

Analysis of migration paths in fast-ion conductors with Voronoi–Dirichlet partition

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Received 1 July 2006

Accepted 26 September 2006

In terms of the Voronoi–Dirichlet partition of the crystal space, definitions are given for such concepts as ‘void’, ‘channel’ and ‘migration path’ for inorganic structures with three-dimensional networks of chemical bonds. A number of criteria are proposed for selecting significant voids and migration channels for alkali cations Li^+ – Cs^+ based on the average characteristics of the Voronoi–Dirichlet polyhedra for alkali metals in oxygen-containing compounds. A general algorithm to analyze the voids in crystal structures has been developed and implemented in the computer package *TOPOS*. This approach was used to predict the positions of Li^+ and Na^+ cations and to analyze their possible migration paths in the solid superionic materials $\text{Li}_3\text{M}_2\text{P}_3\text{O}_{12}$ ($M = \text{Sc}, \text{Fe}$; LIPHOS) and $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ (NASICON), whose framework structures consist of connected M octahedra and T tetrahedra. Using this approach we determine the most probable places for charge carriers (coordinates of alkali cations) and the dimensionality of their conducting sublattice with high accuracy. The theoretically calculated coordinates of the alkali cations in MT frameworks are found to correlate to within 0.33 Å with experimental data for various phases of NASICON and LIPHOS. The proposed method of computer analysis is universal and suitable for investigating fast-ion conductors with other conducting components.

1. Introduction

Traditionally, analysis of the geometry and (to a smaller extent) the topology of atomic three-dimensional nets (Wells, 1986) has attracted much attention in inorganic crystal chemistry. At present, computer methods allow similar investigations for ‘empty’ (containing no atoms) crystal space considering the geometrical–topological properties of cavities and channel networks (Thomas, 1991; Adams & Swenson, 2002; Blatov & Shevchenko, 2003; Blatov *et al.*, 2005; Foster *et al.*, 2006; Küppers *et al.*, 2006). The properties of the ‘empty’ crystal space are important in many crystallochemical tasks and physical applications. The equivalent concept of excluded volume is well known in solid-state physics, enabling the migration paths for mobile ions to be modelled, for instance, in framework fast-ion conductors. Analysis of electron-density distributions in various superionic conductors shows that mobile particles easily migrate through the whole crystal, except the volume occupied by the framework ions (excluded volume). In the crystalline matrix a connected conducting space may be separated that consists of cavities, where ions are located for a long period of time, and of migration channels connecting the cavities. The geometrical properties of the

'empty' crystal space allow the study of the energetic peculiarities of the material responsible for the anomalously high ionic (superionic) conductivity (Hong, 1976):

(i) the number of energetically equivalent positions has to be larger than the number of mobile ions;

(ii) the ion-disordering energy and the energy of ion motion have to be small in comparison with the kT magnitude that, together with the first condition, leads to a random distribution of mobile ions over acceptable Wyckoff positions (voids). Topologically the 'empty' crystal space has to possess an infinite network of channels to provide the ion migration through the material.

The geometrical-topological analysis of the 'empty' crystal space can be performed by various modifications of the 'grid' methods (Thomas, 1991; Adams & Swenson, 2002; Küppers *et al.*, 2006), by constructing the Voronoi–Dirichlet partition (Niggli, 1927; Fischer, 1986; Blatov & Shevchenko, 2003) or the dual Delaunay partition (Foster *et al.*, 2006). The main restrictions of the 'grid' methods are:

(i) they ordinarily use the 'spherical-atom' model and the atomic radii must be dependent on the nature of the chemical bonding;

(ii) the precision of their results depends on the grid density. For instance, this model leads to 'cusp' areas appearing around the cavity (Küppers *et al.*, 2006). The Voronoi–Dirichlet approach seems to be more useful because many parameters of the atomic Voronoi–Dirichlet polyhedra (VDP) have a clear physical meaning (Blatov, 2004). Also the Voronoi–Dirichlet partition naturally maps onto the system of cavities and channels (Fischer, 1986). It is the polyhedral representation that closely conforms to the real shape of an atom in the non-spherical crystal field (Zou & Bader, 1994; Blatov, 2004). Moreover, this representation naturally results in two interpenetrating three-dimensional graphs; graphs of atomic and void nets, whose nodes symbolize atoms and void centres, and whose edges correspond to the interatomic bonds and possible channels, respectively. The usefulness of this approach has been known for some time (Niggli, 1927; Fischer, 1986), but it has only been applied to some simple and high-symmetry structures. Recently it was implemented in the computer package *TOPOS* and successfully used to study microporous crystal structures of various types (Blatov & Shevchenko, 2003; Blatov *et al.*, 2005). However, the main focus was on the analysis of cavities; the possibility of analyzing the connecting channels was hardly mentioned.

In this work we consider in detail the basic problems of applying the Voronoi–Dirichlet partition to the analysis of solid superionic materials, using the example of the framework structures of $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ (NASICON) and

