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Homometrism in Close-Packed Structures

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Abstract

Homometric structures are non-congruent structures having identical X-ray intensity distributions. It has so far been assumed that such structures, while theoretically interesting, would not be realized in practice. Homometrism in close-packed structures is shown to be a realistic possibility. Some general rules applicable to homometric pairs are presented; it is shown that an infinite number of them can be derived from one-dimensional homometric pairs. An exhaustive search of close-packed structures with periods of up to 26 reveals that the smallest period of a homometric pair is 15 and that their number increases rapidly with the period. Homometrism in polytypic structures is further discussed.

Introduction

The term 'homometric pair' was introduced by Patterson (1939, 1944) to denote two non-congruent structures having the same set of distances $\mathbf{r}_i - \mathbf{r}_j$ $(i, j = 1, \ldots, N)$, where N is the number of atoms in the unit cell and $\mathbf{r}_i$ is the coordinate vector of the ith atom. As X-ray intensities depend on the distance $\mathbf{r}_i - \mathbf{r}_j$ and not on the individual $\mathbf{r}_i$'s, the two members of a homometric pair will have the same set of intensities even though they are not congruent structures. Two structures are considered to be congruent if they can be brought into coincidence by a combination of translation, rotation and reflection operations. Patterson (1944) discusses in some detail the characteristics of homometric structures consisting of one type of atom in one, two and three dimensions and gives a large number of examples of such structures. Patterson's work made it clear that the information included in X-ray intensity sets is not sufficient in all cases to determine a structure uniquely. As a consequence, X-ray structure determination must be followed by an examination of possible homometric structures and, if found, other methods must be utilized for a unique structure determination.

In the years following Patterson's publication, the importance of the possible ambiguities associated with X-ray structure determination was played down. Lipson & Cochran (1966) quote Robertson's conclusion that the chance of finding homometric pairs is small and, even if discovered, it would be unlikely that both would present structures that are chemically possible. Stout & Jensen (1968) referring to homometric sets state: 'Although of theoretical interest, these are exceedingly unlikely to appear in practice and do not pose a real difficulty'.

In their discussion of homometric pairs in close-packed structures, Jain & Trigunayat (1977) point out that, in structures based on the closest packing of spheres where each sphere is replaced by more than one atom, two identical stacking sequences may under certain conditions constitute a homometric pair. This type of homometrism cannot exist in close-packed structures of only one kind of atom.

In the above case of homometrism, the two members of the pair are simply related to one another and both have the same stacking sequence of layers, a property important for many investigations in close-packed structures. It turns out that a much more bothersome case of homometrism can take place in close-packed structures where structures with two *different* stacking sequences, which are not simply related, are found to be homometric even when they consist of one kind of atom. This type of homometrism is a property of the closest packing of spheres in three dimensions.

The closest packing of spheres: characterization and notations

A detailed discussion of the symmetry and notations of close-packed structures is given by Patterson & Kaspar (1959). We shall here present and expand those aspects which are directly relevant to this manuscript.

A three-dimensional closest packing of spheres consists of planar layers of spheres arranged in hexagonal arrays, the layers are stacked one on top of another with an interlayer spacing of c_0. In a hexagonal coordinate system with the unit vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{c}_0$, the position of each layer with respect to its neighboring one is given by either $\mathbf{c}_0+(\mathbf{a}_1-\mathbf{a}_2)/3$ or $\mathbf{c}_0-(\mathbf{a}_1-\mathbf{a}_2)/3$. In the first case the layer is said to follow its preceding one in a cyclic order and in the second case in an anti-cyclic order.

In the classical notation, an arbitrary layer in the stacking sequence is denoted as an '*A*' layer, a layer following it in a cyclic order as a '*B*' layer and one that follows in an anti-cyclic order is denoted a '*C*' layer. For example, in the stacking *ABCAB*... all layers are stacked in a cyclic order and in *BACBA*... all are in an anti-cyclic order.

While there are three possible layer positions, *A*, *B* and *C*, there are only two possible relative positions of a layer in relation to its preceding one: cyclic and anti-cyclic. Hägg (1943) denotes them respectively by + and − so that a stacking sequence is specified by the sequence of relative layer positions, *e.g.* −+++−−−++... denotes the sequence *BABCACBABC*....

