Acta Crystallographica Section A
Foundations of Crystallography
ISSN 0108-7673

Received 12 September 2002
Accepted 11 November 2002

Analysis of voids in crystal structures: the methods of 'dual' crystal chemistry

V. A. Blatov* and A. P. Shevchenko

Samara State University, Ac. Pavlov Street 1, Samara 443011, Russia. Correspondence e-mail: blatov@ssu.samara.ru

The theoretical basics of the analysis of voids in crystal structures by means of Voronoi–Dirichlet polyhedra (VDP) and of the graph theory are stated. Topological relations are considered between VDPs and atomic domains in a crystal field. These relations allow the separation of two non-intersecting topological subspaces in a crystal structure, whose connectednesses are defined by two finite 'reduced' graphs. The first, 'direct', subspace includes the atoms (VDP centres) and the network of interatomic bonds (VDP faces), the second, 'dual', one comprises the void centres (VDP vertices) and the system of channels (VDP edges) between them. Computer methods of geometrical–topological analysis of the 'dual' subspace are developed and implemented within the program package *TOPOS*. They are designed for automatically restoring the system of channels, visualizing and sizing voids and void conglomerates, dimensional analysis of continuous void systems, and comparative topological analysis of 'dual' subspaces for various substances. The methods of analysis of 'dual' and 'direct' subspaces are noted to differ from each other only in some details that allows the term 'dual' crystal chemistry to be introduced. The efficiency of the methods is shown with the analysis of compounds of different chemical nature: simple substances, ionic structures, superionic conductors, zeolites, clathrates, organic supramolecular complexes.

1. Introduction

Most methods of crystallochemical analysis traditionally consider the crystal as a set of atoms represented by points, spheres or ellipsoids joined by a system of bonds (in the case of covalent or coordination compounds) or forming a packing (if interatomic interactions are mainly non-direct as in the case of ionic or molecular substances) (Vainshtein *et al.*, 1983). As a result, the crystal space becomes divided into two non-intersecting parts: the subspace of atoms whose topology is determined by a system of interatomic valent or non-valent contacts, and the subspace of interatomic voids joined by a system of channels. The crystallochemical study of a crystal structure comes to the analysis of the first subspace, as a rule, while the subspace of voids is merely considered in special cases when it associates with special properties of a substance, such as ionic conductivity, absorption, molecular recognition, capabilities to form intercalate compounds or to play the role of a molecular sieve *etc.* Reliable results in assessing the amount, positions and sizes of voids, and the topological properties of the system of channels between them can usually be obtained in the case of high-symmetry crystal structures of simple chemical composition where voids have a regular polyhedral atomic environment as in close packings or zeolites (Wells, 1986). In other cases, one has to be satisfied with semi-quantitative or qualitative results and to judge the void properties using indirect data (for instance, the substance's capability to absorb ions or molecules of a given size or the substance's anisotropy in ionic conductivity). Widespread crystallochemical software packages provide no visualization of void subspace and comprise no special tools to study voids. Several algorithms and computer programs are known to estimate the void sizes (Langlet *et al.*, 1977; Alard & Wodak, 1991; Thomas, 1991; McArdle & Cunningham, 2000) but they require using the systems of atomic and van der Waals radii and are not widely exploited. At the same time, the role of void analysis arises in modern crystal chemistry owing to investigation of new classes of substances (ionic and molecular sieves, supramolecular complexes, superionic conductors). Therefore, this study is devoted to the development and computer implementation of methods for the analysis of 'empty' space in crystal structures.

First of all, let us note that the aforementioned division of crystal space into two parts is relative since it assumes an atom to be a sphere with the size determined according to one of the systems of crystallochemical radii. However, the most valid crystal space pattern that conforms to the data of structural experiment is a continuous distribution of electronic density $\rho(r)$ whose local minima can be considered to be void centres. The most physically consistent interpretation of the $\rho(r)$ function, first proposed by Bader (1990) for molecular systems, at present finds more and more applications within

Table 1
Relations between VDP elements, $\rho(r)$ features and topological elements of crystal structure.

VDP element	Geometrical object that can intersect VDP element	Type of critical point according to Bader (1990)	$\rho(r)$ feature	Topological element of crystal structure
Central point	None	(3, −3)	Global maximum	Atomic nucleus
Face	Segment joining two atoms whose VDPs are incident to the face	(3, −1)	Saddle point	'Centre' of chemical bond
Edge	Polygon confined with the atoms whose VDPs are incident to the edge	(3, 1)	Saddle point	Centre of channel
Vertex	Polyhedron whose vertices coincide with the atoms whose VDPs are incident to the vertex	(3, 3)	Local minimum	Centre of void

the framework of fast developing 'electronic' crystal chemistry (Tsirelson *et al.*, 1986).

Bader (1990) defined the atomic domain in a crystal space as a union of nucleus–attractor and its basin in the vector field of the electronic density gradient $\nabla\rho(r)$. He showed that the global maximum and local minima of $\rho(r)$ within the atomic domain should be interpreted as the positions of atomic nucleus and voids, respectively, whereas the saddle points between the $\rho(r)$ maxima and minima correspond to the centres of chemical bonds and the channels between voids, respectively. In crystal structures, the numbers of critical points of different types are determined by the Poincaré–Hopf formula (Zou & Bader, 1994):

$$n - b + r - c = 0, \tag{1}$$

where n, b, r and c are the numbers of nuclei, bonds, channels (rings) and voids (cages), respectively.

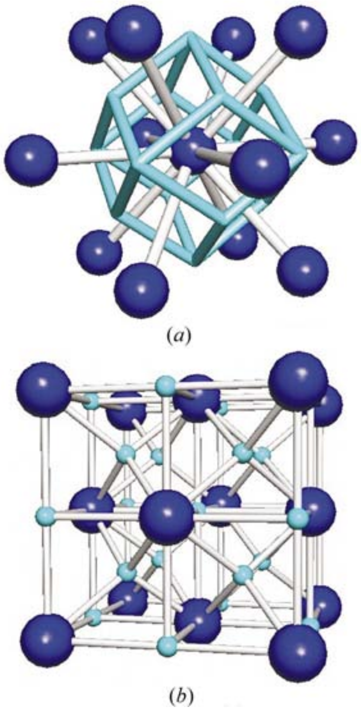


Figure 1
(*a*) Atomic VDP and (*b*) unit-cell contents for the f.c.c. lattice. Small balls indicate the positions of void centres.

To use Bader's method, one needs the $\rho(r)$ function obtained from a quantum-chemical *ab initio* calculation or from a precise structural experiment that essentially restricts the applicability of the method in crystal chemistry. However, Bader's ideas have evident methodological merits and can be used in simpler analytical schemes.

Blatov & Serezhkin (2000) showed that the aforementioned topological features of $\rho(r)$ could be associated with combinatorial properties of the atomic Voronoi–Dirichlet polyhedron (VDP, Fig. 1) as is given in Table 1. According to Table 1, formula (1) is a special case of the Euler–Poincaré formula for the closed odd-dimensional manifold (Pontryagin, 1986):

$$\sum_{i=0}^{d} (-1)^i \alpha_i = 0, \tag{2}$$

where d is the manifold dimensionality, α_i is the number of i-dimensional cages in the manifold. In our case, Voronoi–Dirichlet partition is a three-dimensional (odd-dimensional) manifold; VDPs, their faces, edges and vertices are three-, two-, one- and zero-dimensional cages in the partition, respectively; their numbers ordinarily correspond to n, b, r and c values in (1). Thus, the crystal space partition by atomic domains is homeomorphic to the Voronoi–Dirichlet partition, and atomic domains are homeomorphic to atomic VDPs. Following Table 1, we equate the void geometrical centre [a local $\rho(r)$ minimum] to a VDP vertex. Note that the void centre defined like that does not always conform to the centre of a physical cavity which can contain a set (conglomerate) of VDP vertices (see §2.1).

