

Bedeutung zuzukommen als ihre formale Definition erkennen lässt.

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Topological Analysis of Crystal Structures

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Abstract

Topological analysis of crystal structures is used for studying the topological symmetry of complex ionic compounds. Such analysis can show either that the topology of the arrangement will not allow the structure to be described in a more highly symmetric space group or that the crystalline arrangement would allow a higher symmetry. In the first case the analysis gives a proof that the structure is already described in the

highest admissible space group. In the second case the diffraction evidence must be evaluated in order to ascertain whether or not a higher space-group symmetry is actually realized. A topological analysis of various complex compounds shows that a distinction should be made between those which are only topologically complex and those which are both topologically and geometrically complex. Pauling's rule V, the rule of parsimony, is shown to be of limited value in its application to complex ionic compounds.

Introduction

Topological analyses of crystal structures are useful for detecting similarities or differences between them. They can be of help in classifying structures of different symmetries and stoichiometries. For example, when the structure of cubic SiP_2O_7 was solved (Tillmanns, Gebert & Baur, 1973) the question arose whether or not the cubic phase was simply a highly symmetric version of one of the monoclinic polymorphs of SiP_2O_7 . The question could be answered by describing all three forms as three-dimensional nets (Wells, 1977, 1979). Since cubic SiP_2O_7 was found to be based on a net consisting entirely of 5-gons while the monoclinic forms are composed of 4-, 5- and 6-gons the monoclinic phases cannot be lower-symmetry distortions of the cubic structure. On the other hand, cubic SiP_2O_7 is based on the same type of net as SiP_2 ; that is, it has the same topology. Both structures share the topology of the pyrite-type net (Wells, 1977).

Another potential application of topological analysis lies in the checking of structures of low symmetry for the possible presence of higher symmetries. Marsh & Schomaker (1979), Herbstein & Marsh (1982) and Marsh & Herbstein (1983) have shown that a surprisingly large number of recent crystal structure determinations were performed in space groups of unnecessarily low symmetry. Many of the cases discussed by these authors involve the assumption of a wrong Laue group, a case which does not reveal itself by singularities in the least-squares refinement. A thorough topological analysis of a low-symmetry structure can give an indication whether or not the topology of the structure would admit of a higher symmetry. If the topology does not allow a higher symmetry the case is settled. Otherwise one has to search the diffraction data for evidence of the occurrence of a more highly symmetric space group.

Topological analysis of crystalline environments

Based on single-crystal and X-ray powder patterns O'Bryan, Grodkiewicz & Bernstein (1980) reported for $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ a monoclinic cell with a possible space group $P2_1/m$ and $a = 14.815$ (5), $b = 14.283$ (6), $c = 7.109$ (2) Å, $\beta = 98.37$ (7)° and $V = 1488.6$ Å³. The crystal structure of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ was recently solved and found to be triclinic in space group $P1$ with $a = 7.471$ (1), $b = 14.081$ (2), $c = 14.344$ (2) Å, $\alpha = 89.94$ (2), $\beta = 79.43$ (2), $\gamma = 84.45$ (2)° and $V = 1476.2$ Å³ (Tillmanns, Hofmeister & Baur, 1983). The residual for 3301 observed reflexions is $R = 0.03$. No obvious relationship between the two different sets of cell constants was found. Was the relationship overlooked and is the structure of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ not truly triclinic?

The structure consists of hexagonally closest packed layers of Ba and O atoms stacked in the sequence $(hch)_3$ along \mathbf{b}^* . All the Ti atoms reside in octahedral interstices of this closest packing. The various Ti coordination octahedra share only corners and edges with each other; face sharing does not occur. One half of the Ba atoms are twelve coordinated by O atoms, the other half are eleven coordinated. The eleven coordination is caused by one O-atom vacancy located between a pair of Ba atoms in the same row of the close-packed arrangement. The 40 crystallographically independent O atoms in the unit cell are three- to five-coordinated by Ba and Ti atoms. Because of the varying numbers of contacts of the O atoms to each of the three types of cations ($\text{Ba}^{[11]}$, $\text{Ba}^{[12]}$, $\text{Ti}^{[6]}$) there are at least eleven topologically different O atoms present in $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ (see Table 1). One could try to analyze the topology of this structure in terms of a net description. However, nets with many 12-, 11- and 6-connected nodes would be unwieldy.