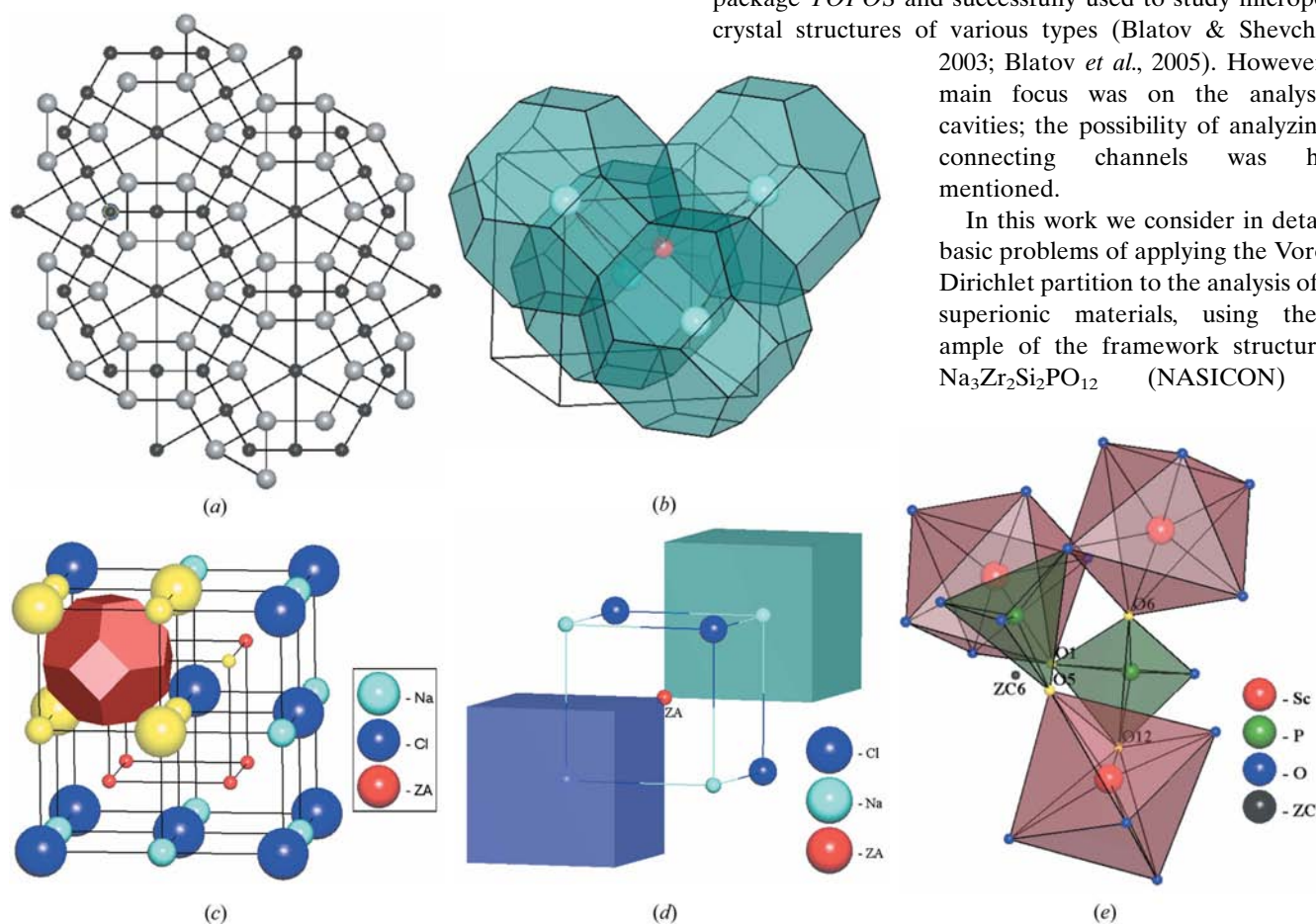


Figure 1

(a) The Shubnikov plane net 3464 (grey balls) and the corresponding net of voids (black balls). (b) Four VDPs meeting in the same vertex (red ball) in a b.c.c. (body-centred cubic) lattice. (c) The form of an elementary void in the NaCl crystal structure. All environmental atoms and one void are yellow; $R_{\text{sd}} = 1.38 \text{ \AA}$, $G_3 = 0.07854$. (d) A major elementary void (ZA) in the NaCl crystal structure. VDPs of Na and Cl ions are selected. (e) A minor void (ZC6) located outside the tetrahedron of the yellow atoms O1, O5, O6 and O12 determining this void in the crystal structure of $\alpha\text{-Li}_3\text{Sc}_2\text{P}_3\text{O}_{12}$. All distances from ZC6 to the O atoms are equal to 2.298 \AA .

$\text{Li}_3\text{M}_2\text{P}_2\text{O}_{12}$ (LIPHOS; $M = \text{Sc}, \text{Fe}$), which consist of connected M octahedra and T tetrahedra. The main goals were to define the selection criteria for significant cavities and channels, and to determine the most probable positions of the alkali cations together with their migration paths. We also intended to evaluate the predictability of the method by comparing the generated models of channel systems with the data of X-ray experiments and conductivity measurements for a number of superionic conductors.

2. Terminology and general principles of analyzing cavities and channels

The basic concepts used to describe the cavities and channels in terms of the Voronoi–Dirichlet partition are *elementary voids* and *elementary channels*. Recall that the Voronoi–Dirichlet partition is a normal (face-to-face) partition of crystal space by VDPs, *i.e.* by the polyhedra constructed around atoms in such a way that each internal point of a VDP is closer to the internal atom than to other atoms. All the VDP vertices and edges in the Voronoi–Dirichlet partition form a three-dimensional graph: the *Voronoi–Dirichlet graph* (*cf.* Fischer, 1986).

2.1. Properties and classification of elementary voids

The *elementary void* is a region of crystal space with its centre on a vertex of an atom VDP. The atoms whose VDPs meet in the centre of a given elementary void are referred to as atoms *determining* the elementary void; these atoms are equidistant to the void centre. The properties of elementary voids are mainly determined by the features of the Voronoi–Dirichlet partition.

(i) In a two-dimensional net the centre of an elementary void is surrounded by no less than three noncollinear atoms at the same distances (Fig. 1*a*). In the three-dimensional case the elementary void is equidistant to at least four noncoplanar atoms (tetrahedral void) since in a three-dimensional Voronoi–Dirichlet partition no less than four VDPs meet in the same vertex (Fig. 1*b*).

(ii) Besides the atoms determining the elementary void, there are additional atoms at longer distances that can strongly influence the geometrical parameters of the elementary void, in particular, its size and shape. To find these parameters one should construct the void VDP, taking into account all atoms and other symmetrically equivalent elementary voids (Fig. 1*c*). Let us name the atoms and voids participating in the VDP formation *environmental*. Obviously, the atoms determining the elementary void are always environmental. Thus, in the crystal structure of NaCl all environmental ions determine the elementary void (Fig. 1*c*). Physically, the void VDP reflects the size and shape of an atom that could occupy the void, which is in contact with all the environmental atoms. Since other equivalent elementary voids would also be occupied in this case, they form the void VDP along with environmental atoms.