Let us emphasize that a VDP element does not correspond to a crystal structure topological element in all cases (Blatov & Serezhkin, 2000) since an atomic domain hyperface does not always contain a critical point (Bader, 1990). According to Blatov & Serezhkin (2000), the correspondence exists if a VDP element intersects the geometrical object given in the second column of Table 1. For instance, if the segment joining two atoms does not intersect corresponding VDP faces, these atoms are 'indirect' neighbours and the bond between them seems to be lost (O'Keeffe, 1979). The same reasons can be used for correspondences between VDP edges and vertices (Table 1). Blatov & Serezhkin (2000) called a VDP element *major* if it satisfies the condition of intersection, otherwise such a VDP element is called *minor* and is to be taken into account only in special cases.

At the same time, topological similarity of atomic domains and VDPs does not mean their geometrical similarity. In particular, unlike VDP faces, the hyperfaces of atomic domains are always curved. Besides, if a VDP has small faces or edges, the corresponding combinatorial elements of an atomic domain can be lost. In this case, the aforementioned homeomorphism of two partitions is violated. In general, the simple geometrical approach based on Voronoi–Dirichlet partition gives a rougher crystal structure pattern than Bader's method. However, as was mentioned above, $\rho(r)$ cannot often be determined by direct *ab initio* calculation or precise experiment; in this case, the Voronoi–Dirichlet method becomes a real possibility to investigate geometrical and topological features of atomic domains. In particular, the Voronoi–Dirichlet partition can successfully be used to solve a number of problems concerning the atomic subspace, namely:

(i) search, determination of type and strength of interatomic and intermolecular contacts (Blatov & Serezhkin, 2000);

(ii) estimation of relative sizes of atoms and molecules (Fischer & Koch, 1979; Blatov & Serezhkin, 2000; Peresypkina & Blatov, 2000*a*);

(iii) estimation of degree of distortion for atomic domains and corresponding coordination polyhedra in a crystal field (Blatov & Serezhkin, 2000);

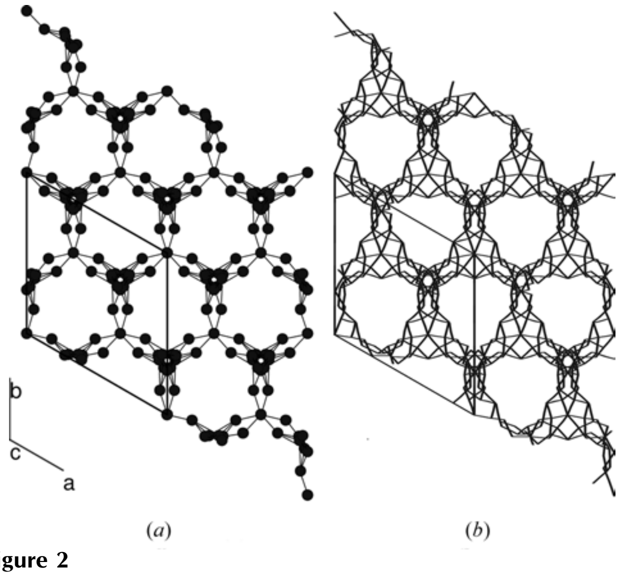
(iv) calculation of uniformity degree for atomic and molecular packings (Blatov, 2001; Peresypkina & Blatov, 2002);

(v) analysis of topological properties of atomic and molecular nets and packings (Peresypkina & Blatov, 2000*b*; Blatov, 2001).

However, the Voronoi–Dirichlet partition has not practically been used to investigate the subspace of voids, although the principal possibility of such an application was earlier mentioned (Wells, 1986). A number of algorithms to analyse pores in non-periodic systems use elements of Voronoi–Dirichlet partition (Medvedev, 2000). Table 1 shows that the set of VDP centres with the topology determined by the system of VDP faces unambiguously corresponds to the atomic subspace. Similarly, the set of VDP vertices with the topology determined by the system of VDP edges corresponds to the void subspace. Thus, Figs. 2(*a*), (*b*) show that the set of VDP vertices constructed without disordered Ag atoms follows, as a whole, the motif of conductivity channels in the crystal structure of superionic conductor $RbAg_4I_5$ (Geller, 1976). Either of the systems can be represented by a three-dimensional graph (*graph representation*); the two graphs (the graph of atoms and the graph of voids) interpenetrate but never intersect each other. Let us emphasize that in the graph representation a void is equated with its centre (VDP vertex) just as the term 'atom' denotes the point corresponding to a $\rho(r)$ maximum.

While the atomic subspace can be related to polyhedral Voronoi–Dirichlet partition, the polyhedral partition where the centres of polyhedra coincide with the centres of voids is the Delone partition (Medvedev, 2000). Voronoi–Dirichlet and Delone partitions are dual to each other and are *polyhedral representations* of atomic and void subspaces. It will be shown below that the void subspace can also be represented by a Voronoi–Dirichlet partition that has clearer physical meaning.

Thus, topological structures of both subspaces are similar to each other. This similarity allows us to suppose that the methods of geometrical and topological analysis of the atomic subspace (Blatov & Serezhkin, 2000) can substantially be used to investigate the void subspace. Actually, the matter concerns a '*dual*' crystal chemistry where similar methods are used to analyse the sets of $\rho(r)$ minima, not maxima. However, the physical properties of both subspaces have a number of important differences, therefore the methods of Blatov & Serezhkin (2000) cannot be applied as is and require an improvement that is considered below.



(*a*) (*b*)

Figure 2

(*a*) Migration channels for Ag^+ ions and (*b*) the edge network for the VDPs of Rb and I atoms in the crystal structure of the superionic conductor $RbAg_4I_5$ (Geller, 1976).

2. The methods of analysis of the void subspace

2.1. Generating the void subspace

The methods of the void subspace investigation are implemented within the program package for multipurpose crystallochemical analysis, *TOPOS* (Blatov *et al.*, 2000). The program *Dirichlet* (part of the *TOPOS* package) performs searches for the void centres (VDP vertices). While constructing the Voronoi–Dirichlet partition, all atoms of the crystal structure are taken into account, as a rule; however, any subset of basic atoms can also be considered. It can be useful, for instance, to investigate voids in intercalates when some voids are already occupied (in this case one needs to forget the interstitial atoms), or to analyse supramolecular receptors when ignoring hydrogen atoms can substantially simplify the void map.

The void subspace differs from the atomic subspace in two principal features, which should be taken into account when restoring its connectedness:

Table 2
Results of VDP construction for the void A89 in the crystal structure of the zeolite SSZ-42 (Chen *et al.*, 1997) with the program *Dirichlet*.

In the program *Dirichlet*, the radius of sphere with the VDP volume ($R_{\rm sd}$), VDP sphericity parameter (G_3, see §2.2.2) are specified as the general VDP parameters in addition to the VDP volume. In each line of the table, the name of an atom or a void that is a neighbour of the void A89, its coordinates (x, y, z), the distance (R) between the neighbour and A89, and solid angle (Ω) of the VDP face are given.

