

occurrence of dual epitaxy. The reduction in interfacial mismatch introduced by dual epitaxy promotes the occurrence of dual epitaxy. In dual epitaxy, the factors that impair the quality of interface and epilayer, such as interfacial mismatch, interfacial net charge and some twins, can be remitted or avoided by adopting suitable planes of substrate and epilayer and appropriate surface reconstruction. Of course, the achievement of an ideal dual epitaxy depends on growth conditions and surface reconstruction and therefore on energy in the final analysis, which includes surface energy, interfacial energy, and kinetic and thermodynamic energies.

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## Crystal Space Analysis by means of Voronoi–Dirichlet Polyhedra

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### Abstract

The method of analysis of crystal space topology by means of Voronoi–Dirichlet tessellation is described. The possibilities of using Voronoi–Dirichlet polyhedra in the investigation of local and global geometrical/topological properties of the crystal lattice in structures of simple and complex substances are discussed. Examples of the application of the proposed method in crystal-chemical analysis are given.

### 1. Introduction

At present, geometrical analysis of crystal structure is one of the fundamental methods that are used by crystal chemists in solid-state investigation. Within this approach, the continuous crystal space is replaced by the discrete (pointal) space, and geometrical properties of a set of points, symbolizing centres of gravity of maxima of electron density or structural units (atoms or atomic groups), are analysed. This set, otherwise known as the multiregular system (MRS), is a set of  $N$  regular systems of points (where  $N$  is a number of crystallographically

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independent structural units) and a special type of Delauney system (Galiulin, 1984). The crystal space is usually considered as space  $\mathbf{R}^3$  in which the MRS is embedded (space  $\mathbf{M}^3$ ), or as space  $\mathbf{M}^3$  in each point of which the function of electronic density  $\rho(x, y, z)$  is determined, and positive integer  $Z_i$ , which is equal to the charge of a corresponding atom, is compared with each point  $\mathbf{p}_i$  of the MRS (space  $\mathbf{P}^3$ ).

According to numerous investigations, the geometrical/topological properties of a MRS are connected with the energy characteristics of a crystal. In crystal chemistry analysis, however, very little attention is paid to topological properties of a MRS and  $\mathbf{M}^3$  as a rule. Although such terms as ‘topology of a coordination polyhedron’ or ‘topology of a complex group’ are commonly used, they do not usually assume the performance of a comprehensive analysis of topological properties of the discussed objects. A theoretical foundation for the topological part of geometrical crystallography has been carried out by a number of authors (particularly Galiulin, 1984; Wells, 1977; Pearson, 1972; Engel, 1986), but the methods of mathematical analysis of  $\mathbf{M}^3$  topology features are far

from perfect. Further, we shall take into account two important crystal-chemical problems which are at present mainly being solved empirically:

(i) The problem of restoration of  $M^3$  connectedness, which consists of the detection of domains belonging to separate atoms in  $M^3$ , the determination of their sizes and form, and the fixing of contacts (*i.e.* chemical bonds) among domains. Here, atoms are mainly represented as hard spheres and interatomic bonds are restored by means of the analysis of interatomic distances. In this case, a MRS is explicitly or implicitly represented as a three-dimensional unoriented infinite graph. However, the model of hard spheres only works well for ionic compounds: for structures of coordination compounds, the analysis of interatomic distances does not always permit chemical bonds to be found clearly.

(ii) The problem of the qualitative and quantitative description of  $M^3$  topological features after connectedness restoration. As a rule, the solution of this problem is restricted by giving atomic coordination numbers, types of coordination polyhedra and the ways of their connecting, *i.e.* local topological characteristics. How can one describe  $M^3$  topology as a whole? Only in the case of close-packed structures is this problem solved completely.

The above-mentioned problems must be solved within the incipient new part of crystal-chemical science: topological crystal chemistry. This paper is the first in a series of articles devoted to  $M^3$  topology analysis methods and their application in descriptive and comparative crystal-chemical analysis.

One of the main methods of topological crystal chemistry is the analysis of Voronoi-Dirichlet tessellation (VDT) of space  $M^3$  with Voronoi-Dirichlet polyhedra (VDPs). It is known that a VDP of the point  $p_i$  of the MRS in  $M^3$  [ $\Pi(p_i)$ ] is convex, all internal points of which are positioned nearer to  $p_i$  than to any other point  $p_j$  of the MRS.  $\Pi(p_i)$  can be considered as an intersection of half spaces  $\sigma_j$  containing  $p_i$  and as being formed by planes  $S_j$ , which are perpendicular to segments connecting  $p_i$  with other points  $p_j$  of the MRS, and the division ratio of each segment for plane  $S_j$  is  $K_d = \rho_j/R_j = 0.5$ , where  $\rho_j$  and  $R_j$  are the distances from  $p_i$  to  $S_j$  and  $p_j$ , respectively.

Suppose that  $K_d \neq 0.5$  while constructing  $S_j$ . As a result, a polyhedron will be obtained that is similar to  $\Pi(p_i)$  with similarity coefficient  $\kappa = 2K_d$ . Evidently, it will be combinatorially equal to  $\Pi(p_i)$  and dual to the coordination polyhedron of  $p_i$  [ $CP(p_i)$ ]. Henceforth, we shall call polyhedra, which are constructed as VDPs but with  $K_d \neq 0.5$ , dual CPs.

