

Search for isotypism in crystal structures by means of the graph theory

V. A. Blatov

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

A method for the classification of crystal structures of chemical compounds is proposed, which is based on the representation of the system of interatomic bonds in a crystal as a finite 'reduced' graph. The program *IsoTest* is described, allowing one to find automatically the topological similarity (isotypism) for large groups of stoichiometrically and structurally different compounds. The analysis of crystal structures of simple and double sulfates and binary inorganic compounds was carried out and numerous examples of topological isotypism of the representatives of these groups of substances were found. It is shown that in many cases the ionic sublattices, constructed according to one of the close packings, can be selected in the sulfate crystal structures.

© 2000 International Union of Crystallography
Printed in Great Britain – all rights reserved

1. Introduction

The classification of crystal structures is one of the main problems of crystal chemistry. The most important step for its solution is the choice of the taxonomic system, which allows one to group compounds with similar features in their crystal structures. Most of the modern classification schemes are based on considering the space symmetry of a crystal and also of the short-distance atomic environment. Thus, the typical classification criteria are: belonging to the same space group, distribution of atoms or crystallographically nonequivalent structural groups on similar regular systems of points (Wyckoff sites) and identical coordination numbers of atoms. The first two criteria allow one to define the concepts of *isopointal structures* (Lima-de-Faria *et al.*, 1990) and of *structural class* (Belsky *et al.*, 1995); if the third is taken into account, then the concept of *structure type* can be introduced (Lima-de-Faria *et al.*, 1990). In other schemes, the main attention is paid to geometrical features of packing of structural units. They include the model of close packing of hard spheres and the model of cation matrices (Borisov & Podberyozskaya, 1984). All these methods of classification can be called 'geometrical' because their key criteria are the geometrical properties of a crystal structure. The concept of structure type provides the analysis of the system of interatomic bonds, however, within the first coordination sphere of atoms only. The technique of the crystal-chemical analysis, considering long-range coordination spheres, was proposed by Aslanov (1988) but it is also 'geometrical' because it is based on the analysis of the form of appropriate coordination polyhedra and is oriented towards the description of compounds with mainly nondirected interatomic interactions. The main problem of all 'geometrical' classification schemes is the complexity of the search for relations between compounds

whose crystal structures are distorted to some extent, although some progress in its solution has been achieved (Malinovskii *et al.*, 1998). At the same time, the contacts between structural groups are not frequently broken as a result of such distortion. Therefore, the kind of organization of the whole system of interatomic bonds in a crystal structure can be considered as the most important 'chemical' criterion for a crystal-chemical analysis. We shall call classification schemes that rely on this criterion '*topological*' because a certain topology specified on a set of atoms corresponds to each variant of such an organization. Note that the identification of interatomic contacts is a special crystal-chemical problem, which forms a bridge between geometrical and topological descriptions of crystal structure but is so far solved incompletely. We shall return to this problem in §3. For instance, the topological properties of atomic subnets have been taken into account in the descriptions of silicates (Liebau, 1985), alloys (Pearson, 1972) and clathrates (Wells, 1986). However, in these cases, the local topological properties are only considered (in particular, the size of silicon–oxygen circles in silicates, the topology of two-dimensional subnets selected in a three-dimensional framework in alloys, combinatorial topological properties of polyhedral cavities in clathrates *etc.*) and the description of crystal-structure topology as a whole usually is not given. The method of analysis of global topological properties of crystal structures and separate atomic subnets, which is widely used especially in crystal chemistry of zeolites (*Atlas of Zeolite Structure Types*, 1996), will be discussed in §2.

The global topology of a system of interatomic bonds in a crystal is completely specified by a three-dimensional infinite non-oriented graph, each vertex and edge of which correspond to an atom and an atomic interaction, respectively (Wells, 1977). Such a graph keeps information on all contacts between atomic domains or, in other words, on crystal space *connect-*

