruent to one another, which is not found to be the case. The structural pairs 5423 and 3245, 8723 and 3278, *etc.* are examples of homometric pairs of this category. The symmetrical structures like 2233 and 3322 are simply TC and, therefore, not homometric. Obviously, there exist an infinite number of possible homometric pairs in this class as well. The list of homometric structures in the known polytypes of SiC is presented in Table 3.

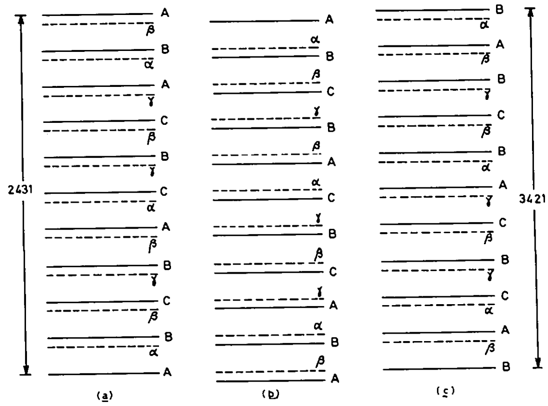

Fig. 1. The sequence of atomic planes in MX-type compounds (*a*) for the polytype 2431, (*b*) after reversing the stack and (*c*) after interchanging in (*b*) the positions of the M and X layers, which have been denoted by continuous and dotted lines respectively.

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