Therefore we began by studying just one type of nodes, namely the ones at the Ti atoms. In Table 2 we list the types of O atoms (as defined in Table 1) surrounding each of the Ti atoms. We see that there are 15 different Ti-atom environments present in $\text{Ba}_2\text{Ti}_9\text{O}_{20}$. Twelve of the Ti atoms are unique in each having different numbers and types of O atoms which surround them. Three arrangements occur in topologically equivalent pairs: Ti(2) with Ti(5), Ti(3) with Ti(4), and Ti(8) with Ti(16). We call two Ti coordination octahedra topologically equivalent when all of their coordinating O atoms have themselves identical coordination environments. The correspondence can be either direct or by enantiomorphism. We could have distinguished in addition the relative spatial orientations of the cations around the O atoms or else

Table 1. *Coordination environments of the eleven different O-atom types in $\text{Ba}_2\text{Ti}_9\text{O}_{20}$*

Also given are the coordination numbers (CN), the sums of bond strengths at the O atoms [$p(\text{O})$: Pauling (1929); Baur (1970)] and the mean O—Ti distances from the O atoms to their surrounding Ti atoms.

Label	Number of such atoms	Number of neighbors			CN	$p(\text{O})$ (v.u.)	$(\text{O}-\text{Ti})_{\text{mean}}$ (Å)
		Ti	$\text{Ba}^{[11]}$	$\text{Ba}^{[12]}$			
A	3	2	0	1	3	1.500	1.839
B	1	2	1	0	3	1.515	1.832
C	5	2	0	2	4	1.667	1.892
D	5	2	1	1	4	1.682	1.869
E	1	2	1	2	5	1.848	1.884
F	7	3	0	0	3	2.000	1.969
G	2	3	0	1	4	2.167	1.982
H	12	3	1	0	4	2.182	2.012
I	1	3	1	1	5	2.348	2.017
J	1	4	0	1	5	2.833	2.121
K	2	4	1	0	5	2.848	2.115

Table 2. Ti-atom environments in $Ba_2Ti_9O_{20}$ characterized by the different kinds of O atoms coordinating them

The labels of the O-atom types are defined in Table 1.

		O-atom types						
Ti(1)	A		D	F	3H			
Ti(2)				2F	4H			
Ti(3)			D	2F	3H			
Ti(4)			D	2F	3H			
Ti(5)				2F	4H			
Ti(6)	2A		D		3H			
Ti(7)	A		D	F	2H	I		
Ti(8)				3F	3H			
Ti(9)				F	G	2H		2K
Ti(10)	A	C			2G		J	K
Ti(11)		2C	2D	E			J	K
Ti(12)	B	C			G	H	J	K
Ti(13)		2C	D	E	G		I	
Ti(14)	B	2C			G	H		K
Ti(15)		C	2D		F	H	I	
Ti(16)					3F	3H		
Ti(17)					2F	3H		K
Ti(18)	A	C			F		J	2K

the O atoms around the Ti atoms. In this instance we did not do so because we could decide the case without going into that much detail.

In space group $P2_1/m$ the general equivalent position is fourfold, while in $P\bar{1}$ it is twofold. Therefore, all Ti atoms in the triclinic description should occur in topologically equivalent pairs and not just six of them if the true space group of $Ba_2Ti_9O_{20}$ were $P2_1/m$. Actually the argument can be extended to all monoclinic space groups with a center of symmetry because they are all at least of rank four. We also can exclude all noncentrosymmetric monoclinic space groups because the triclinic structure has a center of symmetry. Naturally symmetries higher than monoclinic are also excluded.