edness. However, within the framework of this model, the immediate analysis of only local topology is possible. For the study of the global topological properties and also for the machine representation of an infinite graph, it is convenient to use the method of reducing it to a finite 'reduced' graph (RG) or so-called labeled *quotient* graph, as was suggested by Chung *et al.* (1984). The operation of reducing can be visually represented by closing the edges of an infinite graph, which are extended outside or are on the boundary of a unit cell, to translationally identical vertices, being inside the unit cell or on its boundary (Fig. 1a). Apparently, the number of vertices of a RG obtained is equal to the number of atoms in the unit cell. Also, a RG can have loops and multiple edges. A loop or a multiple edge appears if there are bonds between two translationally equivalent atoms or between an atom and several atoms, which are translationally identical to each other. Algebraically, the operation of reducing corresponds to the decomposition of space group G on a subgroup of all translations T , resulting in generation of a factor group G/T . Then we neglect bond lengths and angles in a crystal structure, keeping its connectedness only. This enables one to draw a RG on a plane (Fig. 1b). Generally, each vertex of a RG corresponds to a primitive (without a basis) periodic subnet and each edge corresponds to a system of bonds between primitive subnets inserted into each other. Hereinafter, we use the term 'subnet' to pay attention to a system of interatomic bonds and the term 'sublattice' to emphasize that the topological properties are insignificant in such a context. According to Chung *et al.* (1984), it is necessary to mark properly the RG vertices, which are incident to loops and multiple edges to store the information on the topology of these subnets. For this purpose, let us select in each subnet an origin atom being inside a given unit cell and assign to it the code $(0, 0, 0)$. The codes of other atoms of a given subnet will correspond to the coordinates of the vector translations, which start at an origin atom. If there are bonds between atoms of different subnets, the edges of a RG must be labeled properly (Fig. 1b). Thus, a vector of labels is compared to each vertex and edge in a RG. A labeled RG describes an appropriate infinite graph accurate to isomorphism. It should be noted that this approach has been applied by Klee (1987) for analysis of the topology of polysilicate ions, *i.e.* when the vertices of a RG correspond to atoms of the same chemical sort. The quotient RGs were used, for which the labels were omitted, which resulted in the loss of a considerable part of the information on the topology of a crystal structure.

2. Search for topological similarity of 'reduced' graphs

Further, we shall consider the compounds with the same topology of crystal structure as representatives of the same *topological type*, irrespective of their chemical composition and space symmetry, and call them *topologically isotypic*. Note that this term gives emphasis to the topological properties of a system of interatomic bonds, unlike the terms '*configurationally isotypic*' and '*crystal-chemically isotypic*'

(Lima-de-Faria *et al.*, 1990), which are related to geometrical and/or physical properties of atomic sublattices.

As mentioned above, to find the topological isotypism of a pair of crystal structures, it is enough to answer the question whether the appropriate RGs are isomorphic to each other. However, during the crystal-chemical analysis, the search for compounds having some similarity in the crystal structure is more interesting than for the completely topologically isotypic compounds (it is trivial, as a rule). A method for the detailed analysis of RG topology and for the search of topological relationships between RGs is proposed below.

For example, let us consider the topological properties of crystal structures of binary compounds AX . RGs of such substances comprise vertices of two 'colors' corresponding to atoms of a different chemical nature, *i.e.* they are bipartite. Then let us divide a bipartite graph into two subgraphs, which contain vertices of the same color, keeping graph connected-