VDP central point: A89 (0.500, 0.245, 0.000); $R_{\rm sd}$ = 1.196 Å; VDP volume = 7.174 Å^3; G_3 = 0.0860

Atom or void	x	y	z	R (Å)	Ω (%)
A90	0.480	0.120	−0.046	1.739	10.52
A90	0.520	0.120	0.046	1.739	10.52
A53	0.571	0.338	−0.008	1.817	9.82
A53	0.429	0.338	0.008	1.817	9.82
A55	0.409	0.309	−0.054	1.853	10.01
A55	0.591	0.309	0.054	1.853	10.01
A49†	0.528	0.399	−0.040	2.173	3.23
A49†	0.472	0.399	0.040	2.173	3.23
O1	0.563	0.143	−0.172	2.345	5.91
O1	0.438	0.143	0.172	2.345	5.91
O2	0.424	0.186	−0.265	2.345	5.87
O2	0.576	0.186	0.265	2.345	5.87
A84†	0.411	0.116	−0.068	2.373	1.27
A84†	0.589	0.116	0.068	2.373	1.27
A82	0.519	0.285	−0.355	2.834	3.37
A82	0.481	0.285	0.355	2.834	3.37

† 'Indirect' neighbours.

(i) distances between the void centres can be arbitrarily small;

(ii) voids are not *a priori* differentiable by type as atoms are by chemical nature.

N void centres located close to each other represent an N-conglomerate, which actually corresponds to the same rather large cavity whose centre coincides with the conglomerate centroid. Such a situation is standard in the compounds containing voluminous cavities decorated with many atoms (Fig. 3). To some extent, this case is similar to atomic disorder. One can differentiate voids by additional parameters, for instance, by void size or by the nature of void atomic environment. In addition to the differentiation of major and minor voids described above, the program Dirichlet implements one more classification variant to be considered below.

First of all, note that not all of the VDP vertices correspond to real cavities in the crystal structure even in the case of the 1-conglomerate. In general, any four non-coplanar interconnected atoms correspond to a VDP vertex. If all or some of these atoms are valently bonded and, hence, are close to each other, the volume of the corresponding void would be small to fit the size of an interstitial atom (metal hydrides are the single exception). Obviously, if large cavities are only of interest and there are long-distance non-valent contacts between neighbouring atoms, such VDP vertices might be excluded from consideration. Since six contacts between four atoms correspond to each VDP vertex located in a general position, it is convenient to introduce the rank of VDP vertex to be equal to the number of *non-valent* contacts around it and to be varied from 0 to 6. One can expect that the vertices of the highest rank will conform to the largest cavities. For instance, in the crystal structure of the zeolite Dodecasil 1H (Gerke & Gies, 1984), there are VDP vertices of ranks 3 and 6. A vertex of rank 3 is incident to four VDPs of one Si and three O atoms joined by three Si—O valent bonds, and is located within an $\mathrm{SiO_3}$ pyramid. A vertex of rank 6 is formed by the intersection of four VDPs of oxygen atoms without valent contacts. Forgetting the vertices of a lower rank results in a consecutive simplification of the channel map and in a clarification of large cavities (Figs. 4a, b). Note that in all examples of this study all VDP vertices are forgotten except the vertices of the highest (for a given crystal structure) rank, however, all minor vertices of the highest rank are taken into account together with major ones.

An automated determination of void connectedness can be performed by means of the program *AutoCN* from the *TOPOS* package. This procedure is based on constructing a 'secondary' Voronoi–Dirichlet partition where void centres are the centres of VDPs, however, while VDP constructing all other voids and atoms are to be taken into account (Fig. 5, Table 2). By analogy of the criterion of existence of interatomic contact (Blatov & Serezhkin, 2000), a connecting channel (Fig. 6) is assumed to exist between two voids if (i) they are 'direct' neighbours and (ii) the solid angle of the VDP face separating void centres is more than a certain value (normally 1.5% of the total solid angle 4π sr). In fact, this value corresponds to the channel of the minimum section.

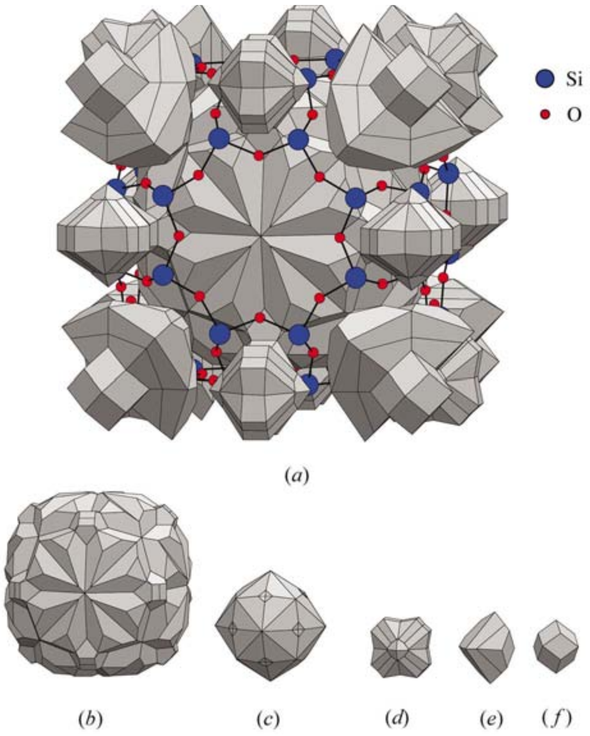


Figure 3
(a) Polyhedral representation of voids in the sodium-free sublattice of the crystal structure of $\mathrm{NaAlSiO_4}$ zeolite (Smith & Dowell, 1968) and molecular VDPs for unconnected void N-conglomerates with the following values of N, volume (Å^3) and G_3: (b) 60, 799.0, 0.09466; (c) 33, 119.1, 0.07735; (d) 15, 23.8, 0.08151; (e) 3, 16.0, 0.08264; (f) 1, 9.5, 0.07875. The conglomerate (b) embraces the conglomerate (c).

Note that such an approach is a simpler alternative to the system of VDP edges as a topology on the void subspace, since a clear criterion to neglect narrow channels is difficult to introduce in the later variant.

If the void subspace is not simply connected (*i.e.* it contains void conglomerates not connected to each other), one needs to divide it to simply connected domains before analysing. This operation corresponds to separating molecular (including polymeric) groups when providing an ordinary crystallochemical analysis of the atomic subspace. It can be performed with the program *ADS* of the *TOPOS* package, which simultaneously determines the dimensionality (0D, 1D, 2D or 3D) of simply connected domains and the orientation of chain and layer (1D or 2D) conglomerates along crystallographic directions (Figs. 7*a*, *b*). When the contacts between voids in a conglomerate are substantially heterogeneous (which can be fixed by large lengths of the contacts or by small solid angles of VDP faces), it is reasonable to make an additional division of the conglomerate into simpler fragments. Such a problem is typical for continuous channels in zeolites connecting voluminous cavities when the cavity properties should be analysed (Fig. 8).

Visualization of voids in polyhedral and graph representations is implemented in the program *IsoCryst* of the new 32-bit *TOPOS* 4.0, which was used to prepare all figures in this paper.

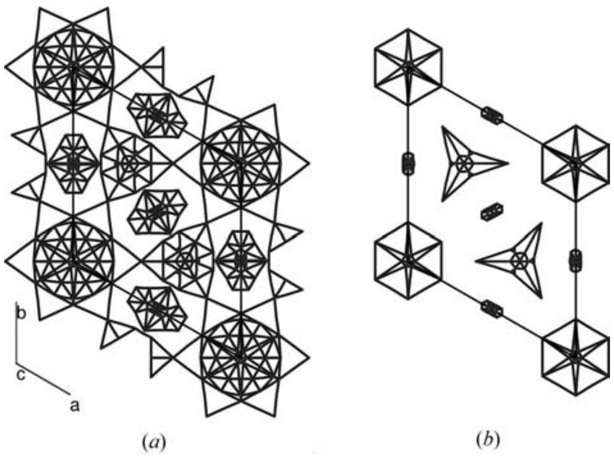


Figure 4
Void conglomerates in the crystal structure of the zeolite Dodecasil 1*H* (Gerke & Gies, 1984): (*a*) without removing voids; (*b*) removing all the voids of rank less than 6.