Without looking at the details one could argue that the twelve unique Ti atoms might all be located on symmetry elements in a more highly symmetrical space group. However, this is contradicted by the environment of Ti(12) which is coordinated by six topologically different O atoms. Consequently Ti(12) must be in a general position in any higher symmetry group. Since Ti(12) is not paired (Table 2) with any other Ti atom we can again exclude all higher symmetries. The only pairing occurs with the centrosymmetrically related other Ti(12) atom in $\bar{x}\bar{y}\bar{z}$. Therefore, we see that Ti(12) is not symmetrically related by a mirror plane, a glide plane, a twofold axis or a 2_1 axis to any other Ti atom in any higher symmetric cell of a volume equal to the triclinic cell. That the primitive cell does not correspond to a larger centered cell can be ascertained by inspection of the Niggli matrix (*International Tables for X-ray Crystallography*, 1969). Thus we conclude that the topological symmetry of $Ba_2Ti_9O_{20}$ is so low that its structure cannot be of any symmetry

higher than $P\bar{1}$. By topological symmetry we mean the highest symmetry which can be attained by a crystal structure given a certain topology of the connexions of its bonds. In Megaw's (1973) nomenclature we would say that $Ba_2Ti_9O_{20}$ is already an aristotype and not a hettotype which could possibly attain a higher crystallographic symmetry. The term 'topologic symmetry' was previously used in the discussion of framework silicates (see Gottardi, 1979, and literature cited therein); for a definition see Klee (1979).

Another example of the application of a topological analysis is the triclinic structure ($P\bar{1}$) of $Cu_2Li_2P_6O_{18}$ (Läugt & Durif, 1974). The authors of this structure determination remark on the presence of a pseudo-mirror plane in the P_6O_{18} ring. In addition there are similarities in cell constants ($b \simeq c$; $\beta \simeq \gamma$). The topological analysis, however, shows clearly that the ring is topologically triclinic. It contains two O atoms [O(E22) and O(E52)] which are topologically unique and are not located in the pseudo-mirror plane. This is obviously a case where a further search for a possible higher symmetry is pointless.

So far we have been talking about the topology of arrangements of primary bonds. There is no reason not to include more distant connexions, say between atoms in different molecules. As an example we can take the crystal structure of $KB(SO_3Cl)_4$ which was described by Mairesse & Drache (1978) in space group $P1$. Marsh & Schomaker (1980) showed that the structure can be described equally well in space group Cc . The two crystallographically independent molecules $KB(SO_3Cl)_4$ in the triclinic description become crystallographically identical in the monoclinic setting. A topological analysis of the original triclinic structure taking into account intermolecular approaches shows that the two molecules are not only internally identical but that all of their intermolecular contacts are identical as well (compare Table 3 of Mairesse & Drache, 1978). Any case in which even the non-bonding distances for independent molecules agree with each other should alert the crystallographer to the possibility of a higher symmetry. Thus the topological analysis can also be applied to structures of organic or metalloorganic molecular compounds.

When a centrosymmetric structure is refined in a noncentrosymmetric space group then atoms which are paired in the centrosymmetric case, but independent in the lower-symmetry description, can have positional errors amounting to about 0.2 Å. In order to avoid mistakes in the topological description resulting from such scatter in the bond lengths it is advisable to be generous in the inclusion of bonding contacts. In the case of $Ba_2Ti_9O_{20}$ we called bonds all those Ti—O distances ranging from 1.75 to 2.32 Å and all the Ba—O distances from 2.75 to 3.21 Å. It is also useful to compare the bond lengths of topologically equivalent bonds with each other. In the case of $Zn_3(BO_3)_2$ the