(iii) The *radius* of the elementary void (R_{sd}) is the radius of the sphere, whose volume is equal to the volume of the void VDP which is constructed taking into account all the environmental atoms and voids. Physically, the radius of the elementary void corresponds to the radius of an atom that can be located in the void under the influence of the crystal field distorting the spherical shape of the atom. Let us emphasize that this parameter is used only to characterize the void volume; it does not mean that the void is considered to be spherical. In the Voronoi–Dirichlet approach the voids (and atoms) have polyhedral shape and fill the whole space, which is in contrast to the model of the spherical atom used in the ‘grid’ methods (Thomas, 1991; Küppers *et al.*, 2006).

(iv) The *shape* of the elementary void is determined by the void VDP which is constructed with all the environmental atoms and voids (Fig. 1*c*). It is estimated to be the dimensionless-normalized second moment of inertia of the VDP (G_3). The more spherical the elementary void, the lower the G_3 value; the sphere has a minimum G_3 value of 0.07697. We assume that an elementary void is essentially distorted if $G_3 > 0.10$. The distorted voids are hardly accessible even though they are a reasonable size.

There are two kinds of elementary void: *major*, if its centre is located inside the polyhedron, whose vertices coincide with the atoms determining the elementary void (for instance, inside the tetrahedron for a tetrahedral void, Fig. 1*b*, or inside the cube in the NaCl crystal structure, Fig. 1*d*); and *minor*, if its centre lies outside or on the boundary of the polyhedron (Fig. 1*e*).

The physical sense of the major elementary voids means that they usually correspond to real cavities and cages in framework structures. Minor elementary voids often correspond to transition regions between cavities, for instance, to channel necks.

2.2. Properties and classification of elementary channels

The *elementary channel* is a space belonging to two elementary voids; the channel connects the voids and corresponds to a VDP edge; the VDP refers to an atom determining either of the voids. Such an edge is termed a *line* of the elementary channel. Accordingly, the atoms *determining* the elementary channel are those atoms whose VDPs have a common edge coinciding with the channel line (Fig. 2*a*). The properties of elementary channels are similar to the properties of elementary voids.

(i) Generally speaking, each elementary channel is determined by at least three noncollinear atoms, since in the Voronoi–Dirichlet partition each VDP edge is shared by no less than three VDPs. The plane passing through these atoms is perpendicular to the line of the elementary channel (Fig. 2*a*).

(ii) The *section* of the elementary channel is a polygon whose vertices are the atoms determining the channel; the section always corresponds to the narrowest part of the channel. The line of the elementary channel is always

perpendicular to its section; ordinarily, the channel section and the channel itself are triangular (Figs. 2*a* and *b*).

(iii) The *radius* of the elementary channel section is estimated to be the geometric mean for the distances from the barycentre of the elementary channel section to the atoms determining the channel. In fact, the radius corresponds to an average distance from the centres of the atoms surrounding the channel to the centre of an atom passing through it. An atom can freely pass through the channel if the sum of its radius and the average radius of the atoms determining the channel does not exceed the channel radius.

(iv) The *length* of the elementary channel is the distance between the elementary voids connected by the channel, *i.e.* is the length of the corresponding VDP edge.

An elementary channel can be of two types: (i) *major* if its line intersects its section (Fig. 2*a*) and (ii) *minor* if the line and section have no common points, or one of the line ends lies on the section (Fig. 2*b*).

With respect to the ion-transport processes in fast-ion conductors, the major elementary channels correspond to the most spacious parts of the real migration channels; the minor elementary channels ordinarily connect the major elementary channels and relate to the bends of the migration paths.

2.3. Terminology for the systems of elementary voids and channels

The following terms define the properties of the systems of elementary voids and channels.

(i) The '*significant*' elementary void and the '*significant*' elementary channel are accessible voids and channels for mobile particles within the scope of a given task. In the present work the cationic conductors are studied and the elementary voids and channels which are accessible for cations are assumed to be significant. If the superionic conductors

with anionic conductivity, molecular sieves or other substances with different mobile particles are under consideration, then an additional definition of the 'significance' is required. Only significant voids and channels are important in the analysis of superionic conductors; other elementary voids and channels should be ignored. Significant voids and channels are referred to as *probabilistic* if the migration of particles through them is not forbidden, but is hindered for some reason. The criteria for determining probabilistic voids and channels depend on the problem to be solved.

(ii) The *migration channel* for mobile particles is a set of significant elementary voids and elementary channels connecting the voids. The passage defined in this way provides charge transport in fast-ion conductors. If the migration channel contains no probabilistic elementary voids and channels, the ion transport is not bottle-necked and a high ionic conductivity can be expected at the temperature of the structural experiment; otherwise the conductivity is at a high temperature.

(iii) The *migration path* of mobile particles is a set of elementary void centres and channel lines which compose the migration channel (*cf.* Fischer, 1986). Thus, the migration path unambiguously corresponds to a migration channel and is a graph whose vertices and edges correspond to elementary void centres and elementary channel lines. To provide conductivity, the migration path has to be infinite (one-dimensional, two-dimensional or three-dimensional), otherwise the mobile ions will be located in finite zero-dimensional cages. Thus, the infinite migration paths are of special interest in the analysis of the electrical properties of superionic conductors. Obviously, an infinite migration path has to be formed by the elementary voids being incident to at least two elementary channels, otherwise the elementary void would be a dead end in the migration path, or even isolated.