A notation introduced by Pauling (1945) is based on the relation of a layer's two nearest neighbors; they can be either of the same type, such as for *B* in *ABA*, or of different types, as for *B* in *ABC*. The two nearest neighbors are of the same type for a hexagonal or '*h*' layer and of different types for a cubic '*c*' layer. A stacking sequence can thus be represented as a sequence of *h* and *c*, *e.g.* *hcchcch*... for the sequence given above.

A concise representation of both Hägg's and Pauling's notations was introduced by Zhdanov (1945). A stacking sequence is given by a sequence of numbers: in terms of Hägg's notation each number represents the number of +'s or −'s in a consecutive sequence of these symbols, while in terms of Pauling's notation each number represents the distance (in units of c_0) of an *h* layer to the following *h* layer. For example, ...2 3... represents the two identical sequences ...(−)++−−−(+)... and ...*hchcc*(*h*)...; the number of layers represented by a group of Zhdanov elements is equal to the sum of the elements. The Zhdanov notation of close-packed structures is the most convenient notation for many applications; while the notation is not confined to periodic structures we shall use it here to represent only such structures. The number of elements in the Zhdanov symbol of a periodic stacking sequence must be an even number equal to the number of hexagonal layers in the period of the structure. The basic period of the Zhdanov elements is not necessarily equal to that of the unit cell (as represented by the *ABC* sequence). The two periods are equal only for non-rhombohedral structures whereby the basic period of the Zhdanov elements of a rhombohedral structure is equal to 1/3 that of the unit-cell period. For example, the structure |*ABCACABCBCAB*|*AB*... is a rhombohedral structure with a period and thus a unit cell of 12 layers; its Zhdanov symbol is 3 1 3 1 3 1... with a period of 4. In order to maintain uniformity we shall henceforth refer to the period *M* of a structure as that of the basic period of its Zhdanov symbol and not to the true period of its unit cell; the structure in the above example will therefore be denoted as 3 1 and not the commonly accepted form $(3\ 1)_3$.

The elements of the Zhdanov symbol can be divided into two groups: elements in the odd positions and those in the even positions. Each group represents layers stacked with the same type of transition. The elements in the odd and even positions will represent layers with cyclic and anti-cyclic transitions, respectively; reversing the cyclicity of these two groups would give a congruent structure. The sums of the elements in the odd and even positions will be respectively denoted by *I* and *J*, which are the numbers of + and − symbols in Hägg's notation; clearly $I+J=M$.

In all notations discussed so far there is no unique representation of a set of congruent structures. There are a number of ways in which such a unique representation can be introduced, the one which we shall adopt here was found to be convenient for many applications.

The first layer in the notation of a structure will be selected to represent a hexagonal layer (the cubic structure *ABCABC*... is the only exception); this layer will be denoted as an '*A*' layer, the second layer will be selected as a '*B*' layer. With these two requirements, the Hägg notation will always start with a group of +'s and end with a group of −'s, the elements of the Zhdanov symbol in the odd and even positions will respectively represent layers in cyclic and anti-cyclic order. We shall further require that $I \geq J$.

While the above agreement reduces the number of possible notations for a set of congruent structures it is still not unique. For example, the structure 4 3 2 1 can also be represented as 4 1 2 3, 2 1 4 3 and 2 3 4 1. In order to select a unique representation, we shall view the elements of a Zhdanov symbol as the digits of a base M number. This number is defined as the 'value' of the Zhdanov symbol; the values of the above symbols for which $M = 10$ are therefore the numbers (base 10) 4321, 4123, 2143 and 2341. The Zhdanov symbol with the highest value is selected to represent the set of congruent structures. As examples let us first consider the set of congruent structures 5 6 1 2 3 1, 1 6 5 1 3 2, 3 1 5 6 1 2 *etc.* For this set, $I = J = 9$ and the representative symbol will be 6 5 1 3 2 1. For the set 5 6 1 1 3 1, 1 6 5 1 3 1, 3 1 5 6 1 1, *etc.*, $I = 9$, $J = 8$. As I has to be larger than J the representative symbol will be 5 6 1 1 3 1 (not 6 5 1 3 1 1).