At present, a number of algorithms and computer programs of VDP construction are known (Koch, 1972; Hsu & Rahman, 1979; Tanaka, 1986; Engel, 1986). They are based on the search of the intersection of half spaces  $\sigma_j$ . The above-mentioned algorithms are very difficult and therefore the number of points  $p_j$  considered during  $\Pi(p_i)$  construction does not exceed several tens (Tanaka,

1986). In the computer program *DIRICHLET* that is included in the structure topology program package *TOPOS* (Blatov, Shevchenko & Serezhkin, 1993), we used for the first time a very effective algorithm, 'gift wrapping' (Preparata & Shamos, 1985), in which the search of  $S_j$ , forming  $\Pi(p_i)$  faces, is based on the construction of the convex hull for the image points  $p_j^*$  with coordinates  $(2x_j/R_j^2, 2y_j/R_j^2, 2z_j/R_j^2)$ , where  $(x_j, y_j, z_j)$  are the coordinates of point  $p_j$ . According to our practice, it is necessary to consider no less than 100  $p_j$  points around  $p_i$  within a sphere of a given radius to construct a VDP successfully. Recently, we have computed more than 250 000 VDPs for MRS points in real and model crystal spaces using *DIRICHLET*. It should be noted that *DIRICHLET* may be used for combinatorial comparison of a pair of VDPs by means of the search of their edge net graph isomorphism and for automatically forming a library of combinatorial topological types of polyhedra.

In the case of complex substances, when the  $Z_i$  values differ from each other, the choice of  $K_d = 0.5$  is not well founded and this circumstance has been the principal cause of the rare application of VDPs in crystal-chemical analysis. However, in this case, under some conditions, VDPs may be successfully used to investigate geometrical/topological properties of the crystal structure.

Firstly, it has been physically substantiated that VDP can be used for the topology analysis of sublattices consisting of single-type atoms  $p_i$ . Among these sublattices, it will be interesting to explore mainly those of complexing atoms in crystal structures of inorganic and coordination compounds and sublattices of gravity centres of molecules in molecular crystals. It should be noted that at the same time VDP approximately represents the form of an atomic or group domain of the conforming structural unit only in the case of its sufficient 'compactness', considered as the absence of prolonged 'salients' and 'hollows', which are typical for many organic compounds, and 'sphericity', *i.e.* proximity of the group volume to the volume of the sphere inscribed or described around this group. It should be noted that the concept of 'sphericity' will give a quantitative expression regarding the characteristic  $G_3$  that will be introduced in the second part of this paper.

Secondly, VDPs may be used to analyse  $M^3$  local characteristics at points  $p_i$  with single-type environment  $p_j$  (at the same time,  $Z_i \neq Z_j$  in general). Then, all characteristics of an atomic domain, which are invariant for a similarity transformation, will be independent of the  $K_d$  value, which may be set equal to 0.5.

## 2. Physical meaning of VDP geometrical characteristics

In this section, we shall discuss how VDP geometrical characteristics may be connected with local and global geometrical/topological properties of  $P^3$ .

### 2.1. A number of VDP faces

The fundamental VDP property, determining the VDP employment in crystal chemistry, is the possibility of calculating the coordination number of  $p_i$ ,  $[CN(p_i)]$  using the number of  $\Pi(p_i)$  faces during the solving of the above-mentioned problem (i). Frank & Kasper (1958) suggested applying VDP for  $CN(p_i)$  determination in simple substances. In complex substances, the  $CN(p_i)$  search while using VDP is possible under the conditions of uniformity of surrounding atoms or similarity of their characteristics, e.g. in the case of an oxofluoride environment. As an example, a VDP of the U atom in  $UO_2B_2O_4$  (Gasperin, 1987) is displayed in Fig. 1, and in Table 1 the computation results for its geometrical characteristics, according to *DIRICHLET*, are given. It should be noted that in the cited paper (Gasperin, 1987) the CN of the U atom was taken as six whereas the VDP analysis (Fig. 1, Table 1) shows that it is also necessary to consider atoms that are at a distance of 2.607 Å from the U atom. It should be taken into account that, when the sizes of atoms  $p_i$  and  $p_j$  differ from each other and consequently  $|K_d - 0.5| > 0$ , the faces with small area may vanish when considering the curvature of VDP boundaries.