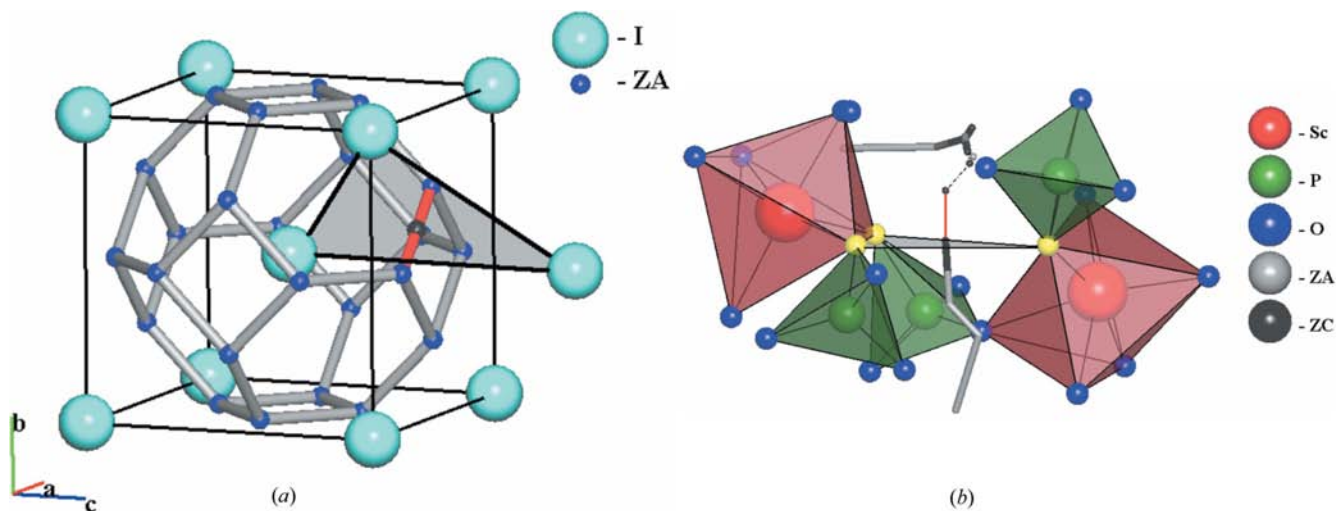


Figure 2

(*a*) Section of a triangular major elementary channel in the crystal structure of α -AgI. The channel line is red. The atoms determining the channel are at the vertices of the triangular section. The channel line intersects the section in the black ball. (*b*) Fragment of the channel system in the crystal structure of α -Li₃Sc₂(PO₄)₃. The line of a minor elementary channel is red, the O atoms determining this channel are yellow. Other minor elementary channels are shown by dashed lines. The line does not intersect the shaded triangular section.

Table 1

Average geometrical parameters of VDPs for alkali and alkaline-earth cations (Blatov, 2004).

Atom	$V_{\text{VDP}} (\text{Å}^3)$	$R_{\text{sd}} (\text{Å})$	$G_3 \times 10^3$	Atom	$V_{\text{VDP}} (\text{Å}^3)$	$R_{\text{sd}} (\text{Å})$	$G_3 \times 10^3$
Li	11.1 (1)	1.38 (1)	89.1 (6)	Be	7.3 (1)	1.20 (1)	99.8 (5)
Na	15.2 (1)	1.54 (1)	84.5 (1)	Mg	9.3 (1)	1.30 (1)	84.4 (2)
K	20.8 (1)	1.70 (1)	81.9 (1)	Ca	13.3 (1)	1.47 (1)	83.0 (1)
Rb	23.4 (2)	1.78 (1)	81.1 (2)	Sr	15.7 (1)	1.55 (1)	81.5 (2)
Cs	27.7 (2)	1.88 (1)	80.8 (2)	Ba	18.6 (1)	1.64 (1)	80.6 (1)

(iv) All migration paths form a *conduction pattern* of the substance (*cf.* Fischer, 1986). The dimensionality of the conduction pattern determines the dimensionality of the conductivity (one-dimensional, two-dimensional or three-dimensional).

2.4. Computer implementation of the method

The Voronoi–Dirichlet approach has been implemented in the program package *TOPOS* (Blatov, 2004) for multipurpose crystallochemical analysis. The program *Dirichlet*, a part of the package, provides the following operations:

- (i) constructing VDPs for all the independent framework atoms, *i.e.* a Voronoi–Dirichlet partition of the crystal space (interstitial particles including mobile ions are omitted);
- (ii) determining the coordinates for all the independent vertices of atomic VDPs and, as a result, the coordinates of all the elementary voids;
- (iii) determining all the independent VDP edges and, hence, all the elementary channels;

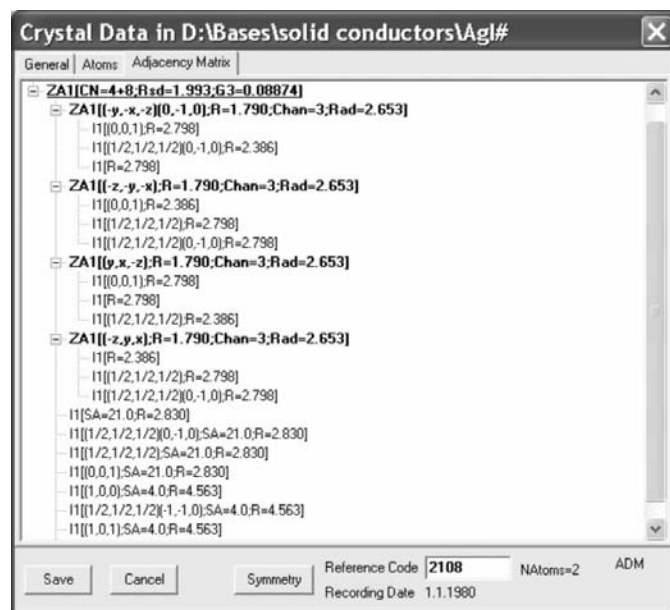


Figure 3
A *TOPOS* window containing the information on the adjacency matrix of the Voronoi–Dirichlet graph for α -AgI.

(iv) calculating the numerical parameters of the elementary voids and channels.

Information on the resulting conduction pattern is stored as a three-level adjacency matrix of the Voronoi–Dirichlet graph (Fig. 3).

The first level contains information on a reference elementary void. A major elementary void is designated as ZA, a minor one is marked as ZB or ZC if it lies on the boundary or outside, respectively, the polyhedron of the atoms determining the void. The void radius (R_{sd} , Å)

and second moment of inertia of its VDP (G_3) are also shown.