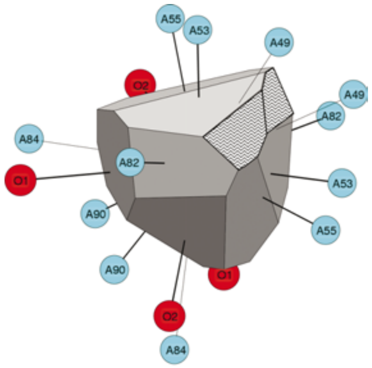


Figure 5
VDP and the near environment of the void A89 in the crystal structure of the zeolite SSZ-42 (Chen *et al.*, 1997).

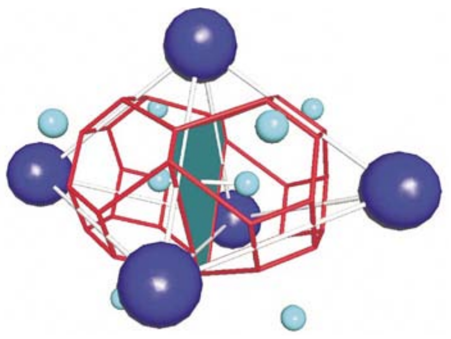


Figure 6
Crystal structure fragment for h.c.p. Atoms and voids are shown by dark and light balls, respectively. VDPs are constructed for tetrahedral voids. The face corresponding to the connecting channel is filled.

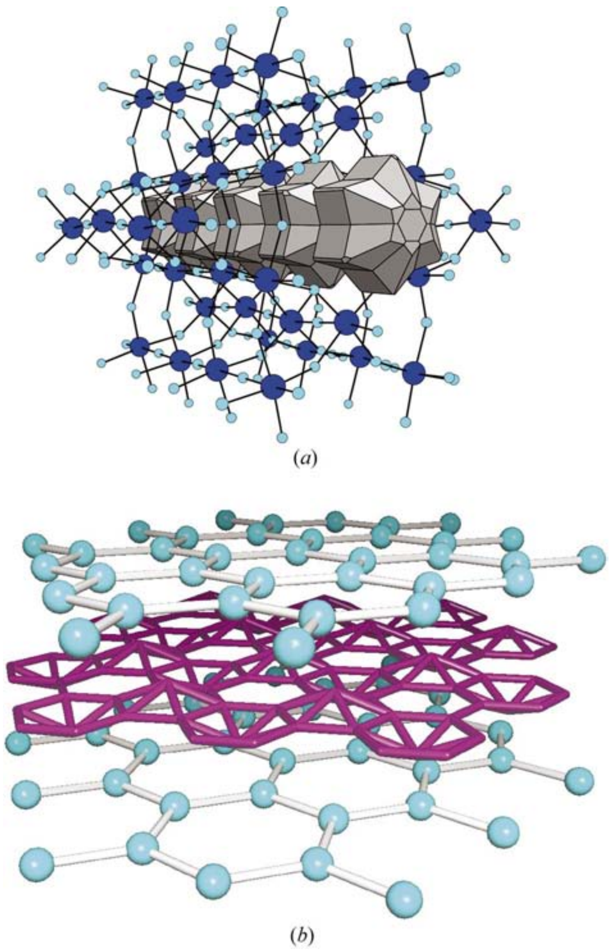


Figure 7
(*a*) Polyhedral representation of 1D chain void conglomerate in the crystal structure of $Rb_{0.28}WO_3$ (Labbé *et al.*, 1978); (*b*) graph representation of 2D layer void conglomerate in the crystal structure of graphite.

Table 3
R_{sd} values for N-conglomerates and their centroids in the environment of oxygen atoms for some crown ethers.

			R_{sd}, Å	
CSD reference code	Crown ether	N	Conglomerate	Centroid
Li complexes				
CELHAC	14-Crown-4†	5	1.542	1.349
CEVNAS	12-Crown-4	7	1.478	1.386
JOJNOL‡	12-Crown-4	9	1.639	1.408
	12-Crown-4	7	1.535	1.437
KEVRAE	12-Crown-4	7	1.451	1.385
KOCXUV	14-Crown-4†	2	1.361	1.352
POWZOQ	14-Crown-4†	2	1.398	1.365
XACKUH	10-Crown-3†	4	1.409	1.313
Mean value			1.48 (9)	1.37 (4)
R_{sd} of Li atoms§				1.38 (1)
Na complexes				
FOPPOP	12-Crown-4	7	1.503	1.458
JEGFIK	14-Crown-4†	5	1.624	1.529
JUNGAA	24-Crown-8†	3	1.561	1.539
HOJFAN	12-Crown-4	7	1.490	1.444
HOWGOP	12-Crown-4†	7	1.476	1.439
TEGCEN	12-Crown-4	8	1.494	1.446
YATBIE‡	12-Crown-4	7	1.506	1.456
	12-Crown-4	7	1.521	1.462
Mean value			1.52 (5)	1.47 (4)
R_{sd} of Na atoms§				1.54 (1)
K complexes				
CALYOD	15-Crown-5†	13	1.904	1.666
CIRDUC	30-Crown-10†	13	1.938	1.685
HOFGOE	12-Crown-4	8	1.952	1.774
FIWVUC	15-Crown-5†	12	1.809	1.646
LAWFIY	15-Crown-5†	13	1.849	1.648
NAYKON	15-Crown-5	14	1.840	1.651
YEKLUV‡	12-Crown-4	7	1.779	1.682
	12-Crown-4	9	1.853	1.675
Mean value			1.87 (6)	1.68 (4)
R_{sd} of K atoms§				1.704 (3)
Rb complexes				
CAXSUP	18-Crown-6	10	1.942	1.744
FOJJAP	15-Crown-5†	13	1.838	1.700
GOKXUZ	18-Crown-6†	20	2.113	1.821
HEWNAY	15-Crown-5	8	1.850	1.726
PAQPEC	18-Crown-6	10	1.864	1.755
YISTID	15-Crown-5†	14	1.897	1.668
Mean value			1.9 (1)	1.74 (5)
R_{sd} of Rb atoms§				1.775 (5)
Cs complexes				
CENQIV	18-Crown-6	15	2.279	1.911
DOSKIF	15-Crown-5†	15	2.421	1.868
DUBCIM	18-Crown-6	18	2.215	1.874
FUJCUI	18-Crown-6	19	2.305	1.843
SILREK01	15-Crown-5	13	2.048	1.906
TAGFEM	15-Crown-5	16	2.250	1.820
Mean value			2.3 (1)	1.87 (4)
R_{sd} of Cs atoms§				1.88 (1)

† Substituted crown ether. ‡ This compound contains two non-equivalent crown ether molecules. § According to Blatov *et al.* (1998).

2.2. Determination of void geometrical parameters

2.2.1. Void volume and area of channel section. The notion of volume makes sense only for 0D conglomerates. When a conglomerate consists of a single void (1-conglomerate), its volume is equal to the volume of the void VDP constructed with all neighbouring atoms, and its R_{sd} is equal to the void R_{sd} (*i.e.* to the radius of a sphere of the void VDP volume). The volume and R_{sd} of the 1-conglomerate correspond to the atomic parameters whose correctness was shown by numerous examples (Blatov & Serezhkin, 2000). Actually, the volume of the 1-conglomerate is equal to the volume of an atom in a given atomic environment, and R_{sd} of the 1-conglomerate is equal to the atom radius. It is the void volume that can be compared with the atomic volumes assumed to be equal to the volumes of atomic VDPs in a given atomic environment. In this case, the main problem hindering VDPs to be applied in crystal chemistry disappears, the problem of choosing the coefficient of division of segments joining atoms by VDP faces (Blatov & Serezhkin, 2000), because VDP construction both of voids and of atoms is performed with the same coefficient (its value is taken to be equal to 0.5, which corresponds to the VDP definition). Note that the coefficient being equal to 0.5 was substantiated for comparative crystallochemical analysis by Blatov & Serezhkin (2000).