$CN(p_i)$  analysis in sublattices of single-type complexing atoms permits the determination of the packing features of structural units. Thus, in Blatov, Shevchenko & Serezhkin (1994), using data on the crystal structures of 4124 coordination compounds of titanium, zirconium, hafnium, molybdenum, thorium, uranium and neptunium, we verified the efficiency of the 12-neighbours rule (Belov, 1976), according to which the leading atoms or atomic groups of the structure (in the case of complex groups) are disposed in  $M^3$  in a way resembling the close packing of equal hard spheres. The analysis of  $CN(p_i)$  in sublattices of complexing atoms, considered as centres

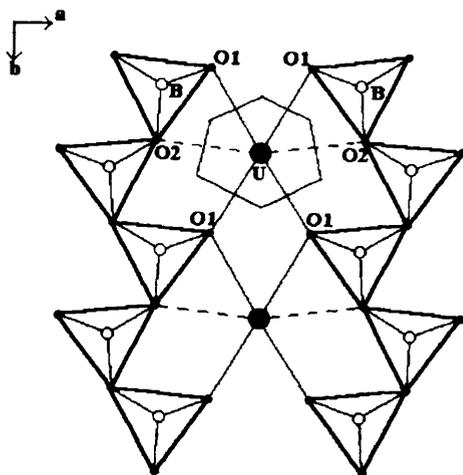


Fig. 1. The projection of the  $UO_2B_2O_4$  crystal structure fragment on the (001) plane (Gasperin, 1987). The dashed lines indicate the U—O<sub>2</sub> bonds which were not taken into account by Gasperin (1987). The VDP of uranium is shown by the thin lines.

Table 1. An example of the output from the program *DIRICHLET*

In columns 'Dist.', 'SAng.',  $s_j$  and  $s_j$  (Brown), the value of the distance (Å) between the central atom and the atom listed, the solid angle (%), and the bond strength calculated with formulae (2)–(5) and according to the method of Brown & Altermatt (1985) are given, respectively.

Compound:  $UO_2B_2O_4$

Central atom: U1 0.500 0.259 0.750

VDP volume = 9.45 Å<sup>3</sup>

CP volume = 18.80 Å<sup>3</sup>

	x	y	z	Dist.	SAng.	$s_j$	$s_j$ (Brown)
O3	0.411	0.256	0.551	1.758	22.04	2.06	2.36
O3	0.589	0.256	0.949	1.758	22.04	2.06	2.36
O1	0.603	0.743	0.756	2.379	10.90	0.41	0.44
O1	0.397	0.743	0.744	2.379	10.90	0.41	0.44
O1	0.603	-0.257	0.756	2.494	9.11	0.30	0.32
O1	0.397	-0.257	0.744	2.494	9.11	0.30	0.32
O2	0.702	0.183	0.739	2.607	7.95	0.23	0.24
O2	0.298	0.183	0.761	2.607	7.95	0.23	0.24

Central atom: B1 0.301 0.148 0.251

VDP volume = 7.69 Å<sup>3</sup>

CP volume = 21.97 Å<sup>3</sup>

	x	y	z	Dist.	SAng.	$s_j$	$s_j$ (Brown)
O1	0.397	0.257	0.244	1.323	29.67	1.12	1.14
O2	0.202	0.317	0.239	1.376	28.53	0.95	0.99
O2	0.298	-0.183	0.261	1.393	27.44	0.88	0.94
O3	0.411	0.256	0.551	2.713	8.23	0.04	0.03
O2	0.298	0.817	0.261	2.800	1.14	0.01	0.02
O3	0.089	-0.244	-0.051	3.283	3.66	0.01	0.01
O3	0.411	-0.256	0.051	3.482	0.27	<0.01	<0.01
O3	0.589	-0.256	0.449	3.489	0.04	<0.01	<0.01
O3	0.089	0.756	-0.051	3.814	0.52	<0.01	<0.01
O1	0.103	0.243	-0.244	4.403	0.48	<0.01	<0.01

of corresponding complex groups, demonstrated that Belov's rule is performed in no more than 11.5% of situations, whereas 56–75% of all groups are surrounded in the structure by 14 neighbours. In following papers, we intend to examine in detail geometrical interpretation of the 14-neighbours rule, which was formulated by Shevchenko, Blatov & Serezhkin (1992).

### 2.2. VDP volume

When simple substances or sublattices of single-type complexing atoms are considered, the VDP volume characterizes the size of an atom or a structural group in  $P^3$ . It should be noted that the volume per atom in structures of simple substances is commonly calculated according to the formula

$$V[\Pi(p_i)] = V_{\text{cell}}/Z_{\text{at}}, \quad (1)$$

where  $V_{\text{cell}}$  is the volume of a unit cell and  $Z_{\text{at}}$  is a general number of atoms in the cell (Pearson, 1972). However, when  $N > 1$ , crystallographically different atoms with the same chemical nature can have different sizes. For example, in  $\alpha$ -Mn and  $\alpha$ -Pu structures, the volumes of VDPs of atoms vary within the range of 11.56–13.38 and 18.93–22.14 Å<sup>3</sup>, respectively. The VDP volume should depend on the type of atom  $p_i$  (i.e. on the  $Z_i$  value), its degree of oxidation, electronic configuration and the environment ( $Z_j$  values).