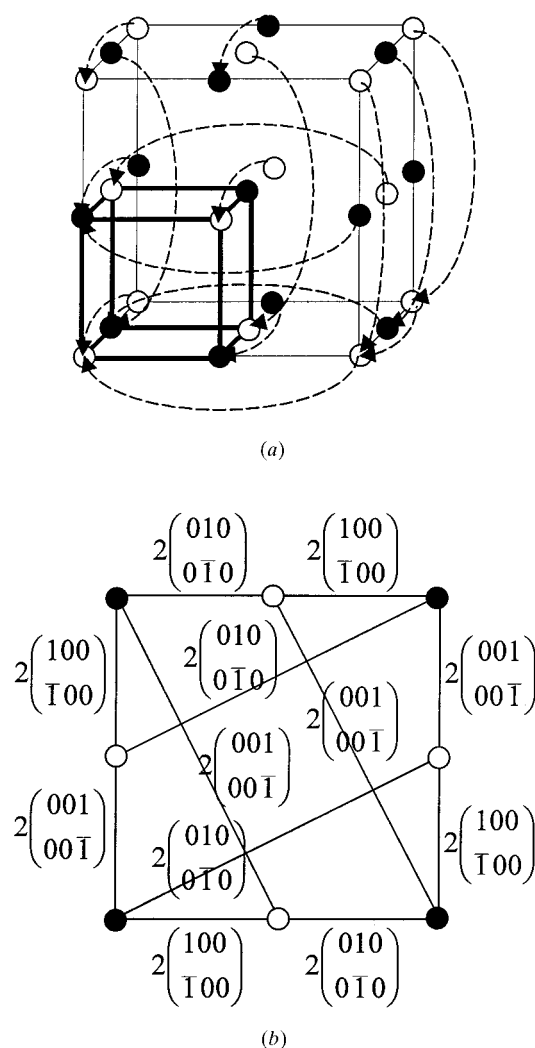


Figure 1
(a) Operation of reducing an infinite graph of NaCl. The arrows indicate the direction of the closing edges (edges are not drawn). The volume containing all vertices of a 'reduced' graph is shown. (b) The 'reduced' graph of NaCl. The multiplicity of each edge of the RG is equal to 2. Open circles Na, filled circles Cl.

ness. For this purpose, we shall make a division by contraction of graph edges or vertices (Fig. 2). Namely, we shall sequentially remove all vertices of one color, closing opened ends of edges. The division of a RG of NaCl is shown in Fig. 3. In terms of crystal chemistry, such an approach means a separate analysis of cationic and anionic sublattices. We shall call the graphs obtained 'lattice' graphs (LG) because they describe the topology of bond systems in atomic multilattices. A multilattice corresponding to a LG can comprise any subset of basis atoms (including ones with different chemical nature). For example, one can consider a RG as a special type of LG, which include all basis atoms of a crystal structure. If there is an infinite system of bonds between the contracted atoms (this means crystal-chemically the presence of infinite ligands in a crystal structure), the construction of LG of corresponding complexing atoms is impossible. We shall call such LGs *forbidden*. Thus, a set of LGs corresponds to each RG. This set includes the RG itself, all possible variants of selecting atomic sublattices in it and also forbidden LGs. The method of the division of the complete graph of a crystal structure into LGs enables one to find the topological similarity of separate atomic subnets in compounds whose structures are topologically different and, as will be shown below, to determine the

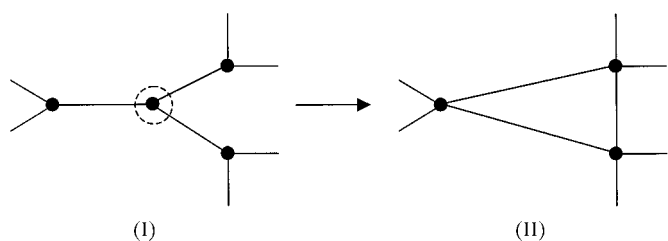


Figure 2
Procedure of contracting the graph fragment (I) to the fragment (II). The contracted vertex is marked.

relations between crystal structures of chemically and stoichiometrically different substances.

In terms of the graph theory, we consider a topological type as an abstract finite graph corresponding to a set of all mutually isomorphic RGs or LGs and also as an appropriate abstract infinite graph. A topological type is called by the name of one of its representatives, from which the ancestor of one of the known structure types can be selected. Note that we consider crystallographically nonequivalent atoms (also with different chemical nature) as atoms of the same *topological sort* if corresponding LGs are isomorphic. Thus, the role of the terms 'topological isotypism', 'topological type', 'topological sort of atoms' in this 'topological' scheme of classification is similar to the role of the terms 'isostructurality', 'structure type', 'crystallographic sort of atoms' in the 'geometrical' schemes.

In turn, several topological types can be combined into one *crystal-chemical group*. According to Serezhkin (1986), the crystal-chemical group includes the compounds with identical stoichiometric composition of complex groups, with the same relation of coordination centers and ligands of a given coordination type, with equal coordination numbers (CN) of complexing atoms, and also with equal maximum possible quantities $H_i = CN_A(CN_A - 1)$ of the complexing atoms A connected with a basis atom by all bridge ligands (CN_A is the number of ligands connected with the atom A). In terms of the graph theory, this means that the degree of a vertex of a LG conforming to a sublattice of complexing atoms of a compound cannot exceed an appropriate H_i value. In other words, the crystal-chemical group describes the local topology of a complex group within the first and second coordination spheres of complexing atoms. The degree of a LG vertex corresponds to the H_p quantity proposed by Serezhkin (1986) and can be calculated without taking into account the multiplicity of edges of an infinite graph (*i.e.* the multiplicity of