scatter of topologically equivalent Zn—O bonds (1.86 to 2.13 Å) and B—O bonds (1.22 to 1.54 Å) indicated that the original description in *Ic* was wrong and that the structure could actually be described in space group *I2/c* (Baur & Tillmanns, 1970). On the other hand, the large scatter in cation—O bond lengths in Ba₂Ti₉O₂₀ can be explained by the different topologic environments of the various O atoms. As a matter of fact there is usually a strong correlation between the sum of the bond strengths received by an anion (which in turn is based on the topology of its surroundings) and the lengths of the bonds it forms to its neighbors (Table 1). Such correlations can be exploited for the prediction of bond lengths (Baur, 1981). The comparison of observed and predicted bond lengths is another diagnostic tool useful for judging the correctness of published structures.

The approach we take is topologic inasmuch as the length of a Ti—O distance which we consider to be a bond does not matter as long as it is in the usually observed range between 1.6 and 2.5 Å. However, if a distance Ti—O is clearly longer, let us say 3.0 Å, we would not consider it to be a bonding contact. Thus far, crystal-chemical experience imposes a metric limitation on the topologic analysis.

Topological and geometrical complexity

In Ba₂Ti₉O₂₀ we have eleven topologically different types among the 40 crystallographically unique O

atoms. The corresponding ratio for Ti is 15 of 18, for Ba four of four. In total there are 30 essentially different kinds of atoms among the 62 crystallographically distinguishable atoms in one unit cell of Ba₂Ti₉O₂₀. Pauling's (1929) rule V, the rule of parsimony, states: 'The number of essentially different kinds of constituents in a crystal tends to be small'. In the light of this rule is Ba₂Ti₉O₂₀ parsimonious or lavish?

In order to answer this question we have analyzed topologically the atomic environments in a number of crystal structures. Within one cationic species we regarded as essentially different constituents cations with different coordination numbers. Therefore, for instance, in K₂Mg₅Si₁₂O₃₀ the K^[12], K^[9], Mg^[4], Mg^[6] and Si^[4] are all counted as being different (the coordination numbers are given as superscripts in square brackets). Since each crystallographically unique O atom in this compound is surrounded differently by the cations we have a total of eight topologically distinct (*t* = 8) atomic species in the asymmetric unit, as compared with eight crystallographically different constituents (*c* = 8) and four different chemical elements (*e* = 4). We now define a topological parsimony index as $I_t = (t - e)/t$. For a completely parsimonious structure I_t tends to a limiting value of zero. An example for that is the sodium chloride type (Table 3). In contrast, K₂Mg₅Si₁₂O₃₀ with $I_t = 0.50$ is a relatively lavish structure. The entries in Table 3 are

Table 3. Parsimony indices [$I_t = (t - e)/t$ and $I_c = (c - e)/c$] for a number of selected crystal structures

In addition are given the number of crystallographically unique atoms per asymmetric unit (*c*), the number of topologically different atomic species per asymmetric unit (*t*) and the number of different chemical elements per compound (*e*). References to older work are given by volume and page numbers of Wyckoff (1963): W, 1; Wyckoff (1964): W, 2; and Wyckoff (1968): W, 4.