Table 2. VDP volume versus degree of oxidation ( $\xi$ ) and composition of the CP of uranium

$\xi(\text{U})$	CP composition	Number of types of U atom	VDP volume ( $\text{\AA}^3$ )
II	UO <sub>6</sub>	1	14.9
III	UO <sub>6</sub>	1	12.6
IV	UO <sub>6</sub>	7	12 (1)
	UO <sub>8</sub>	15	11.1 (4)
	UO <sub>8</sub>	3	11.1 (3)
	UO <sub>10</sub>	10	11.2 (6)
	UO <sub>11</sub>	1	11.6
	UO <sub>12</sub>	11	11.1 (5)
V	UO <sub>6</sub>	5	9.9 (5)
	UO <sub>7</sub>	6	10.0 (4)
	UO <sub>8</sub>	1	9.8
	UO <sub>9</sub>	1	10.1
VI	UO <sub>6</sub>	28	9.2 (3)
	UO <sub>7</sub>	209	9.1 (2)
	UO <sub>8</sub>	110	9.3 (2)
	UO <sub>9</sub>	1	9.7
	UO <sub>10</sub>	5	9.5 (3)
	UO <sub>12</sub>	1	9.2

We examined the dependence of  $V[\Pi(\mathbf{p}_i)]$  on  $\text{CN}(\mathbf{p}_i)$  using the example of oxygen-containing compounds of hexavalent uranium (Serezhkin, Blatov & Shevchenko, 1995). Although in the considered structures the precise value of the uranium atomic domain volume is not the same as in the VDP (thus, in general,  $K_d \neq 0.5$ ), the comparison of VDP volumes of different U atoms in a similar environment (in this example the environment consists of O atoms) is correct according to the reasons mentioned in the previous section. We demonstrated (Serezhkin, Blatov & Shevchenko, 1995) that, for reasonable values of  $K_d$  (within the range 0.2–0.8), the volume of conforming dual CPs is practically independent of the CN value. According to recently obtained data (Table 2), this conclusion is also correct for U atoms with other degrees of oxidation. It should be noted that the CP volume increases as the CN value increases. A hypothesis that the atomic volume in a crystal is constant when degree of oxidation and type of environment are given may therefore be proposed.

### 2.3. Size of VDP faces

Since in VDT the polyhedra touch each other with whole faces and each face conforms to a contact between two atoms in  $\mathbf{P}^3$ , the size of this face can characterize the pair atomic interaction in a crystal. The most substantiated characteristic seems to be the value of the solid angle  $\Omega_j$  (O'Keefe, 1979), corresponding to face  $S_j$ , which is numerically equal to the segment  $\beta_j$  of the sphere which is cut by a pyramid with atom  $\mathbf{p}_i$  at the top and face  $S_j$  at the bottom (Fig. 2). Within the proposed approach, it is assumed that valence abilities of atom  $\mathbf{p}_i$  are distributed among  $\text{CN}(\mathbf{p}_i)$  bonds  $\mathbf{p}_i-\mathbf{p}_j$  proportionally to the values of solid angles  $\Omega_j$  conforming to faces  $S_j$  of  $\Pi(\mathbf{p}_i)$ . In this case,  $\sum_{j=1}^{\text{CN}(\mathbf{p}_i)} \Omega_j = 4\pi$  sr and we assume that  $\Omega_j$  is proportional to a portion of the valence electrons of atom  $\mathbf{p}_i$ , which are taking part in the formation of bond  $\mathbf{p}_i-\mathbf{p}_j$ . 'Bond strength'  $s_j$ , corre-

sponding to bond  $\mathbf{p}_i-\mathbf{p}_j$ , can be interpreted as an analogue of valence-electron density in space among interacting atoms (Ivanenko, Blatov & Serezhkin, 1992a) and represented as

$$s_j = \zeta_i s \Omega_j^*, \quad (2)$$

where

$$\Omega_j^* = K \Omega_j / R_j^3, \quad (3)$$

$\zeta_i$  is the degree of oxidation of atom  $\mathbf{p}_i$ ,  $\Omega_j/R_j^3$  is an analogue of the solid angle of the  $j$ th face describing non-sphericity of the domain of atom  $\mathbf{p}_i$  and possessing the dimensionality of electronic density. The coefficient of proportionality  $K$  is the normalization factor and is determined by the formula

$$K = 1 / \sum_{j=1}^{\text{CN}(\mathbf{p}_i)} \Omega_j / R_j^3. \quad (4)$$

In the suggested method in accordance with Pauling's second rule (Pauling, 1929), the balance of valences on atoms  $\mathbf{p}_i$ , *i.e.* complexing cations, is assumed, for which

$$s = \sum_{j=1}^{\text{CN}(\mathbf{p}_i)} s_j \quad (5)$$

is equal to their degree of oxidation. Balance of valences on atoms  $\mathbf{p}_j$  of ligands is calculated as the sum of valence contributions of all atoms  $\mathbf{p}_i$  whose VDPs have common faces with those of atoms  $\mathbf{p}_j$ . In contrast to the classical one-dimensional approach, when 'bond strength'  $s_j$  of two atoms is determined only by the  $R_j$  value (Pyatenko, 1972; Brown & Wu, 1976; Brown & Altermatt, 1985), the proposed method considers the influence of atomic crystal environment on intensity of interaction between a pair of atoms and permits the examination of not only ionic compounds but also coordination and covalent