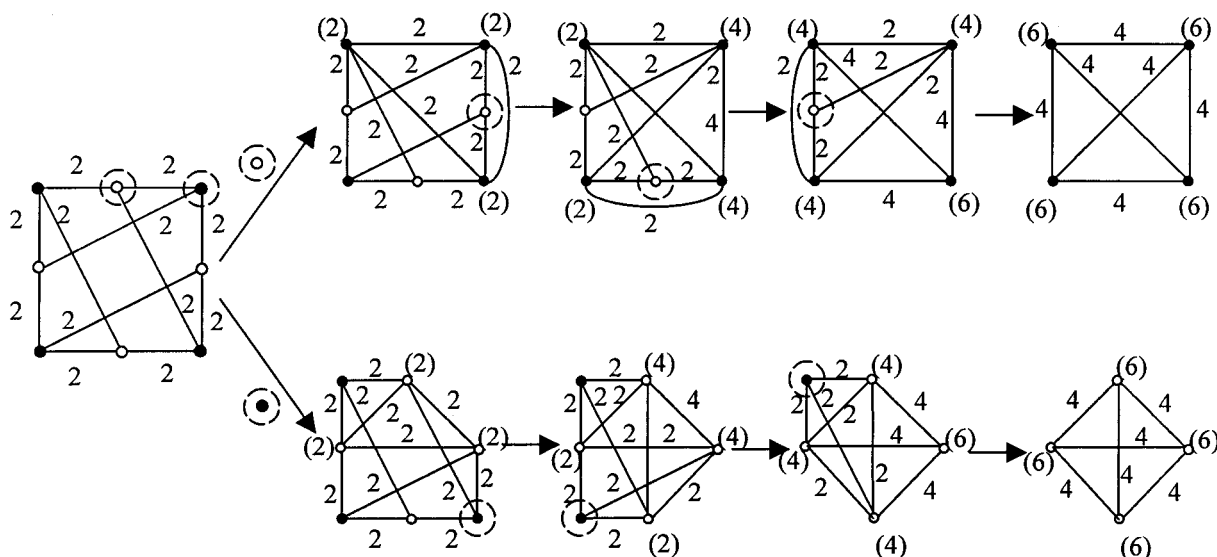


Figure 3
Dividing a 'reduced' graph of NaCl (see also Fig. 1) into the 'lattice' graphs by the operation of contracting its vertices. The numerals at vertices (in brackets) and at edges specify the number of loops and edge multiplicity, respectively. The dashed lines indicate removed vertices.

chemical bonds) according to the formula $H_p = v + e + f$, where the quantities v , e and f specify the number of coordination polyhedra with which the coordination polyhedron of an atom A shares vertices, edges and faces, respectively. H_p and H_i are connected by the formula

$$H_p = H_i - e - \sum_i (n_i - 1)f_i, \quad (1)$$

where n_i is the number of vertices of the i th face of a coordination polyhedron and f_i is the number of such faces.

The characteristics H_p , v , e and f can be used during the search of isomorphism of LGs because a difference in their values unambiguously indicates that the compared LGs are not isomorphic. For the deeper search of isomorphism, one can consider the composition of long-range coordination spheres of atoms in the subnets by calculation of *coordination sequences* (Brunner & Laves, 1971). Following Grosse-Kunstleve *et al.* (1996), we mean under the k th coordination sphere (shell) a set of such vertices in an infinite graph corresponding to a LG, for which the length of the shortest simple chain connecting this vertex with the vertex accepted as central is exactly equal to k . In terms of the graph theory, the k th coordination sphere corresponds to the k th layer of vertices of the infinite graph. According to Grosse-Kunstleve *et al.* (1996), we designate the number of vertices (atoms) in the k th coordination sphere as N_k . In particular, $H_p = N_1 = v + e + f$. It is a set $\{N_k\}$ that forms a coordination sequence.