Structure	<i>c</i>	<i>t</i>	<i>e</i>	I_t	I_c	Reference
Ba ₂ Ti ₉ O ₂₀	62	30	3	0.90	0.95	Tillmanns, Hofmeister & Baur (1983)
Ba ₆ Ti ₁₇ O ₄₀	34	27	3	0.89	0.91	Tillmanns & Baur (1970)
Ba ₄ Ti ₁₃ O ₃₀	15	13	3	0.77	0.80	Tillmanns (1982)
BaTi ₆ O ₁₃	20	12	3	0.75	0.85	Tillmanns (1972)
Cu ₂ Li ₂ P ₆ O ₁₈	28	15	4	0.73	0.86	Laüdt & Durif (1974)
BaTi ₅ O ₁₁	17	7	3	0.57	0.82	Tillmanns (1969)
Ca ₂ Mg ₅ Si ₈ O ₂₂ (OH) ₂ , tremolite	13	11	5	0.55	0.62	W, 4, 304
K ₂ Mg ₅ Si ₁₂ O ₃₀	8	8	4	0.50	0.50	Khan, Baur & Forbes (1972)
Si ₂ Al ₃ O ₂₀ (OH) ₁₈ Cl, zunyite	10	9	5	0.44	0.50	W, 4, 434
K(Al,Si) ₄ O ₈ , sanidine	8	5	3	0.40	0.60	W, 4, 450
KB(SO ₃ Cl) ₄	22	8	5	0.38	0.77	Marsh & Schomaker (1980)
Ba(Ti,Pr)O ₃ , hexagonal	6	6	4	0.33	0.33	Fischer & Tillmanns (1981)
CaMgSi ₂ O ₆ , diopside	6	6	4	0.33	0.33	W, 4, 295
ZrO ₂ , baddeleyite	3	3	2	0.33	0.33	W, 1, 243
KAl ₂ (AlSi ₃)O ₁₀ (OH) ₂ , muscovite	10	6	5	0.17	0.50	W, 4, 346
SiP ₂ O ₇ , cubic	50	3	3	0.00	0.94	Tillmanns, Gebert & Baur (1973)
SiO ₂ , meteoritic tridymite	36	2	2	0.00	0.94	Dollase & Baur (1976)
Na ₂ MgSiO ₄	16	4	4	0.00	0.75	Baur, Ohta & Shannon (1981)
SiO ₂ , coesite	7	2	2	0.00	0.71	W, 1, 321
BaTiO ₃ , hexagonal	6	3	3	0.00	0.50	W, 2, 414
Mg ₂ SiO ₄ , olivine	6	3	3	0.00	0.50	W, 4, 159
SiO ₂ , high-temp. tridymite	3	2	2	0.00	0.33	W, 1, 316
BaTiO ₃ , cubic	3	3	3	0.00	0.00	W, 2, 390
TiO ₂ , rutile	2	2	2	0.00	0.00	W, 1, 251
NaCl	2	2	2	0.00	0.00	W, 1, 85

arbitrarily selected from well known structure types and from our own experience.

Whenever one tries to express a complex phenomenon by a single measure as we are doing here with the parsimony index it certainly is possible to do so in many different ways. Actually we considered about a dozen of such indices, using as variables e , t and c . Since t by itself already contains a count of chemical elements and of their topology (see the example of $K_2Mg_3Si_{12}O_{30}$ given above) it reflects the main requirements of parsimony as defined by Pauling (1929): the polyhedra about all chemically identical cations should be chemically similar and similar in the nature of the sharing of corners, edges and faces with other polyhedra. By subtracting from t the number of different chemical elements we are correcting for the number of constituents which must be distinct because of their chemistry.

We can subdivide the entries according to the value of I_t in lavish ($I_t > 0.66$), intermediate ($0.66 > I_t > 0.33$) and parsimonious ($I_t < 0.33$) structures. The parsimonious structures are either simple structure types or their superstructures. The intermediate group is just that. It contains many of the typical silicate minerals. Worth mentioning is the observation that partial statistical substitutions of one chemical element by another (as often encountered in minerals) can quickly increase the lavishness of a structure. Witness hexagonal $BaTiO_3$ which has been shown to be stable only if one of the Ti-atom positions is substituted partly by Pt. The index I_t increases consequently from 0.00 to 0.33. However, if several sites are uniformly occupied by two elements in the same ratio we count this only as one element for purposes of counting e [see (Al,Si) in sanidine], because statistically all occupants of the tetrahedral sites are uniform here.