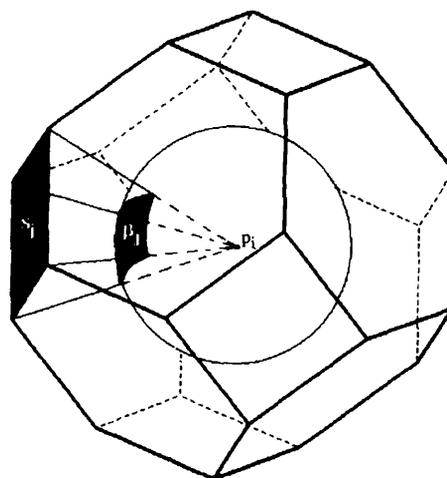


Fig. 2. The VDP of atom  $\mathbf{p}_i$  in a b.c.c. lattice  $\beta_j$  is a segment of the sphere with a unit radius, which is cut by the pyramid with atom  $\mathbf{p}_i$  at the top and face  $S_j$  at the bottom.

compounds. Also, its advantage is the absence of adjusted parameters in estimated formulae (2)–(5). We demonstrated (Ivanenko, Blatov & Serezhkin, 1992a) the efficiency of this method on the example of oxygen-containing coordination compounds of uranium(VI) when the calculation of the balance of valences, according to traditional methods, gave an abnormally large value for the total structural imbalance or required the modification of values of fitting parameters (Ivanenko, Blatov & Serezhkin, 1992b). For example, let us consider the balance of valences in the above-mentioned crystal structure of  $\text{UO}_2\text{B}_2\text{O}_4$ . Table 1 shows the geometric data for VDPs of U and B atoms and the  $s_j$  values for all the contacts U—O and B—O, which are necessary for the calculation based on formulae (2)–(5). The balance of valences (in bond-strength units) on the crystallographically independent O1, O2 and O3 atoms is 1.83 (1.90), 2.06 (2.17) and 2.06 (2.36), respectively [the values calculated according to the method of Brown & Altermatt (1985) are given in parentheses]. It should be noted that this method gives satisfactory balance of valences on U atoms (6.24) only under the condition of ignoring U—O2 contacts, and as a result the error in determination of the CN of U atoms appears, as mentioned above.

### 3. VDT application for the evaluation of the degree of uniformity of crystal structures

In the previous sections, the possibilities of the application of VDPs for the analysis of local properties of  $\mathbf{M}^3$  space were considered. Below we shall describe the method of the analysis of the  $\mathbf{M}^3$  global topological property, the uniformity, using characteristics of the corresponding VDT.

It is well known that, under the influence of central attractive forces, atoms or more complex structural units of a crystal try to arrange themselves so that the number of shortest contacts among them will be a maximum [the so-called principle of maximum filling of space (Vainshtein, Fridkin & Indenbom, 1983)]. On the other hand, in the presence of repulsive forces with the same nature, atoms and atomic groups tend to locate at the greatest distance possible from each other. Thus, a two dimensional model (an arrangement of negative charges on a sphere), used specifically in Gillespie's theory (Gillespie & Hargittai, 1991), leads to the conclusion of uniform distribution of like charges on a spherical surface.

The formation of a three-dimensional structure of the crystal is a result of superposition of interatomic attractive and repulsive forces. In the approximation of central forces by analogy with the two-dimensional model, it may be assumed that the most 'uniform' arrangement of atoms or structure-forming groups in a space should conform to the energy minimum of the crystal lattice, and space  $\mathbf{M}^3$  should possess the global property of uniformity. According to the above, it should

be noted that the problem of the uniform arrangement of points in space  $\mathbf{R}^n$  was considered by Delauney, Dolbilin, Ryshkov & Shtogrin (1970) and the value of the coefficient of space covering ( $K_c$ ) by equal crossing spheres with centres at points of the considered system was proposed as a criterion of uniformity. According to Delauney, Dolbilin, Ryshkov & Shtogrin (1970), the minimum of  $K_c$  conforms to the most uniform system of points. Among three-dimensional periodic structures, this is a body-centred (b.c.) lattice with  $K_c = 1.4635$  (Conway & Sloane, 1988). The other uniformity criterion may be formulated with the help of the parameters of discreteness ( $R_d$ , *i.e.* minimum distance between the points of a system) and covering ( $R_c$ , *i.e.* maximum distance from any point of space to the nearest point of the system), which are used in the theory of Delauney's systems (Galiulin, 1984). The ratio  $R_c/R_d$ , whose minimum value conforms to the most uniform system of points, may be applied as a quantity evaluation of uniformity. The b.c. lattice also has the minimum value of  $R_c/R_d = 0.646$  for a three-dimensional periodic lattice (Galiulin, 1984). It should be noted that the above-mentioned criteria of uniformity can be applied only to the limited set of MRSs, when all points are crystallographically equivalent ( $N = 1$ ). When  $N > 1$ , it is necessary to take into account the difference of forms and sizes of atomic domains.