The second level gives information on other elementary voids connected to the reference void by channels, and on the environmental atoms. Every elementary void is characterized by the length (**R**, Å) of the elementary channel connecting it to the reference void, by the number of channel atoms (**Chan**) and by the channel radius (**Rad**, Å). If a channel is major, the text is marked as bold, otherwise a normal font is applied. Every environmental atom of the central void is characterized by the distance to the void centre (R , Å), and by the solid angle of the corresponding VDP face (SA as a percentage of 4π steradian); the greater the SA, the more significant the atom–void contact.

The third level contains information on the atoms determining the channel; the distances between the atoms and the centre of the channel section are also given.

A number of factors should be taken into account when determining the significant elementary voids and channels in solid electrolytes with cationic conductivity. An elementary void is significant if:

- (i) it is determined only by anions (for instance, by O or I atoms);
- (ii) the void radius and G_3 value conform to the average values for the cations (Table 1).

Obviously, if the void radius is greater than the radius of the cation, the void can store the cation. Moreover, if the G_3 value for the void is smaller or slightly greater than the G_3 value for the cation, the void is suitable by shape. If the value of G_3 is large ($G_3 > 0.1$), the void can only be a transfer point in a migration channel, *i.e.* is probabilistic. Besides, the environmental atoms of the void must be considered; the most significant voids have a purely anionic environment. If there are cations with SA > 5% in the environment, such a void cannot store cations permanently, even if it has a suitable volume and G_3 value. However, it can also serve as a transfer point, *i.e.* is probabilistic.

An elementary channel is significant if:

- (i) it is only determined by anions, and
- (ii) its radius is similar to a typical cation–anion distance (R_{ca}).

As in the case for voids, the first condition is unambiguous and determines the principal possibility of passing the cation through the channel; the channel radius characterizes the migration obstacles and is related to the migration energy. If R_{ca} is 10% or more greater than the channel radius, the channel is probabilistic.

3. Examples of the analysis

Below we consider how the method is applied to the study of ionic conductivity in some typical superionic conductors. In all the cases studied the alkali cations were removed from the structure before constructing the voids and channels.

3.1. NASICON $\text{Na}_4\text{Zr}_2(\text{SiO}_4)_3$

A high ionic conductivity in the $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ NASICON (NA-SuperIonic CONductor) phases was revealed by Hong (1976) when studying the $\text{NaZr}_2(\text{PO}_4)_3\text{--Na}_4\text{Zr}_2(\text{SiO}_4)_3$ system. The conductivity of the $\text{Na}_3\text{Zr}_2\text{PSi}_2\text{O}_{12}$ material was found to be similar to sodium β -alumina and is of great interest in the NASICON family.

The NASICON crystal structure is based on a three-dimensional $[\text{M}_2\text{T}_3\text{O}_{12}]_\infty$ framework consisting of $[\text{MO}_6]$ octahedra and $[\text{TO}_4]$ tetrahedra. All the O atoms are bridges between the octahedra and tetrahedra; each octahedron connects with six tetrahedra and each tetrahedron joins four octahedra (Fig. 4). Sodium ions occupy two Wyckoff positions: the Na1 ions belong to distorted $[\text{NaO}_6]$ octahedra and the Na2 ions lie in the framework cavities, each formed by ten O atoms. The rhombohedral NASICON phase was first investigated in detail for terminal representatives of the solid-solution series $\text{NaZr}_2\text{P}_3\text{O}_{12}$ ($x = 0$) and $\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}$ ($x = 3$). In the $\text{NaZr}_2\text{P}_3\text{O}_{12}$ crystal structure only Na cations are located in the octahedral Na1 positions, but in the $[\text{Zr}_2\text{Si}_3\text{O}_{12}]_\infty$

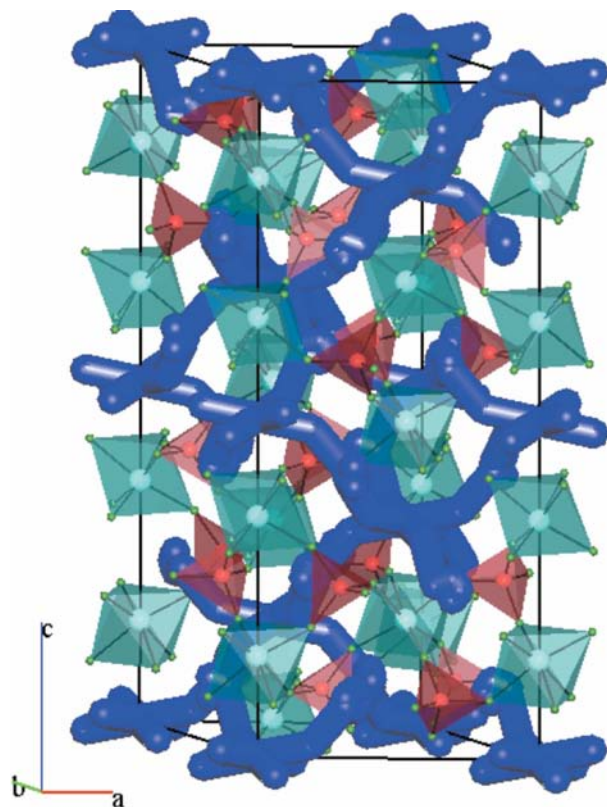


Figure 4
The $[\text{M}_2\text{T}_3\text{O}_{12}]_\infty$ framework and three-dimensional conduction pattern in the NASICON crystal structure.

framework the Na1 and Na2 positions are completely occupied. An increase in temperature leads to a significant decrease in the occupancy of the Na2 positions.

We used the crystallographic data for NASICON determined at 298 K (Kohler *et al.*, 1983). The following steps enabled us to construct the conduction pattern; this algorithm is the same for any fast-cation conductor.