Generally, each crystallographically nonequivalent atom of a crystal structure can be characterized by an individual *collection* (v , e , f , N_k). The system of such collections for all crystallographically nonequivalent atoms included in a LG characterizes its topology within the first k coordination spheres. If a (generally speaking homomorphic) relation can be specified for a pair of LGs on a set of collections (v , e , f , N_k), then one can assume that the topology of these LGs is the same in the range of the first k coordination spheres. Let us emphasize that the homomorphism (or isomorphism) of collections (v , e , f , N_k) does not mean the strict isomorphism of compared LGs. However, it indicates that the topology of appropriate atomic subnets is more similar the greater the k value is. At present, we do not know any examples of non-isomorphic LGs with identical sets of N_k at $k \leq 5$ for the real crystal structures.

If the way of binding coordination polyhedra is not taken into account and only the sequences $\{N_k\}$ are considered, one can detect the further topological similarity of LGs. Hereinafter, we shall call two RGs (or LGs) *essentially* isomorphic/non-isomorphic if their coordination sequences are identical/different at $k \leq 3$. First of all, this term has chemical meaning because the similarity of the topology of the system of interatomic bonds within the first three coordination spheres allows one to assume that the influence of the nature of chemical interaction in the considered compounds on their topology is of the same type.

Further, if an isomorphic mapping of the set of LGs, corresponding to a RG of one of the compared crystal struc-

tures, into the set of LGs of other crystal structures can be found according to the above-mentioned criterion of identity of the topology of LGs, then one can assume that these crystal structures are similar to each other up to the n th coordination sphere. For example, a unit cell of the triclinic polymorphic modification of tridymite (Konnert & Appleman, 1978) contains 80 and 160 nonequivalent atoms of silicon and oxygen, respectively. The same number of collections (v , e , f , N_k) will characterize LGs of these atoms. However, all such collections are the same for silicon atoms and for $k \leq 4$ look like (4, 0, 0, 4, 12, 25, 44), whereas there are only two different collections for oxygen atoms: (6, 0, 0, 6, 18, 48, 82) and (6, 0, 0, 6, 18, 48, 86). Therefore, one can find the isomorphism between three indicated sets of collections and three collections for one nonequivalent silicon atom and two nonequivalent oxygen atoms in the crystal structure of a hexagonal two-layer modification of tridymite containing the same values of v , e , f , N_k . This fact indicates the identity of the topology of the silicon–oxygen framework in both compounds. Note that this method allows one to find the relationship of crystal structures of the compounds, the systems of interatomic bonds of which are not completely isomorphic, and also does not depend on the value of their geometrical distortion.

These principles of topological analysis can be used for a study of crystal structure not only as a whole but also of any of its components. As a typical example, let us give the determination of a type of packing of particles (atoms, molecules, ions) forming a sublattice in a crystal structure. In this case, the atoms that do not belong to this sublattice are not taken into account at the construction of the RG of a crystal structure. Since the atoms of a sublattice do not form the chemical bonds with each other, as a rule, on restoring the connectedness of such an ‘incomplete’ RG one must take into account nonvalent (weak ionic or van der Waals) contacts between them. The topological analysis of an ‘incomplete’ RG can be fulfilled according to the scheme described above. For this, the preliminary division into LGs is not usually required because the selection of a necessary sublattice has already been made at the stage of the construction of an ‘incomplete’ RG. The N_k values obtained should be compared with the coordination sequences, which are typical for various close packings (Table 1) (see also O’Keeffe, 1995; Conway & Sloane, 1997). This approach enables one to identify the type of packing at any degree of distortion.

Below, we shall consider a problem of computer automation of the search for the topological isotypism of crystal structures and also for the topological relationship of not completely topologically isotopic compounds within the framework of the described ‘topological’ method of classification.

3. Comparing the topology of crystal structures with the program *IsoTest*

To search the topological relationship through large groups of chemically different compounds, we have developed the program *IsoTest* as part of the package of structural topo-

logical programs *TOPOS* (Blatov *et al.*, 1999). The algorithm of the program *IsoTest* is based on the representation of a crystal structure as a RG. The problem of restoring the connectedness of a crystal lattice (or, otherwise, the problem of determination of an adjacent matrix of a RG, that is a way of computer representation of a RG) is solved with the program *AutoCN*, which is also integrated into *TOPOS*. For automatic identification of interatomic (including nonvalent) bonds, the method of intersected spheres (Serezhkin *et al.*, 1997) is applied in *AutoCN*, which is based on the representation of an atom in a crystal field as its Voronoi–Dirichlet polyhedron. This method enables one to determine unambiguously the CNs of all atoms of a crystal structure, including ones that form bonds of various strength and chemical nature. The comparison of collections (v, e, f, N_k) or only of coordination sequences $\{N_k\}$ is stipulated for the search of a degree of topological relationship of RGs. Then various variants of simplification of a complete RG are considered in the program *IsoTest*, which correspond to various levels of detailing the structure of a crystal, namely:

(i) Not the whole set of LGs is taken into account, but only some of its subsets. Otherwise, several atomic sublattices are selected in a crystal structure, which can be considered as sublattices of complexing ('central') atoms. Other atoms will belong to ligands and provide the connectedness of complexing atoms (*i.e.* of LG vertices). Generally speaking, the number of different variants of selecting a subset of LGs (n_{LG}) is determined only by the number of LGs (m) (*i.e.* by the number of chemically different atoms in the composition of a substance):

$$n_{LG} = \sum_{i=1}^m m!/(m-i)! \quad (2)$$

and is not too large in practice [for example, for a quaternary compound ($m = 4$), $n_{LG} = 15$].

(ii) For each of the indicated n_{LG} ways of selecting atomic sublattices, all variants are considered for removing the atoms that do not belong to LGs of complexing atoms, together with the bonds formed by them. For example, during the study of zeolites, it is reasonable to exclude all atoms inside channels if the topology of a silica–alumina framework is considered or, *vice versa*, to exclude all cations of the framework if the structure of channels should be analyzed. Apparently, the number of variants of removing other atoms at a given number of LGs of complexing atoms [the i variable in formula (2)] can also be calculated with formula (2) if one assumes that $m = m - i$.

(iii) Lastly, all variants of 'contracting' other atoms to complexing atoms can be considered for each variant of selecting LGs of complexing atoms and removed atoms. From the viewpoint of the crystal-chemical description of a crystal structure, the operation of contracting is equivalent to considering some polyatomic groups as quasimonoatomic. For example, it is known that the crystal structures of NaNO_3 and NaCl are similar to each other if one associates the nitrate ion with the chloride ion, *i.e.* considers it as quasimonoatomic. The same result can be drawn by comparing RGs of these crystal

Table 1
Coordination sequences for some close packings with L layers.

L^\dagger	Layer type	k							
		1	2	3	4	5	6	7	8
2 (h)‡	h	12	44	96	170	264	380	516	674
3 (c)§	c	12	42	92	162	252	362	492	642
4 (hc)	h	12	42	96	170	264	378	516	674
	c	12	44	96	170	264	380	516	674
5 (hhc ₁ c ₂ c ₁)	h	12	43	94	165	260	375	508	661
	c ₁	12	43	94	168	260	372	508	661
	c ₂	12	42	96	168	260	372	504	666
6 (hcc)	h	12	42	92	168	264	380	516	672
	c	12	43	96	169	264	380	516	673
7 (c ₁ hc ₂ c ₃ c ₃ c ₂ h)	h	12	42	94	166	258	375	512	669
	c ₁	12	44	96	168	260	372	512	672
	c ₂	12	43	94	166	262	378	512	666
	c ₃	12	42	94	169	264	378	512	666
8 (c ₁ c ₂ c ₁ h)	c ₁	12	43	94	168	262	379	516	674
	c ₂	12	42	96	170	264	378	516	674
9 (chh)	h	12	42	92	162	260	378	516	674
	c	12	44	96	168	264	378	512	672
	h	12	43	96	169	262	378	514	669

† The sequence of closely packed layers is specified in brackets; c cubic, h hexagonal closely packed layer. ‡ H.c.p. packing. § F.c.c. packing.

structures if one considers nitrogen and chlorine atoms as complexing atoms and we contract oxygen atoms to nitrogen atoms. Thus, each LG is characterized not only by the collection of its topological parameters (v, e, f, N_k) but also by the collection ($\{CA\}, \{TA\}, \{DA\}$), which contains the sets of central (CA), contracted ('tightened' TA) and removed ('deleted' DA) atoms and describes some way to represent a crystal structure. Note that the effect of contracting all atoms of ligands, which results in the selection of the skeleton of a complex group consisting only of complexing atoms, is topologically equivalent to considering a set of LGs of complexing atoms without contracting (the first level of detailing) and, therefore, should not be taken into account. The total number of variants of selecting atomic sublattices in the structure of a crystal (N_{LG}) increases quickly with increasing m . Thus, for $m = 2, 3, 4$ or 5 (a greater number of different elements in one compound is found very rarely), $N_{LG} = 5, 31, 161$ or 751 , respectively. At the same time, a trivial topology (for example, a molecular complex group) corresponds, as a rule, to the majority of these variants (especially to the variants of removing atoms from a crystal structure), therefore the complete topological analysis of a crystal structure can be carried out at reasonable machine time (of the order of several hours on a Pentium 200 MHz for the most complex examples).