Homometric pairs in close-packed structures

Patterson (1944) discusses in detail periodic distributions of points on a line and states a number of theorems related to such distributions. For a set P of p points on a period divided into M equal parts, Patterson defines the complementary set P_c as the set of the $M - p$ points which are not occupied by members of P. A theorem which was later proved by Buerger (1977) states that if P and P' are homometric then P_C and P'_C will also be homometric.

Let us now associate an atom A with an f factor f_A with each of the p points of the set P and an atom B with an f factor f_B with each of the points of P_C. The absolute value of the structure factor can then be written as

$$|F_{hk.l}|^2 = f_A f_A S_{AA} + f_B f_B S_{BB} + f_A f_B S_{AB},$$

where

$$S_{AA} = \sum_A \sum_A \exp 2\pi i \, \mathbf{h}.(\mathbf{r}_s - \mathbf{r}_t)$$

$$S_{BB} = \sum_B \sum_B \exp 2\pi i \, \mathbf{h}.(\mathbf{r}_s - \mathbf{r}_t)$$

$$S_{AB} = \sum_A \sum_B \exp 2\pi i \, \mathbf{h}.(\mathbf{r}_s - \mathbf{r}_t),$$

where the $(\mathbf{r}_s - \mathbf{r}_t)$ are the vector distances; $\mathbf{h} = \sum h_k \mathbf{b}_k$, where the $\mathbf{b}_k$ are the reciprocal-lattice vectors and h_k the Miller indices. In S_{AA}, the summation is over the A atoms, in S_{BB} over the B atoms and S_{AB} includes the mixed terms. Clearly, $S_{AA} + S_{BB} + S_{AB} = S$, where S denotes the sum over all points in the period irrespective of which atom occupies them. Assume now that the sets P and P' form a homometric pair, the complementary sets P_c and P'_c will also form a homometric pair and therefore $S_{AA} = S'_{AA}$ and $S_{BB} = S'_{BB}$ but then we must also have $S_{AB} = S'_{AB}$, which leads to the conclusion that two sets including two types of atoms will be homometric if a subset of one structure including one type of atom is homometric to the subset of the other set including the same atoms.

We can now replace the atoms A and B by two different three-dimensional molecules where the f's will now denote the molecular structure factors - the above conclusion will still hold. Applying the conclusion to close-packed structures we can start with a one-dimensional homometric pair, say 5 4 1 2 3 1 and 4 1 3 5 2 1 (Patterson, 1944); in this example $M = 16$ and $p = 7$. The above notation of the homometric pair (no relation to the Zhdanov symbol!) gives consecutively the number of occupied and missing points in the arrangement; thus the first arrangement consists of five occupied points, four missing, one occupied, two missing *etc.* Now let us assign to each occupied point the group of layers *ABC* and to each unoccupied point the group *ACB*. The first arrangement will therefore be represented by the *ABC* sequence *ABCABCABCABCABC ACBACBACBACB ABC ACBACB ABCABCABC ACB*, which has the Zhdanov symbol 15 12 3 6 9 3 and the other member of the homometric pair is 12 3 9 15 6 3. These two close-packed structures are non-congruent and homometric and indeed have the same set of X-ray intensities.

The two groups of layers substituted for the sets P, P' and P_c, P'_c can be selected in an arbitrary way as long as both include the same number of layers and as long as the first letter of each is different from the last letter of both, *e.g.* *ABCAC* and *ACBAB* is a permissible pair. The first condition ensures correspondence to equal distances on the linear arrangements of points and the second condition ensures that no two neighboring layers in the close-packed structure will be of the same type. Starting from any linear homometric pair, one can create an infinite number of close-packed pairs with the two members of each pair being either congruent or homometric.

The method described above of constructing close-packed homometric pairs does not exhaust all such pairs. Some general properties and examples of other forms of homometric pairs in such structures will be given in the following section.

Distance-distribution arrays and homometric pairs

There are three types of distance vectors possible in a close-packed structure; they will be denoted by

$$\mathbf{d}_k = k\mathbf{c}_0, \qquad \mathbf{d}_k^+ = k\mathbf{c}_0 + (\mathbf{a}_1 - \mathbf{a}_2)/3,$$

$$\mathbf{d}_k^- = k\mathbf{c}_0 - (\mathbf{a}_1 - \mathbf{a}_2)/3 \qquad (k = 0, \ldots, M-1)$$

The number of the $\mathbf{d}_k$, $\mathbf{d}_k^+$ and $\mathbf{d}_k^-$ vectors in a basic period will be denoted respectively by N_k, N_k^+ and N_k^-.