(i) The Voronoi–Dirichlet partition gives 20 nonequivalent elementary voids in the $[\text{Zr}_2\text{Si}_3\text{O}_{12}]_\infty$ framework; eight of them are major and 12 are minor (Fig. 5*a*).

(ii) Insignificant elementary voids are then removed; all of them are minor (ZC1, 2, 4, 6, 8, 9, 11 and 12). For instance, the minor void ZC12 is insignificant, since there are zirconium cations among its determining atoms (1Zr + 3O with $R = 2.092 \text{ \AA}$; Fig. 5*b*). Three of the four elementary channels meeting in this void (ZC12–ZC1) are also insignificant, because zirconium cations participate in their formation. After removing the minor voids and renumbering the remaining

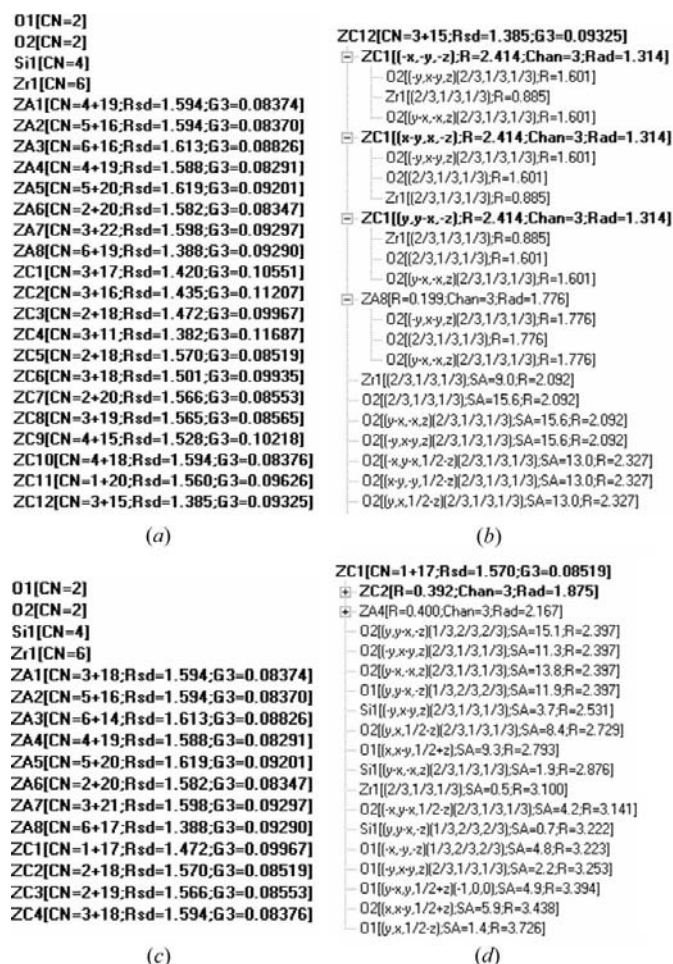


Figure 5
Fragments of TOPOS windows with the NASICON adjacency matrix containing (a) all elementary voids; (b) insignificant elementary void ZC12 and insignificant elementary channels ZC12–ZC1; (c) only significant voids and channels including probabilistic ones; (d) probabilistic channel ZC1–ZC2.

Table 2

Final list of framework atoms and voids in the NASICON crystal structure.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Void	<i>x</i>	<i>y</i>	<i>z</i>
O1	0.1855 (2)	0.1666 (1)	0.0850 (1)	ZA1	0.6669 (1)	0.9663 (1)	0.5774 (1)
O2	0.1842 (1)	0.9828 (2)	0.1912 (1)	ZA2	0.0000	0.0000	0.0000
Si	0.2969 (1)	0.0000	0.2500	ZA3	0.3592 (1)	0.3327 (1)	0.5686 (1)
Zr	0.0000	0.0000	0.1468 (1)	ZA4	0.5375 (1)	0.8501 (1)	0.6493 (1)
				ZA5	0.7168 (1)	0.0000	0.2500

ones (ZC3 → ZC1; ZC5 → ZC2; ZC7 → ZC3; ZC10 → ZC4), the list becomes as shown in Fig. 5(c).

(iii) The probabilistic voids should be revealed in the next step. If we consider the migration of Na⁺ cations at the temperature of the X-ray experiment (298 K), we should ignore such voids. If we are curious about the principal possibility of cation migration at an even higher temperature, the *R*_{sd} and *G*₃ values for the sodium cation should be taken from Table 1. In particular, the ZA8 and ZC1 voids (Fig. 5c) are probabilistic since their *R*_{sd} values are smaller than those for Na⁺. Note that the shapes of all the voids in Fig. 5(c) are rather spherical (*G*₃ < 0.1).

(iv) The probabilistic elementary channels should then be determined among significant ones. Let us assume that the typical Na⁺–O²⁻ distance is equal to the sum of their ionic radii and is estimated as *R*_{ca} = 2.35 Å. Hence, a channel will be probabilistic if its radius is smaller than *R*_{ca} – 0.1*R*_{ca} ≈ 2.1 Å. For instance, the ZC1–ZC2 channel is probabilistic (its radius is too small, 1.875 < 2.1 Å; Fig. 5d). After removing it only one (minor) channel (ZC1–ZA4) ends in ZC1. Thus, the ZC1 void cannot be part of an infinite migration path and should be ignored. As a result seven voids (ZA2, 7, 8; ZC1–4) were removed; the final list of voids after renumbering (ZA3 → ZA2; ZA4 → ZA3; ZA5 → ZA4; ZA6 → ZA5) is given in Table 2.

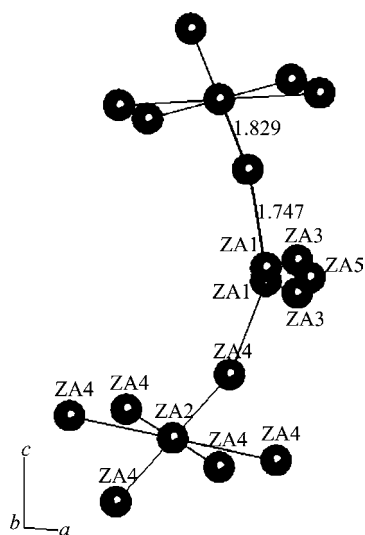


Figure 6

A fragment of the migration path in NASICON. The lengths (Å) of the elementary channels ZA1–ZA4 and ZA4–ZA2 are shown nearby.