However, one often deals with complex 0D N-conglomerates ($N > 1$) owing to complex geometry of cavities. Volume and R_{sd} of a complex N-conglomerate are equal to corresponding parameters of molecular VDP (Fischer & Koch, 1979), which is in this case a set of N VDPs of voids belonging to the conglomerate (Fig. 3). Evaluation of the size of a 0D N-conglomerate can substantially help in solving the problems of supramolecular chemistry, firstly, the problem of molecular recognition when the substrate is a separate atom or a molecule of any complexity. In short, a molecule could not fit a cavity if the VDP of the molecule is greater than the 0D N-conglomerate corresponding to the cavity. We emphasize that this condition is necessary but not sufficient since a receptor and a substrate must coincide with each other not only by sizes but also by physical-chemical properties. Although in most cases the necessary condition becomes sufficient to make conclusions about receptor properties. Some examples are given below.

While analysing the possibility of a cavity to fit the size of an atom, the 0D N-conglomerate should be represented by its centroid. Thus, R_{sd} values for N-conglomerates and their centroids in the environment of oxygen atoms are given in Table 3 for some crown ethers (Fig. 9) in comparison with R_{sd} values of alkali atoms (M) in coordination polyhedra MO_n

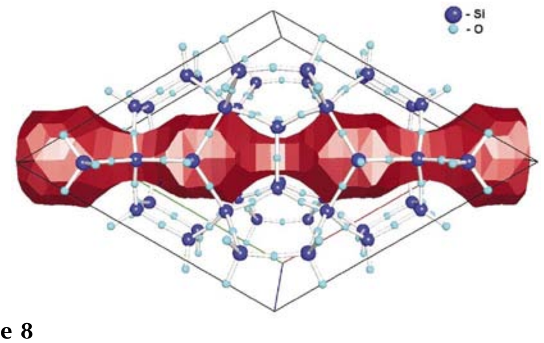


Figure 8
Polyhedral representation of a channel in the crystal structure of the zeolite Dodecasil 1H (Gerke & Gies, 1984).

(Blatov *et al.*, 1998). It is clear that R_{sd} values for the conglomerate centroids better fit the typical radii of M atoms.

The next example is a 14-conglomerate with volume equal to 51.5 Å^3 and R_{sd} = 2.31 Å in the molecule of octaanisyl cavitand (Trueblood *et al.*, 1995; Fig. 10). This cavity volume is insufficient to fit practically all organic molecules, except probably methane with the volume $\simeq$50 Å^3. For instance, dichloromethane and ethanol molecules are solvates in the crystal structures of FUDSIG10, FUDSOM10 and FUDSUS10 (Trueblood *et al.*, 1995) and are not coordinated by the cavitand. Their volumes calculated using crystal structure data of DCLMET10 and ETANOL are equal to 82.1 and 75.5 Å^3, respectively, which substantially exceeds the absorptive capacity of the cavitand. However, the cavity is sufficient to enclose alkali atoms; thus, according to Blatov *et al.* (1998), the VDP volume for caesium ions in the oxygen environment is equal to 27.7 Å^3, R_{sd} = 1.88 Å. Really, in the crystal structure FUDSUS10, a caesium ion occupies the cavity of the octaanisyl molecule and coordinates in addition two perchlorate ions, therefore the cavity volume decreases down to the value required; the VDP volume for the caesium ion surrounded by ten oxygen atoms (eight of them belong to the cavitand and two oxygen atoms belong to two perchlorate ions) is equal to 25.9 Å^3.

Let us consider one more example illustrating the features of the analysis of 0D N-conglomerates. For the crystal structure of the clathrate containing CCl_4 molecules and Xe atoms (McMullan & Kvick, 1990), the calculation without interstitial atoms and molecules gives three void conglomerates (Fig. 11); the centres of A1 and A2 conglomerates coincide with the positions of Xe atoms and centroids of CCl_4 molecules, respectively, while the voids A3 correspond to the channels joining A2 conglomerates and show the directions of C—Cl bonds forming a tetrahedral arrangement for each A2 conglomerate. The volumes 36.5, 51.2 and 25.0 Å^3 were obtained for A1, A2 and A3 conglomerates, respectively. The volume of a tetrahedral molecule to fit the cavity A2 can be evaluated as 51.2 + 4 × 25 = 151.2 Å^3. The volumes of Xe atoms and CCl_4 molecules are equal to 57.6 and 145 Å^3, respectively, for the crystalline state. Therefore the cavity A1 is insufficient in size to enclose Xe atoms, which justifies its filling only by 21–22% (McMullan & Kvick, 1990). Note that the Xe atoms encapsulated into the crystal structure of zeolite A (Heo *et al.*, 1999) conform to the crystalline xenon by volume.

While analysing 1D, 2D or 3D conglomerates, it is important to evaluate the section areas or radii of the channels between cavities. If a channel is represented by N voids separated by approximately equal distances from each other (*i.e.* they group into no additional conglomerates), its maximum, minimum and average section areas (S_{max}, S_{min}, $\langle S\rangle$) can be calculated as follows:

$$S = \pi R_{sd}^2, \tag{3}$$

where R_{sd} corresponds to maximum, minimum and average R_{sd} values for the set of N void VDPs, respectively, and is assumed to be equal to the channel radius. To assess the shape and size of the channel more precisely, one can calculate VDPs and R_{sd} values for several additional equidistant points placed on the channel line (the channel