Some simple relations hold between the N_k's and the Zhdanov elements of a given structure:

$$N_k + N_k^+ + N_k^- = M;$$

$$N_0 = M; \qquad N_0^+ = N_0^- = 0;$$

$$N_1 = 0; \qquad N_1^+ = I; \qquad N_1^- = J;$$

$$N_2 = M_h,$$

where M_h is the number of hexagonal layers in the period, which is also the number of Zhdanov elements in the basis period;

$$N_2^+ = M - I - M_h/2; \qquad N_2^- = M - J - M_h/2;$$

$$N_3 = M - 2M_h + n(1),$$

where $n(1)$ is the number of 1's in the Zhdanov symbol. The following relations hold for non-rhombohedral structures:

$$N_{(M-1)} = N_{(M-1)}^- = 0; \qquad N_{(M-1)}^+ = M;$$

N_k is a symmetric array, namely $N_k = N_{(M-k)}$;

$$N_k^+ = N_{(M-k)}^-.$$

For rhombohedral structures with $I - J = 1 (\mathrm{mod}\ 3)$:

$$N_{(M-1)}^+ = N_{(M-1)}; \qquad N_{(M-1)}^- = M;$$

$$N_k^+ = N_{(M-k)}^+; \qquad N_k^- = N_{(M-k)}.$$

For rhombohedral structures with $I - J = 2 (\mathrm{mod}\ 3)$:

$$N_{(M-1)}^- = N_{(M-1)}^+ = 0; \qquad N_{(M-1)} = M;$$

$$N_k^- = N_{(M-k)}^-; \qquad N_k = N_{(M-k)}^+.$$

It should be stressed that the above relations hold only if the convention given in the previous section for the presentation of the Zhdanov symbol is adopted.

As a consequence of the above relations, the two members of a homometric pair must be of the same type: non-rhombohedral, rhombohedral with $I - J = 1$ (mod 3) or rhombohedral with $I - J = 2$ (mod 3). They also have to have the same values of M, M_h, I, J and $n(1)$.

An exhaustive search for homometric pairs in close-packed structures with $M \leq 26$ was facilitated by these restrictive conditions and by the interrelations given above. It was found that no homometric pairs exist with $M < 15$.

For $M = 15$ there are two homometric pairs: 3 2 3 1 2 2 1 1, 3 2 2 1 3 1 1 2 and 3 1 2 2 1 1 2 1 1 1, 3 1 2 1 1 1 2 2 1 1.

There is one pair with $M = 16$: 3 1 2 3 1 1 2 1 1 1, 3 1 2 1 1 1 2 3 1 1.

There are three pairs with $M = 17$: 3 1 2 3 1 1 2 2 1 1, 3 1 2 2 1 1 2 3 1 1; 3 2 3 1 2 2 1 1 1 1, 3 2 2 1 3 1 1 1 1 2 and 3 1 2 4 1 1 2 1 1 1, 3 1 2 1 1 1 2 4 1 1.

Table 1 gives the number of homometric pairs found in the range $15 \leq M \leq 26$ and the total number of different structures for each M.

Table 1. *Homometric pairs in close-packed structures with periods of* 15 *to* 26

Period	Number of pairs	Number of structures
15	2	607
16	1	1115
17	3	2055
18	8	3886
19	9	7154
20	22	13 631
21	46	25 472
22	58	48 671
23	51	92 204
24	131	176 862
25	107	337 590
26	230	649 342

Table 2. *All homometric pairs found in close-packed structures with* $M = 48$, $M_h = 6$, $I = 27$, $J = 21$, $n(1) = 0$

(1)	12 15 3 3 12 3 21 12 3 3 3 6	(2)	18 6 6 12 3 3 15 12 3 6 9 3 12 3 9 15 6 3
(3)	21 9 3 6 3 6 18 12 3 6 6 3	(4)	18 11 6 2 3 8 15 13 9 6 3 2
(5)	18 10 6 7 3 4 12 14 6 3 9 4	(6)	18 10 6 4 3 7 12 14 9 3 6 4
(7)	18 9 6 3 3 9 15 12 3 3 9 6	(8)	18 12 3 3 6 6 12 15 9 3 6 3
(9)	15 9 9 6 3 6 12 12 9 3 6 6	(10)	15 9 6 9 6 3 12 12 6 6 9 3

There exists the possibility that a structure with a period M will be homometric to a structure M' where M is divisible by M'; these structures were therefore included in the search and are counted in Table 1; such homometric pairs were not found in our search.