(v) Visualization and analysis of migration paths in the program *IsoCryst* of the *TOPOS* package shows that they are infinite and three-dimensional (Fig. 4). Thus, the results obtained agree with the three-dimensional conductivity found in NASICON experimentally. Moreover, since probabilistic elementary voids and channels do not participate in the migration paths one can

expect a high conductivity at the temperature of the X-ray experiment, *i.e.* at room temperature. Also, the centres of the elementary voids ZA2 and ZA1 (Table 2) nearly coincide with the positions of two inequivalent Na cations which were determined experimentally (Kohler *et al.*, 1983): (0, 0, 0) and (2/3, 0.9722, 0.5833). A detailed analysis of the conduction pattern reveals the key role of the void ZA2 (Fig. 6); six channels of the length 1.83 Å and radius 2.11 Å meet in this void. At the same time the voids ZA3 and ZA5 play a secondary role, connecting the close-spaced ZA1 voids disordered over the special positions corresponding to Na cations. ZA4 voids join the ZA1 and ZA2 voids together, and can correspond to the temporary location sites of mobile ions while passing through the channels.

3.2. The LIPHOS family Li₃M₂(PO₄)₃

Superionic conductors were independently discovered among double lithium phosphates (LIPHOS), Li₃M₂(PO₄)₃ (*M* = Sc, Cr, Fe, In), by two research groups from Russia (Genkina *et al.*, 1983) and France (D'Yvoire *et al.*, 1983). The high conductivity of these materials is caused by mobile lithium ions and amounts to 10⁻² Ω⁻¹ cm⁻¹ at 573 K. As in many other superionic conductors the high conductivity of the Li₃M₂(PO₄)₃ materials is determined by the features of the crystal structure: the framework is formed by the [PO₄] tetrahedra and [MO₆] octahedra sharing vertices, and has a network of cavities. As in NASICON each tetrahedron is connected with four octahedra and each octahedron has common vertices with six tetrahedra, but the topology of the framework is not the same. The [M₂P₃O₁₂]^{3∞-} frameworks can have monoclinic or rhombohedral symmetry corresponding to low- (α) or high-temperature (γ) phases.

An analysis of the space distribution of cations in the Li₃Sc₂(PO₄)₃ phases (Bykov *et al.*, 1990; Suzuki *et al.*, 1998; Ivanov-Schits & Murin, 2000) showed that the preferable direction for ion transport is [001], *i.e.* the X-ray investigations confirmed the ionic conduction data. However, the question why the maximum conductivity direction is [100], not [001], in isostructural Li₃Fe₂(PO₄)₃ and Li₃In₂(PO₄)₃ is still unanswered. As was mentioned by Ivanov-Schits & Murin (2000), '... at present there is no clear explanation of this fact...'. Probably, real cation distributions in Li–Sc and Li–Fe phosphates are different since it is difficult to accurately locate lithium ions in high-temperature phases. To resolve this problem it is necessary to perform further precise investiga-

Table 3

 Comparing the positions of the centres of the elementary voids ZA and the coordinates of Li atoms in the crystal structures of $\text{Li}_3\text{M}_2(\text{PO}_4)_3$ ($M = \text{Sc}, \text{Fe}$).

Atom/ void centre	<i>x</i>	<i>y</i>	<i>z</i>	<i>R</i> (Li–ZA) (Å)	<i>x</i>	<i>y</i>	<i>z</i>	<i>R</i> (Li–ZA) (Å)
	$\alpha\text{-Li}_3\text{Sc}_2(\text{PO}_4)_3$ (Suzuki <i>et al.</i> , 1998)				$\alpha\text{-Li}_3\text{Fe}_2(\text{PO}_4)_3$ (Bykov <i>et al.</i> , 1990)			
Li1	0.2900	0.3230	0.2710	0.02	0.2950	0.3220	0.2760	0.03
ZA	0.2898	0.3216	0.2716		0.2945	0.3194	0.2752	
Li2	0.5820	0.1950	0.4070	0.33	0.5770	0.1930	0.4210	0.28
ZA	0.5837	0.2063	0.4414		0.5721	0.2040	0.4498	
Li3	0.9220	0.2460	0.2940	0.20	0.9120	0.2410	0.2970	0.30
ZA	0.9413	0.2394	0.3016		0.9433	0.2365	0.3098	

tions of the physical properties of $\text{Li}_3\text{M}_2(\text{PO}_4)_3$ crystals controlling composition, structure, and history of samples'. Below we present additional data for an interpretation of this contradiction.

We have analyzed in detail the crystal structures of $\text{Li}_3\text{M}_2(\text{PO}_4)_3$ ($M = \text{Sc}, \text{Fe}$; Bykov *et al.*, 1990; Suzuki *et al.*, 1998) for NASICON using the algorithm described above. In the low-temperature form of $\alpha\text{-Li}_3\text{Sc}_2(\text{PO}_4)_3$ there are 26 significant voids forming a three-dimensional conduction pattern. After removing the probabilistic voids and channels ($R_{\text{ca}} = 2.05 \text{ \AA}$ is applied for Li–O contacts) the two-dimensional (110) channel network is separated, where lithium ions pass most easily (Figs. 7*a* and *b*). The result obtained conforms to the experimental conductivity measurements for $\alpha\text{-Li}_3\text{Sc}_2(\text{PO}_4)_3$ (Bykov *et al.*, 1990), according to which conductivity along [001] is the largest among the three main crystallographic axes. This direction in fact lies inside the (110) plane with the channels most accessible for cation migration. At the same time one can also expect a high conductivity along $[\bar{1}10]$.