We suggest the evaluation of the standard deviation of a quantizer (Conway & Sloane, 1988), *i.e.* the lattice laid on the continuous space  $\mathbf{R}^n$ , the coordinates of each point in  $\mathbf{R}^n$  being rounded to those of the nearest point  $\mathbf{p}_i$  of the lattice, as the quantity criterion of  $\mathbf{M}^3$  space uniformity. Thus, all points inside  $\Pi(\mathbf{p}_i)$  are assumed to be equal to  $\mathbf{p}_i$ . The value of the standard deviation of a quantizer is measured by the distance between  $\mathbf{p}_i$  and a point, whose coordinates are rounded. For the quantitative expression of an error that is introduced by a quantizer, the evaluation of the average value of the standard deviation is used, which is normalized on the space dimension ( $n$ ) and the VDP volume  $V[\Pi(\mathbf{p}_i)]$  (Conway & Sloane, 1988):

$$G_n = \frac{1}{n} \frac{(1/N) \sum_{i=1}^N \int_{\Pi(\mathbf{p}_i)} r_i^2 dV[\Pi(\mathbf{p}_i)]}{\left\{ (1/N) \sum_{i=1}^N V[\Pi(\mathbf{p}_i)] \right\}^{1+2/n}} \quad (6)$$

Henceforth, we assume that everywhere the quantizer coincides with the MRS. In this case,  $N$  is the number of base atoms in a unit cell and  $r_i$  is the distance between the  $\Pi(\mathbf{p}_i)$  point and the corresponding atom  $\mathbf{p}_i$ .

In a particular case, when the MRS point coincides with the gravity centre of its VDP,  $G_3$  is equal to the dimensionless second moment of inertia of a polyhedron (Conway & Sloane, 1988). The quantizer, whose points are most uniformly arranged relative to the space, has the minimum  $G_3$  value. The best known lattice quantizer for

$\mathbf{R}^3$  is a b.c. lattice (Conway & Sloane, 1988) with  $G_3 = 0.07854$ .

$G_3$  is an integral parameter, which at the same time takes into account a number of  $\mathbf{M}^3$  characteristics connected with  $\mathbf{M}^3$  uniformity. Let us consider some of them, using terminology customary to crystal chemists.

(1) The spread in values of interatomic distances in  $\text{CP}(\mathbf{p}_i)$ , which are equal to the doubled values of the shortest distances between atom  $\mathbf{p}_i$  and the  $\Pi(\mathbf{p}_i)$  faces.

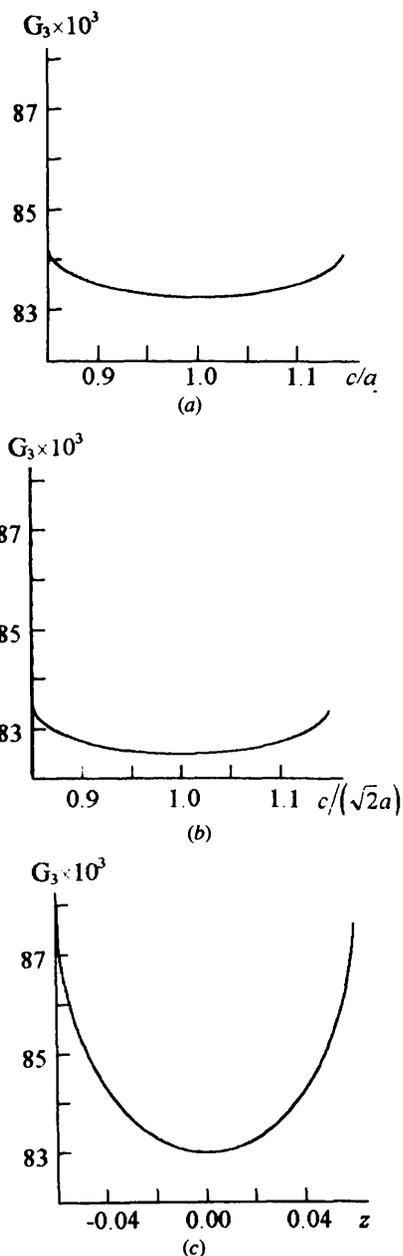


Fig. 3. Value of  $G_3$  for (a) a tetragonal prism versus the value of ratio  $c/a$ , (b) a tetragonal bipyramid versus the value of ratio  $c/2^{1/2}a$ , and (c) for a cube versus the value of shift ( $z$ ) of the central atom from the cube centre of gravity.

Table 3.  $G_3$  and  $R_c/\rho$  values for regular polyhedra and a sphere

Polyhedron	$R_c/\rho$	$G_3(\times 10^3)$
Tetrahedron	3.000	104.00
Cube	1.732	83.33
Octahedron	1.732	82.55
Dodecahedron	1.258	78.13
Icosahedron	1.258	77.82
Sphere	1.000	76.97

For example, in Fig. 3(a) the function of  $G_3$  of VDP, possessing the form of a square prism, versus the ratio of the prism height ( $c$ ) to the length of its base edge ( $a$ ), is given. Fig. 3(a) shows that the minimum value  $G_3 = 0.08333$  conforms to the ratio  $c/a = 1$  when the VDP of an atom transforms into a cube and all six distances in  $\text{CP}(\mathbf{p}_i)$  (an octahedron) coincide in value. Increasing or decreasing the ratio  $c/a$  in comparison with the above-mentioned value is followed by tetragonal distortion of the octahedron and the corresponding appearance of four nearer ( $4 + 2$  coordination) or farther ( $2 + 4$  coordination) neighbours in the coordination sphere of the atom, the result of which is the increase of the  $G_3$  value.