None of the pairs found in the above range of M can be derived from a linear set of points by the method described in the previous section; such pairs are however found for larger values of M. As an example we list in Table 2 all close-packed homometric pairs in the subset $M = 48$, $M_h = 6$, $I = 27$, $J = 21$, $n(1) = 0$.

Group 2 is an example of a homometric triplet which can be derived from a linear triplet; the pairs 1, 3, 7, 8, 9 and 10 can be derived from linear homometric pairs while 4, 5 and 6 cannot.

While the number of homometric pairs increases rapidly with M, it seems that the density of these pairs decreases. The distribution of the pairs among the various values of I, J and $n(1)$ is highly non-uniform with no clear pattern.

Structures based on the closest packing of spheres

ZnS, SiC and CdI_2 are examples of structures based on the closest packing of spheres, where each sphere is replaced by the same group of atoms with identical spatial orientations. The various structures of a given material are known as polytypes and are quite common, hundreds of them have already been identified, their periods can reach values of up to tens of layers.

The former conclusions related to close-packed homometric structures apply directly to such polytypes.

The Zhdanov symbol of a close-packed structure may, in some cases, depending on the symmetry of the structure, define a direction along the *c* axis, *e.g.* the structure 1 2 3 4 has the opposite direction to 4 3 2 1; on the other hand, 1 2, 1 2 3 2 or 1 2 3 4 3 2 do not define such a direction. The group of atoms replacing each sphere may also define a direction along the *c* axis, *e.g.* the Si and C atoms in SiC can have two opposite orientations in each of the closest-packing-of-spheres configurations while the two Si atoms replacing a sphere in a silicon crystal do not define a direction along the *c* axis of the crystal. In those polytypes where both orientations, structural and molecular, can be defined, inverting one direction leads to a structure which is non-congruent to the original but has the same set of X-ray intensities. A pair of homometric structures thus exists, as noted by Jain & Trigunayat (1977). This type of homometrism is superimposed on the structural homometrism of the closest packing of spheres.

There is, for example, a homometric *quadruplet* of ZnS polytypes derived from the close-packed homometric pair 18 10 6 7 3 4, 12 14 6 3 9 4 mentioned before, but there can be only a homometric *pair* of such silicon polytypes.

Discussion

It was stated (Lipson & Cochran, 1966) that if a homometric pair of structures is found it would be unlikely that both members of the pair would represent structures that are chemically possible. The various structures of a compound based on the closest packing of spheres are all chemically identical and thus the members of homometric pairs of these compounds are chemically indistinguishable. It seems that other properties will be similar for both members of a pair: the free energy for example depends mostly on the distribution of the distance vectors which is common to both members. The energy gap and birefringence depend on N_2/M, common to both pair members (Brafman & Steinberger, 1966) and therefore cannot be used to discriminate between them. A way to identify a member of a homometric pair can be envisioned if we notice that the products of martensitic transformations of the two members of a pair will most probably be non-congruent and not homometric.

As a working example let us assume that a ZnS polytype is identified as either one of the two members of the homometric pair 7 4 2 1 3 1 2 4, 5 5 5 1 2 3 2 1. Martensitic transformations in ZnS in the vicinity of room temperature take place in such a direction as to eliminate neighboring hexagonally stacked layers (Mardix, 1986*a*). The product of a martensitic transformations in the above structures will therefore be either 7 4 6 1 2 4 or 7 4 9 4 for the first member of the pair and either 8 5 5 1 2 3 or 8 5 8 3 for the second member. The two possible products of the first member are neither congruent nor homometric to either of the products of the second member. Identification of the transformed structure by regular X-ray methods will unequivocally determine the correct structure of the parent polytype.