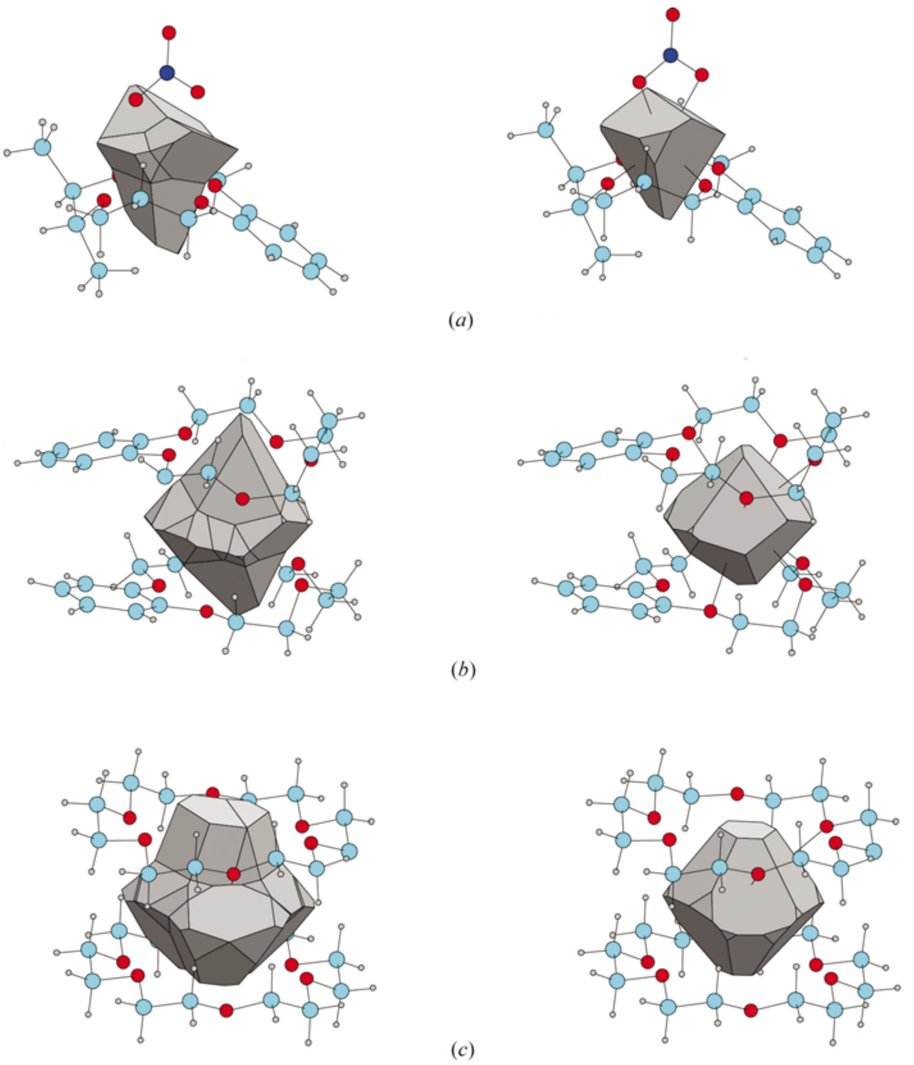


Figure 9
VDPs of void conglomerates and of alkali atoms in the crystal structures of: (*a*) (6,7-dimethyl-benzo-14-crown-4-*O*-1-,*O*-4-,*O*-8-,*O*-11)-nitrato-*O*,*O*′-lithium [CELHAC]; (*b*) bis[bis(benzo-15-crown-5)-potassium]hexaiododimercurate(II) [CALYOD]; (*c*) (μ_2-18-crown-6)-bis(18-crown-6)-dicaesium-decakis(μ_3-iodo)-bis(acetonitrile)-octacopper(I) [CENQIV]. [Reference codes for compounds in the Cambridge Structural Database (CSD, version 5.21, 2001) are given in brackets.]

Table 4
The results of assessing channel size obtained by the channel scan method for the zeolite Dodecasil 1*H*.

Point coordinates				
x	y	z	R_{sd} (Å)	S (Å^2)
1.0000	0.0000	0.5	2.810	24.81
0.9375	0.0625	0.5	2.742	23.62
0.8750	0.1250	0.5	2.515	19.87
0.8125	0.1875	0.5	2.139	14.37
0.7500	0.2500	0.5	2.036	13.02
0.6875	0.3125	0.5	2.150	14.52
0.6250	0.3750	0.5	2.124	14.17
0.5625	0.4375	0.5	1.919	11.57
0.5	0.5	0.5	1.634	8.39

scan method). Thus, the zeolite Dodecasil 1*H* (Fig. 8) has $S_{\max} = 24.81$; $S_{\min} = 8.39$; $\langle S\rangle = 16.04$ Å^2 according to Table 4.

2.2.2. Shape and degree of geometrical distortion for a cavity. The VDP for an *N*-conglomerate immediately reflects the shape of the corresponding cavity (Fig. 3). To assess the degree of geometrical distortion of a 1-conglomerate, it is suitable to use the VDP normalized dimensionless second moment of inertia (G_3) to be generally calculated as follows:

$$G_3 = \tfrac{1}{3}\int\limits_{\mathrm{VDP}} R^2\,\mathrm{d}V_{\mathrm{VDP}}\big/V_{\mathrm{VDP}}^{5/3}, \qquad (4)$$

where V_{VDP} is the VDP volume, R is the distance between the void centre and a point inside the VDP. As is well known (Conway & Sloane, 1988), the G_3 value can be calculated for a solid simplicial dissection:

$$G_3 = \tfrac{1}{3}\sum_i V_i I_i\big/V_{VDP}^{5/3}, \qquad (5)$$

where summation is provided over all simplexes, V_i is the volume of an *i*th simplex, I_i is the normalized second moment of inertia for this simplex relative to the VDP centre:

$$I = \tfrac{4}{5}\,\|\bar{v}\|^2 + \tfrac{1}{20}\sum_{j=0}^{3}\|v_j\|^2. \qquad (6)$$

In (6), the summation is provided over all simplex vertices, $\|v_j\|$ is the norm of the radius vector for a *j*th simplex vertex, $\|\bar{v}\|$ is the norm of the radius vector for the simplex centroid relative to the VDP centre. It is the formulae (5) and (6) that are used in the *TOPOS* package to calculate G_3 values. Blatov & Serezhkin (2000), Blatov (2001) and Peresypkina & Blatov (2002) have shown that the G_3 parameter allows one to evaluate the degree of distortion for a polyhedral atomic domain in comparison with a sphere or regular polyhedra (Table 5) in more detail than other known criteria do.

Formula (5) can also be used to calculate the G_3 value for an *N*-conglomerate represented by its molecular VDP. In this case, the summation is provided over all simplexes of all void VDPs in the conglomerate, while the conglomerate centroid is taken as a coordinate origin. Some typical void conglomerates are given in Fig. 3 together with corresponding G_3 values.

Table 5
G_3 values for some polyhedra and sphere.

Polyhedron	G_3	Polyhedron	G_3
Tetrahedron	0.10400	Rhombododecahedron	0.07875
Cube	0.08333	Truncated octahedron	0.07854
Octahedron	0.08255	Dodecahedron	0.07813
Hexagonal prism	0.08122	Icosahedron	0.07782
Sphere	0.07697		

2.3. Topological properties of channel system and of void arrangement

Blatov (2000), Peresypkina & Blatov (2000*b*) and Blatov (2001) have developed an approach to analyse three-dimensional periodic nets based on their representation as finite 'reduced' graphs. A 'reduced' graph can characterize the atomic subspace in two different ways. In the first one, the graph of an atomic net is constructed whose edges correspond to interatomic bonds; it conforms to the ball-and-stick representation of the crystal structure. The second variant comes from restoring the connectedness of an atomic multilattice whose atoms do not necessarily contact each other in the reference crystal structure. 'Contacts' between such atoms are determined with the Voronoi–Dirichlet partition for the multilattice without taking into account other atoms. The 'reduced' graph constructed in such a way is called the 'packing' graph (Blatov, 2001) since it specifies the topology for an atomic packing within the crystal structure as a whole. The principles of topological analysis of 'reduced' and 'packing' graphs are the same and are used for calculating coordination sequences[1] for all basic atoms in the graph. Comparing the sets of such sequences opens up great possibilities in automation of the procedure of crystallochemical classification (Blatov, 2000). Besides, comparing coordination sequences for 'packing' graphs with reference sequences, one can automatically identify any packings, for instance, close or b.c.c. packings (Blatov, 2001). It is very important to assess the uniformity of the spatial arrangement for the 'packing' graph vertices using the root-mean-square error for the corresponding three-dimensional space quantizer:

$$\langle G_3\rangle = \tfrac{1}{3}\frac{(1/Z)\sum_{i=1}^{Z}\int_{\mathrm{VDP}(i)} R^2\,\mathrm{d}V_{\mathrm{VDP}(i)}}{\left\{(1/Z)\sum_{i=1}^{Z} V_{\mathrm{VDP}(i)}\right\}^{5/3}}, \qquad (7)$$

where Z is the number of basic atoms in the graph. Comparing (4) and (7), one can note that the $\langle G_3\rangle$ parameter is in fact the measure of averaged distortion for the domains of all basic atoms in the packing and can be calculated with formulae (5) and (6). According to Blatov (2001), the least distorted (the most uniform) lattice has the minimum $\langle G_3\rangle$ value among the lattices with a given topology. This criterion also allows one to find the most uniform lattice among geometrically undistorted but topologically different lattices. The b.c.c. lattice with $\langle G_3\rangle = 0.0785433\ldots$ is the most uniform among three-dimensional

---

[1] The oordination sequence (Brunner & Laves, 1971) is a set of integers $\{Nk\}$ where Nk is the number of atoms in a kth coordination sphere of a basic atom in the graph.

lattices (Conway & Sloane, 1988). In the case of ionic compounds, it is the sublattice uniformity that is the important criterion of the sublattice structure-forming role, *i.e.* the sublattice role in the formation of a rigid three-dimensional periodic framework (Blatov, 2001).