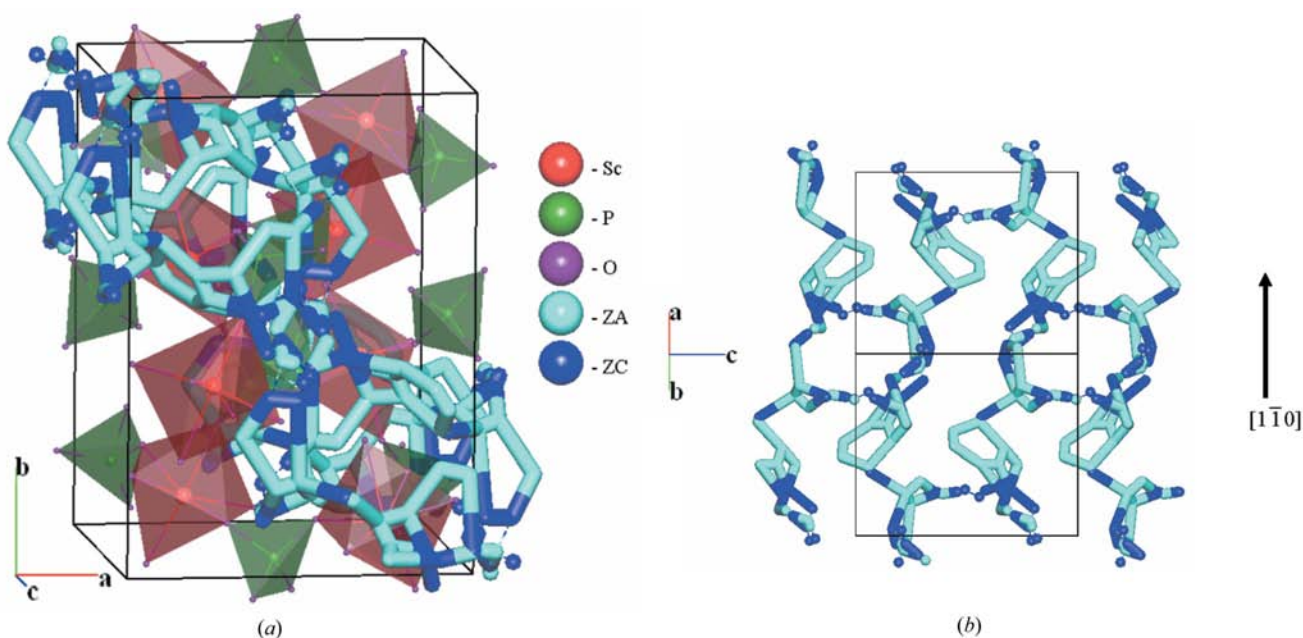
Our calculations have given a similar conduction pattern for $\alpha\text{-Li}_3\text{Fe}_2(\text{PO}_4)_3$, but the most accessible migration channels lie

in the $(\bar{1}10)$ plane with the fast transport axes [110] and [001] (Fig. 8). Thus, orientations of the conduction patterns in $\text{Li}_3\text{M}_2(\text{PO}_4)_3$ ($M = \text{Sc}, \text{Fe}$) are really different and additional conductivity measurements along the [110] and $[\bar{1}10]$ directions are required to elucidate the above-mentioned contradiction in the anisotropy of the conductivity.

Table 3 lists the coordinates of Li cations, according to Bykov *et al.* (1990) and Suzuki *et al.* (1998), compared with the positions of the calculated void centres. It is clear that the proposed method satisfactory fits the experimental data; the discrepancies do not exceed 0.33 Å.

4. Concluding remarks

The results obtained show that the Voronoi–Dirichlet partition allows strict definitions of such characteristics of superionic conductors as ‘void’, ‘channel’ and ‘migration path’, and determines their geometrical and topological parameters. In the proposed method the earlier approach of Fischer (1986) is developed and formalized for cation solid electrolytes of any complexity. The main advantages of the method over traditional ‘grid’ approaches (Thomas, 1991; Adams & Swenson,


Figure 7

(*a*) Atom framework and two-dimensional conduction pattern (110) constructed with only significant elementary voids and non-probabilistic channels in the crystal structure of $\alpha\text{-Li}_3\text{Sc}_2(\text{PO}_4)_3$. (*b*) A projection of the two-dimensional conduction pattern along $[\bar{1}10]$.

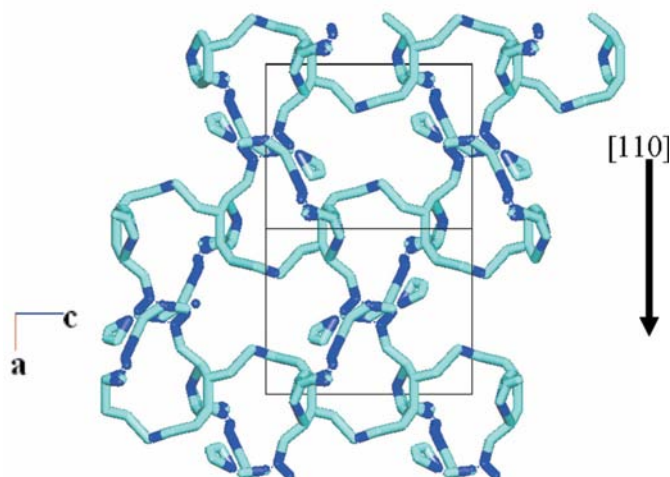


Figure 8
A projection along $[1\bar{1}0]$ of the two-dimensional conduction pattern constructed with only significant elementary voids and non-probabilistic channels in the crystal structure of α - $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$.

2002; Küppers *et al.*, 2006) are its independence of the system of ionic radii, and the application of topological criteria when determining the conduction pattern; the network of elementary channels follows the Voronoi–Dirichlet graph. An important reasoning for the method’s reliability is its implementation as a computer program working in an automated mode. Let us emphasize that the algorithm and basics of the analysis are independent of the nature of the superionic material; there are no principal obstacles to applying them in the investigations of anion conductors or molecular

substances. A demonstration of these abilities is the objective of a further study.

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