The task of structure identification of close-packed structures with large unit cells can be quite complicated and a number of techniques have been employed to deal with it (Mardix, 1986*b*). The main methods are:

(*a*) Trial and error (Verma & Krishna, 1966). A structure with a 'good' fit between its experimental intensities and the calculated ones for a specific stacking order is selected as the identified structure. The method is not expected to discover the existence of homometric pairs. Most SiC and CdI_2 polytypes were identified by this method.

(*b*) The direct method (Tokonami & Hosoya, 1965; Dornberger-Schiff & Farkas-Jahnke, 1970). The set of experimental X-ray intensities is utilized to identify the distance-distribution arrays from which the correct structure is found. This method can detect homometric structures when they are found. However, owing to experimental inaccuracies in intensity measurements, the method is not effective for practical application. Only a few reported polytypes were identified by this method.

(*c*) The elimination method (Mardix, Kalman & Steinberger, 1970). The parameters M, M_h, I, J and $n(1)$ are identified and all structures with this set of parameters are checked for possible fit of their calculated intensity distribution to the experimental one. Homometric structures have the above as common parameters and will therefore be detected. Almost all of the reported ZnS polytypes (Mardix, 1986*a*) were identified by this method.

No ZnS homometric pairs have been so far found. It has already been mentioned that neighboring hexagonal layers constitute an unstable configuration in ZnS structures; as a result it is rare to find a ZnS polytype with $n(1) \neq 0$. However, for most homometric pairs with small periods, $n(1) \neq 0$. As a matter of fact, there are no homometric pairs with periods smaller than 26 for which $n(1) = 0$ and there are only two such pairs with a period of 26 out of 230 pairs. There are only about 30 ZnS identified polytypes with periods larger than 26 (Mardix, 1986*a*). As there has so far been no special effort to discover such homometric pairs, it is not surprising that none have been found.

It should be noted that once a structure is identified the subset within which a homometric pair can be found becomes known. It is therefore suggested that structure identification by the trial-and-error method should be followed by a full search for homometric pairs within the appropriate subset.

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A Method for Calculating Bond Valences in Crystals

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Abstract

A method of calculating the expected bond valences from the connectivity matrix of complex crystals is described. The method is exact (does not require iteration) and is suitable for implementation on a microcomputer.

Introduction

A major advance in inorganic solid-state chemistry has been the development of the bond valence method for predicting and interpreting bond lengths in crystals. In this method valences are assigned to each bond in the crystal and then, from known correlations (Brown & Altermatt, 1985; Brese & O'Keeffe, 1990) between bond valence and bond lengths, the expected bond lengths can be calculated. Alternatively, observed bond lengths can be interpreted in terms of valences. The method, and its historical development, is now well documented (*e.g.* Brown, 1981; O'Keeffe, 1989) and its advantages over other methods (such as using sums of radii) for predicting bond lengths in crystals are well established. This paper is concerned with an algorithm for implementing the method for predicting bond lengths in complex crystals.

The discussion here is restricted to crystals in which there are bonds only between 'cations' and 'anions' (named as such merely for convenience). Let there be m crystallographically distinct cations and n crystallographically distinct anions. Then we recognize the possibility of there being as many as mn kinds of bond, each of which may, in principle have a different valence.

The sum of the individual valences (v) of the bonds from each atom must be equal to the total atom valence (V), so there will be $m+n-1$ independent sums of the sort

$$\sum_j v_{ij} = V_i. \qquad (1)$$

However, if we had mn bonds there would be $mn-m-n+1=(m-1)(n-1)$ degrees of freedom remaining. It may be seen then that, for $m, n>1$, in general bond valence sums do not suffice to determine individual bond valences.

A solution to this problem was proposed by Brown (1977) who suggested that individual valences should be made as nearly as possible equal to each other, subject to the bond valence constraints. Brown developed an iterative method to implement this idea and showed that bond lengths predicted were generally in excellent agreement with those observed. Brown (1987) also remarked that it should be profitable to pursue the apparent similarity (Mackay & Finney, 1973) of a bond valence network to electrical circuits to which Kirchhoff's laws may be applied. This analogy is somewhat misleading (O'Keeffe, 1989); nevertheless the idea is very fruitful and leads to an algorithm for direct computation of valences in complex crystals which overcomes the

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