The methodology of topological analysis described above can easily be extended to the void subspace. In this case, the analog of the graph of an atomic net specifies the topology of the channel system, and the analog of the 'packing' graph

Table 6
Coordination sequences for the voids in the h.c.p. and in alkali peroxides.

Compound or packing	Atom or void	N_1	N_2	N_3	N_4	N_5
H.c.p.	Tetrahedral void	7	21	49	83	133
	Octahedral void	6	18	50	72	134
Li_2O_2	Li1, Li2	6	18	38	86	126
	Li3	6	24	50	84	150
	O	7	21	49	88	133
Na_2O_2	Na1	6	20	46	86	130
	Na2	6	22	48	84	138
	O1	7	22	47	82	133
	O2	7	22	50	88	133
K_2O_2	K	6	20	42	76	114
	O	7	20	44	74	117
$Rb_2O_2(Cs_2O_2)$	Rb (Cs)	6	20	40	72	110
	O	7	19	42	71	111

Table 7
Coordinates and types of voids in the packing of oxygen atoms in the crystal structure of low-temperature magnetite.

Void	*x*	*y*	*z*	Void type
A1	0.5	0.0	0.5	Octahedral
A2†	0.0	0.0	0.5	Octahedral
A3	0.25	0.0	0.625	Tetrahedral
A4	0.5	0.75	0.3787	Tetrahedral
A5†	0.25	0.75	0.25	Octahedral
A6†	0.5	0.75	0.625	Tetrahedral
A7	0.75	0.75	0.75	Octahedral
A8	0.0	0.75	0.6297	Tetrahedral
A9	0.0	0.75	0.3785	Tetrahedral

† Coincides with Fe atom.

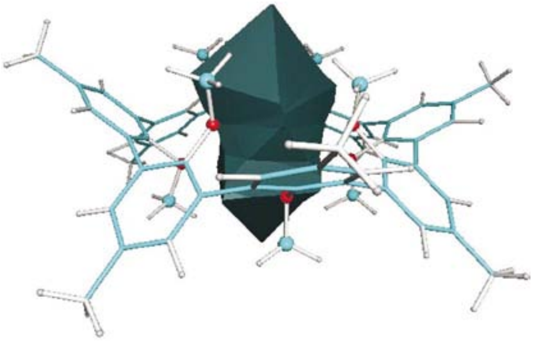


Figure 10
Polyhedral representation of 14-conglomerate in the octaanisyl cavitand (Trueblood *et al.*, 1995).

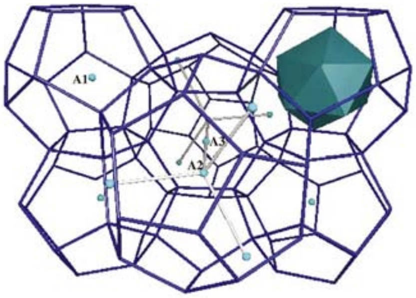


Figure 11
Polyhedral cavities and void centres in the crystal structure of clathrate (McMullan & Kvick, 1990). The VDP of the void A1 is shown.

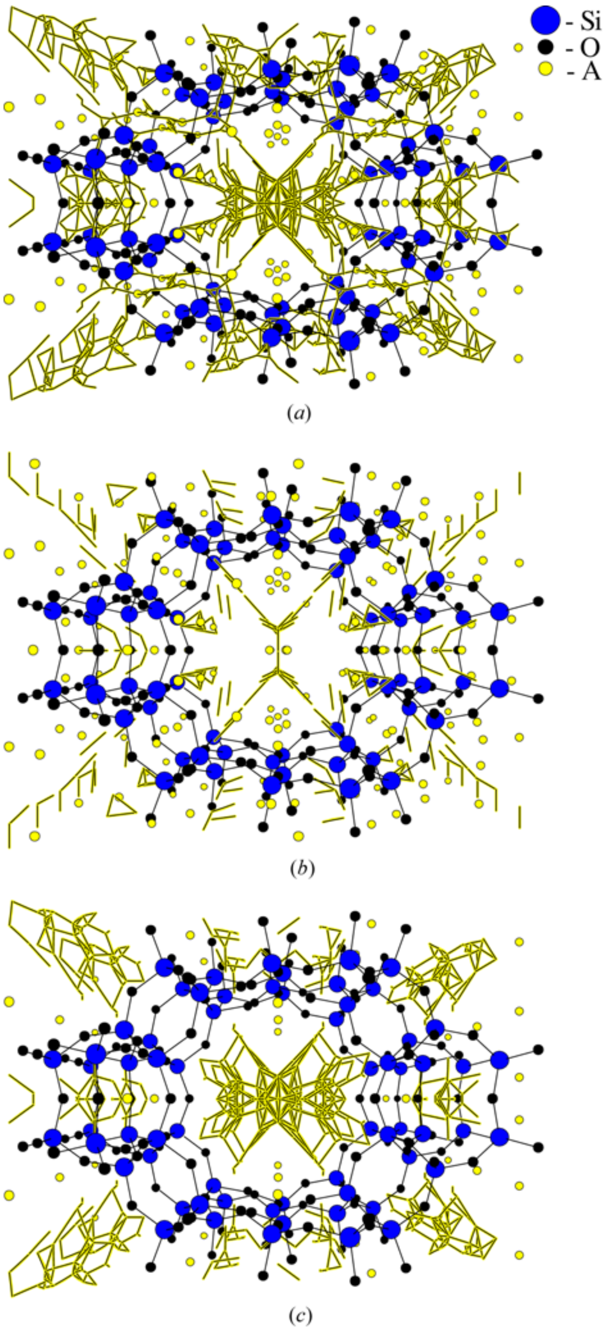


Figure 12
(*a*) Void conglomerates, the results of (*b*) their contraction and (*c*) removing all the voids of the rank less than six in the crystal structure of the zeolite SSZ-42 (Chen *et al.*, 1997). Perspective projections are given along (001).

Table 8
The most uniform arrangements of atoms over the voids of oxygen packing in the crystal structure of low-temperature magnetite.

Topological family	Arrangement	$\langle G_3\rangle$	Void name	N_1	N_2	N_3
I	A6 + A9	0.078551	A6, A9	14	50	110
	A4 + A8	0.078563	A4, A8	14	50	110
II	A1 + A2 + A5 + A7	0.078746	A1, A2, A5, A7	12	42	92
III	A2 + A5 + A6	0.079339	A2, A5	12	50	110
			A6	16	52	130
	A1 + A7 + A9	0.079346	A1, A7	12	50	110
			A9	16	52	130
	A2 + A4 + A7	0.079347	A2, A7	12	50	110
			A4	16	52	130
	A1 + A5 + A8	0.079350	A1, A5	12	50	110
			A8	16	52	130

specifies the topology of a set of voids not connected with each other (for instance, voids of different shape in close packings). To construct such graph analogs, one needs to make only one additional operation after restoring connectedness of the void subspace: to contract[2] each void conglomerate into the same graph vertex. Figs. 12(*a*)–(*c*) show the result of such a transformation for the crystal structure of the zeolite SSZ-42 (Chen *et al.*, 1997). Thus, the following two important problems can be resolved:

(i) comparing the topologies of the systems of cavities and channels in two different compounds or the topology of the system of cavities and channels in one crystal structure with the topology of an atomic net in another crystal structure;

(ii) determination of topological properties for a spatial arrangement of cavities.

All calculations concerning construction and analysis of the graphs of nets and packings can be performed with the program *IsoTest*, part of the *TOPOS* package (Blatov, 2000).