The lavish structures, such as $Ba_2Ti_9O_{20}$ with an I_t of 0.90, have a surprisingly large number of either topological or crystallographic sites per chemical element in the compound. They are lavish whether we use I_t as defined above, or whether we employ $I_c [= (c - e)/c]$, which measures the crystallographic complexity of the structure. This is very different for superstructures of simple compounds (see meteoritic tridymite) where I_c is large, but I_t is still zero, because the topology of the various crystallographic sites does not vary at all. Structural complexity can express itself in very different ways. A superstructure of a simple compound such as tridymite is geometrically complex (as measured by I_c) but topologically exceedingly simple. A superstructure generated by a stuffing of interstices (such as $Ba_2Ti_9O_{20}$) is both geometrically and topologically complex. Structures with very high values of I_c but small values of I_t have a good chance of being superstructures of simpler types.

From the data displayed in Table 3 it appears that Pauling's (1929) rule V, the rule of parsimony, is not

very well obeyed by complex ionic crystals in general. Thus it differs markedly from the other four rules formulated by Pauling (1929) for ionic compounds. Those are today still being applied, extended and reinterpreted (*Structure and Bonding in Crystals*, 1981). It may be significant that the first edition of the *Nature of the Chemical Bond* (Pauling, 1939) does not contain any reference to the rule of parsimony. However, it is still being cited in the literature. Bloss (1971) restates it as 'The number of types of interstitial sites present within a periodically regular packing of anions tends to be small'. Compounds such as $Ba_4Ti_{13}O_{30}$, $Ba_6Ti_{17}O_{40}$ and $Ba_2Ti_9O_{20}$ which can all be described as closest packings of O and Ba atoms with Ti occupying the octahedral interstices are powerful counter examples even to this restated rule of parsimony.

Conclusions

The topological analysis of complex crystal structures is a useful tool for studying the topological symmetry of a structure. The absence of topologically equivalent but crystallographically inequivalent pairs or groups of atoms is an analytical proof that the structure cannot possess a higher symmetry. The discovery of such equivalent pairs shows that the topological symmetry of the structure is higher than the crystallographic symmetry observed so far. Such a finding should be a stimulus to search for higher space-group symmetries in order to avoid the assignments of space groups of unnecessarily low symmetry (Marsh & Schomaker, 1979; Herstein & Marsh, 1982; Marsh & Herstein, 1983). This search for higher symmetries must be based mostly on sifting carefully the diffraction evidence (Niggli matrix, equivalence of pairs of F_{hkl} search for reflexions which violate translational symmetries) or else on numerical relations between atomic coordinates.

The application of the topological and geometrical indices I_t and I_c to a number of structures shows that we should distinguish between those which are only topologically complex and those which are both topologically and geometrically complex. A topological analysis of selected structures shows that the rule of parsimony applies only to the simplest structure types and their superstructures but not to complex ionic crystals in general.

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The $\beta \rightleftharpoons \alpha'$ Phase Transition of Sr_2SiO_4 . I. Order–Disorder in the Structure of the α' Form at 383 K

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Abstract

The high-temperature α' orthorhombic phase of strontium orthosilicate was studied structurally by single-crystal diffractometry at 383 K [$a = 5.682$ (1), $b = 7.090$ (1), $c = 9.773$ (2) Å, $V = 393.7$ Å³, $Z = 4$, space group $Pmnb$ [non-standard setting of $Pnma$ (No. 62); equivalent positions $\pm(x, y, z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z; 0108-7681/83/060674-06\01.50

$\frac{1}{2} - x, y, z; x, \frac{1}{2} + y, \frac{1}{2} - z]$], $M_r = 267.32$, $D_x = 4.510$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 26.6$ mm⁻¹}, using 741 observed reflexions. Least-squares refinements were performed on: (i) an ordered model, with Sr atoms and SiO₄ tetrahedra lying on (100) mirror planes ($R = 0.060$, anisotropic); (ii) a disordered model, with atoms statistically distributed between mirror-related positions ($R = 0.069$, isotropic); (iii) a mixed model, © 1983 International Union of Crystallography