(2) The spread in values of distances between atoms, considered as hard oscillating spheres, and the centres of structure holes (*i.e.* VDP vertices). Let us illustrate the influence of this factor, using the example of VDP in the form of a tetragonal bipyramid with different values of the ratio  $c/a$ , conforming to the tetragonal-prismatic environment of the central atom. In this case, all distances from the central atom to the eight atoms of its first coordination sphere are equal for any values of  $c/a$ , whereas the spread in distances to the centres of the holes (*i.e.* six vertices of the bipyramid) depends on the value of  $c/a$ . Fig. 3(b) shows that the minimum value  $G_3 = 0.08255$  conforms to a VDP in the form of a regular octahedron ( $c/a = 1.414$ ).

(3) The value of the ratio  $R_c/\rho$ , where  $R_c$  and  $\rho$  are the radii of spheres described and inscribed in a VDP, respectively, is used to evaluate the degree of polyhedron sphericity, since in the limiting case the polyhedron with an infinite number of faces, existing at equal distances from the central atom, degenerates into a sphere, whose  $R_c/\rho$  value is minimum and equal to 1. The correlation of the second moment of the VDP and the ratio  $R_c/\rho$  is visible in a number of Platonic solids (Table 3), whose faces and vertices are equivalent to each other, and the above-mentioned factors (1) and (2) do not allow the differences in uniformity of structures containing polyhedra of this type to be revealed. It should be mentioned that the value of  $R_c/\rho$  is identical for dual polyhedra (Table 3), whereas the  $G_3$  value decreases when the number of polyhedron faces increases. The data in Table 3 also demonstrate the possibility of using the characteristic  $G_3$  for the quantity evaluation of the degree of VDP sphericity, since a sphere possesses the minimum  $G_3$  value among all three-dimensional solids.

Table 4.  $G_3$  values for polymorphous modifications of some metals

Poly-morphous modification	Temperature (K)*	$G_3(\times 10^3)$	Poly-morphous modification	Temperature (K)*	$G_3(\times 10^3)$
$\alpha$ -Ga	†	85.67	$\alpha$ -Pu	<394	80.67
$\beta$ -Ga†	110	81.01	$\beta$ -Pu	394–478	79.09
$\alpha$ -Mn	<980	78.94	$\gamma$ -Pu	478–588	78.90
$\beta$ -Mn†	298	79.21	$\delta$ -Pu	588–741	78.74
$\gamma$ -Mn	1358–1373	78.74	$\delta'$ -Pu	741–754	78.56
$\gamma'$ -Mn	1373–1410	78.74	$\epsilon$ -Pu†	>754	78.54
$\delta$ -Mn†	>1410	78.54	$\alpha$ -Sn	<286	91.15
$\alpha$ -Np	<551	81.00	$\beta$ -Sn†	>286	81.10
$\beta$ -Np	551–813	79.51	$\alpha$ -U	<933	79.43
$\gamma$ -Np†	>813	78.54	$\beta$ -U	933–1033	78.83
$\alpha$ -Po	<348	83.33	$\gamma$ -U†	>1033	78.54
$\beta$ -Po†	>348	81.86	$\alpha$ -W	†	78.54
			$\beta$ -W†	923	78.54

\* Data from Tonkov (1979).

† Phase remains stable up to the melting point.

‡ Metastable phase. The temperature is given at which the structural experiment was performed.

(4) The value of the central atom shift from the VDP centre of gravity. Let us consider a VDP in the cubic form, where the central atom is shifted from the centre of gravity towards a face by  $z$ , the value of which is expressed in fractions of the cube edge. The analysis of  $G_3$  versus  $z$  (Fig. 3c) demonstrates that the most uniform arrangement around the central atom is realized when  $z = 0$ , while, when  $|z| \rightarrow 0.5$ , the  $G_3$  value increases greatly.

The given examples indicate that  $G_3$  describes the features of  $M^3$  uniformity in more detail than any of the above-mentioned parameters. Indeed, the criterion, demanding the minimum of the ratio of covering ( $R_c$ ) to discreteness ( $R_d$ ) parameters for structures with a single crystallographic type of atom, is analogous to the above-mentioned factor (3) (since  $R_d = 2\rho$ ) and therefore it is part of the characteristic  $G_3$ . In turn, the criterion of  $R_c/R_d$  minimum includes the condition of  $K_c$  minimum (and also the condition of packing coefficient  $K_p$  maximum) since

$$\begin{aligned} R_c/R_d &= \frac{1}{2}[R_c/\rho] \\ &= \frac{1}{2} \left( \frac{\frac{4}{3}\pi R_c^3/V[\Pi(\mathbf{p}_i)]}{\frac{4}{3}\pi \rho^3/V[\Pi(\mathbf{p}_i)]} \right)^{1/3} \\ &= \frac{1}{2} [K_c/K_p]^{1/3}. \end{aligned} \quad (7)$$