Let us consider as an example of solving the first problem the topology of the system of channels in close packings (h.c.p. and f.c.c.) in comparison with the topologies of atomic nets in binary inorganic compounds using the database of their topological types (Blatov & Zakutkin, 2002). Analysis of coordination sequences shows the system of tetrahedral and octahedral voids and channels joining them in the f.c.c. packing to be topologically similar to the system of atoms and interatomic bonds in the Mg_2Ge structure type (Grosch & Range, 1996): Mg and Ge atoms are topologically equivalent to tetrahedral and octahedral voids, respectively, and have $N_{1-5} = \{10, 34, 82, 142, 218\}$ and $\{8, 36, 78, 140, 230\}$. At the same time, there are no complete topological analogs for the system of voids and channels in the h.c.p. packing among binary compounds though alkali peroxides have similar coordination sequences in the first coordination spheres (Table 6).

The example of solving the second problem is the determination of topology and uniformity for the sublattices of metal atoms at various packings of voids in the f.c.c. packing of oxygen atoms. Consider the low-symmetric (low-temperature) phase of magnetite Fe_3O_4 [spinel family, space group *Imma* (Hamilton, 1958)]. The calculation with the program *Dirichlet* gives nine non-equivalent voids in the oxygen packing; five and four out of them are tetrahedral and octahedral, respectively; three voids coincide with Fe atoms (Table 7). The topological properties and $\langle G_3\rangle$ values for the 'packing' graphs for all possible packings of voids (511 variants) are determined with the program *IsoTest*. Each combination of voids (for instance, A1 + A4 + A9) means physically an atomic arrangement over the oxygen packing (in this case over the voids A1, A4 and A9). When analysing the $\langle G_3\rangle$ value, one can find the most uniform packings of voids. Since in this case voids have to be occupied only by cations, it is the most uniform packing that should conform to the most stable crystal structures. The calculations performed with the *IsoTest* program show $\langle G_3\rangle$ values to be varied within the range 0.07855–0.12543. The most uniform packings ($\langle G_3\rangle < 0.080$, Table 8) are arranged into three topological families according to the values of the first three members of coordination sequences $N_{1-3} = \{N_1, N_2, N_3\}$. When comparing N_{1-3} values with the reference values typical for well known packings, one can conclude that the families I, II and III have the topologies of b.c.c., f.c.c. and Laves phase ($MgCu_2$), respectively. Moreover, when arranging cations (M) over the voids of the families I, II or III, the oxides MO_2, MO and M_3O_4 are obtained with the topologies of SiO_2 (cristobalite), NaCl and spinel, respectively. Obviously, different void packings within each topological family yield the same oxide. Thus, in the case of spinel, the most uniform arrangement of M cations over the voids of the f.c.c. packing is realized, which is possible at the ratio $M:O = 3:4$.

3. Conclusions

The results obtained show that the methods of crystallochemical analysis of the atomic subspace can easily be extended to the void subspace and give additional information about the crystal structure. Dual features of the Voronoi–Dirichlet and Delone partitions emphasize that this information is contained in the standard crystallographic data obtained as a result of structural experiment but it can be extracted merely by constructing these partitions. Such a conclusion reinforces the role of VDP as an object and tool of crystallochemical analysis that allows one to characterize any newly investigated crystal structure with two complementary methods.

This work was financially supported by the Russian Foundation for Basic Research (project No. 01–07-90092).

---

[2] Contracting a graph vertex means its removal and closing together the free ends of the edges to be incident to this vertex (Blatov & Serezhkin, 2000).

References

Alard, P. & Wodak, S. J. (1991). *J. Comput. Chem.* **12**, 918–922.

Bader, R. F. W. (1990). *Atoms in Molecules – a Quantum Theory.* Oxford University Press.

Blatov, V. A. (2000). *Acta Cryst.* A**56**, 178–188.

Blatov, V. A. (2001). *Z. Kristallogr.* **216**, 165–171.

Blatov, V. A., Pogildyakova, L. V. & Serezhkin, V. N. (1998). *Z. Kristallogr.* **213**, 202–209.

Blatov, V. A. & Serezhkin, V. N. (2000). *Russ. J. Inorg. Chem.* Suppl. S105–S220.

Blatov, V. A., Shevchenko, A. P. & Serezhkin, V. N. (2000). *J. Appl. Cryst.* **33**, 1193.

Blatov, V. A. & Zakutkin, Yu. A. (2002). *Z. Kristallogr.* **217**, 464–473.

Brunner, G. O. & Laves, F. (1971). *Wiss. Z.. Techn. Univ. Dresden*, **20**, 387–390.

Chen, C. Y., Finger, L. W., Medrud, R. C. & Crozier, P. A. (1997). *Chem. Commun.* pp. 1775–1776.

Conway, J. H. & Sloane, N. J. A. (1988). *Sphere Packings, Lattices and Groups.* Berlin: Springer-Verlag.

Fischer, W. & Koch, E. (1979). *Z. Kristallogr.* **150**, 245–260.

Geller, S. (1976). *Phys. Rev.* Ser. 3, **14**, 4345–4355.

Gerke, H. & Gies, H. (1984). *Z. Kristallogr.* **166**, 11–22.

Grosch, G. H. & Range, K.-J. (1996). *J. Alloys Comput.* **235**, 250–255.

Hamilton. W. C. (1958). *Phys. Rev.* **110**, 1050–1057.

Heo, N. H., Lim, W. T., Kim, B. J., Lee, S. Y., Kim, M. C. & Seff, K. (1999). *J. Phys. Chem.* B**103**, 1881–1889.

Labbé, P. H., Goreaud, M., Reveau, B. & Monier, J. C. (1978). *Acta Cryst.* B**34**, 1433–1438.

Langlet, G. A., Figueiredo, M. O. & Lima-de-Faria, J. (1977). *J. Appl. Cryst.* **10**, 21–23.

McArdle, P. & Cunningham, D. (2000). *J. Appl. Cryst.* **33**, 993.

McMullan, R. K. & Kvick, A. (1990). *Acta Cryst.* B**46**, 390–399.

Medvedev, N. N. (2000). *The Voronoi–Delone Method for Studies in Structure of Noncrystalline Systems.* Novosibirsk: Nauka. (In Russian.)

O'Keeffe, M. (1979). *Acta Cryst.* A**35**, 772–775.

Peresypkina, E. V. & Blatov, V. A. (2000*a*). *Acta Cryst.* B**56**, 501–511.

Peresypkina, E. V. & Blatov, V. A. (2000*b*). *Acta Cryst.* B**56**, 1035–1045.

Peresypkina, E. V. & Blatov, V. A. (2002). *Z. Kristallogr.* **217**, 91–102.

Pontryagin, L. S. (1986). *Basics of Combinatorial Topology.* Moscow: Nauka. (In Russian.)

Smith, J. V. & Dowell, L. G. (1968). *Z. Kristallogr.* **126**, 135–142.

Thomas, N. W. (1991). *Acta Cryst.* B**47**, 588–597.

Trueblood, K. N., Maverick, E. F., Knobler, C. B. & Goldberg, I. (1995). *Acta Cryst.* C**51**, 894–904.

Tsirelson, V. G., Zorky, P. M., Nozik, Yu. Z., Urusov, V. S. & Ozerov, R. P. (1986). *Electronic Crystal Chemistry.* Moscow: VINITI.

Vainshtein, B. K., Fridkin, V. M. & Idenbom, V. L. (1983). *Modern Crystallography*, Vol. 2. Berlin: Springer.

Wells, A. F. (1986). *Structural Inorganic Chemistry.* Oxford: Clarendon Press.

Zou, P. F. & Bader, R. F. (1994). *Acta Cryst.* A**50**, 714–725.