The described method was used by Blatov, Pol'kin & Serezhkin (1994) for the evaluation of the uniformity of crystal structures of simple substances under thermal phase transitions and also versus the position of the corresponding element in the Periodic Table. Thus, Table 4 shows that the value of  $G_3$  regularly decreases (and consequently the structure uniformity increases) with the temperature increase in all known polymorphous sequences of metals (including the case of such long series as  $\alpha$ -Pu, . . . ,  $\epsilon$ -Pu) with the exception of sequences containing modifications that are metastable under the condition of the structure experiment (such as  $\beta$ -Ga,

$\beta$ -Mn and  $\beta$ -W). Fig. 4 demonstrates the increase of uniformity of crystal structures with the growth of the atomic number of an element in the principal subgroups of the Periodic Table. This fact may be interpreted as a result of the increase of metallic properties of elements and the corresponding growth of the portion of undirected interactions in the whole energy of the crystal lattice. The obtained results have permitted the following principle of crystal lattice uniformity to be formulated: in a thermodynamically stable structure, the atoms and atomic groups, among which the non-directional forces act, try to arrange themselves in space so that the minimum  $G_3$  value will conform to the system of their gravity centres. In our opinion, the uniformity principle expands the principle of maximum space filling (Vainshtein, Fridkin & Indenbom, 1983), resting on the same physical foundations. We assume that the principle of uniformity should also be performed for polymorphous rows of more complex compounds, but evidently in this case striving for uniform arrangement will be typical in structural groups, not in individual atoms.

#### 4. Concluding remarks

In this paper, we considered several methods of topological crystal chemistry. In future publications we

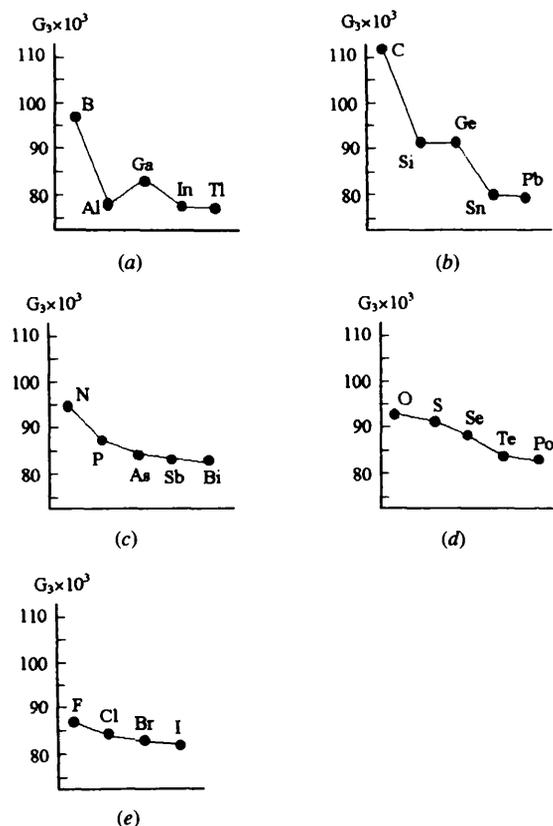


Fig. 4. Values of  $G_3$  for structures of elements of (a) III, (b) IV, (c) V, (d) VI and (e) VII principal subgroups of the Periodic Table.

intend to describe other methods of investigation of local and global geometrical/topological properties of  $M^3$  and also to illustrate each of the suggested methods by examples of the crystal-chemical analysis of various classes of substances and some model systems.

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## Uninodal 4-Connected 3D Nets. III. Nets with Three or Four 4-Rings at a Vertex

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### Abstract

A description is given of 4-connected nets with one kind of vertex in which at least three of the shortest rings containing each pair of edges are 4-rings. 21 such nets are identified and characterized topologically. Some correspond to well known zeolite structures, but most are believed to be new.

### Introduction

This paper continues a description and characterization of 4-connected nets with one kind of vertex (uninodal). Previous papers described nets without 4-rings or 3-rings (O'Keeffe & Brese, 1992) and with 3-rings (O'Keeffe, 1992). Only nets (realizable nets) that have a conformation with four equal edges corresponding to shortest distances between vertices are considered. The reader is referred to O'Keeffe & Brese (1992) for an account of how the nets were discovered, other criteria for inclusion,

Table 1. Correspondence of the numbering of nets in this paper (first column) with earlier names and numbers

The three-letter code is that of Meier & Olson (1992).				
44	#16	W*8	–	O'Keeffe (1991)
45	#13	D8	–	O'Keeffe (1991)
46	203	Faujasite	FAU	Smith & Bennett (1981)
47	202	Zeolite type A	LTA	Smith & Bennett (1981)
48	206	Zeolite rho	RHO	Smith & Bennett (1981)
49	83	Chabazite	CHA	Smith (1978)
50	205	Zeolite ZK5	KFI	Smith & Bennett (1981)
51	82	Gmelinite	GME	Smith (1978)
52	23	Gismondine	GIS	Smith (1978)
53	17	Merlinoite	MER	Smith (1978)
55	46	–	–	Smith (1978)
63	49	–	–	Smith (1978)

and for definitions of terms such as 'coordination sequence' and 'Schläfli symbol' that are used here. That paper also indicates why the data presented here are of interest and are expected to be reasonably complete. It might be noted that other recent enumerations of 4-connected nets (*e.g.* Han & Smith, 1994; Boisen, Gibbs