Let us emphasize that in the known 'topological' schemes of crystal-chemical analysis only a small part of the N_{LG} possible variants of selecting sublattices in a crystal structure is ordinarily considered. For example, the analysis of silicates is usually restricted by the study of the ways of concatenating silicon–oxygen tetrahedra that corresponds in terms of the method described to the selection of a LG of silicon atoms only. At the same time, the study of topology

Table 2

The topological characteristics of atomic subnets in the crystal structures of NaCl and NaNO₃.

No.‡	Method of RG modification†			Topological characteristics of LG					
	CA	TA	DA	<i>v</i>	<i>e</i>	<i>f</i>	<i>N</i> ₁	<i>N</i> ₂	<i>N</i> ₃
NaCl									
1, 2	{Na}, {Cl}	{}	{}	6	12	0	18	66	146
3, 4			{Cl}, {Na}	Molecular groups					
5	{Na,Cl}		{}	6	0	0	6	18	38
NaNO ₃									
1	{N}	{}	{}	Three-dimensional framework NaO ₃					
2, 3, 4			{Na}, {O}, {Na, O}	Molecular groups					
5, 6		{Na}	{}, {O}						
7		{O}	{}	6	12	0	18	66	146
8			{Na}	Molecular groups					
9	{Na}	{}	{}	6	12	0	18	66	146
10			{N}	6	0	0	6	18	38
11, 12			{O}, {N, O}	Molecular groups					
13		{N}	{}	6	0	0	6	18	38
14			{O}	Molecular groups					
15		{O}	{}	6	6	6	18	66	146
16			{N}	6	0	0	6	18	38
17	{O}	{}	{}	12	0	0	12	56	140
18			{N}	10	0	0	10	46	106
19, 20			{Na}, {N, Na}	Molecular groups					
21		{N}	{}	12	0	0	12	56	140
22			{Na}	Molecular groups					
23		{Na}	{}	12	0	0	12	56	140
24			{N}	10	0	0	10	46	106
25	{Na,§ O}	{}	{}	6	0	0	6	18	36
				4	0	0	4	14	38
26			{N}	6	0	6	6	6	30
				2	0	0	2	10	10
27	{N,§ Na}		{}	6	0	0	6	38	90
				12	0	0	12	44	98
28			{O}	Molecular groups					
29	{N,§ O}		{}	3	0	0	3	27	102
				11	0	0	11	55	134
30			{Na}	Molecular groups					
31	{N,§ Na, O}		{}	3	0	0	3	6	27
				6	0	0	6	12	36
				3	0	0	3	12	21

† The sets are indicated of atoms assumed as complexing (CA), of atoms contracted to complexing atoms (TA) and of atoms removed from a crystal structure (DA) at the analysis of the topology of a LG of complexing atoms. ‡ Number of variant of selection of an atomic sublattice (or LG). § The complexing atoms of this LG are characterized by different collections (*v*, *e*, *f*, *N_k*).

both of binding oxygen atoms with cations located in cavities of a framework and of other atomic sublattices (there are 30 additional variants for a simple silicate!) may be of interest.

For each of the compounds investigated, the program *IsoTest* forms a database on the topology of the complete RG of a crystal structure and of atomic subnets obtained by all possible variants of its simplification. The data in the calculation include collections (*v*, *e*, *f*, *N_k*) for each of the complexing atoms selected in the given variant, the user can set the quantity *k*, specifying the depth of the analysis of the LG topology. The depth of the analysis cannot be too large because the rate of calculation of *N_k* quickly decreases with increase of *k*. Experience shows that it is enough to select *k* = 3 during the initial analysis, which enables one to distinguish essentially non-isomorphic LGs and to sort roughly the compounds according to their topology. One can increase *k* for more precise classification. As was mentioned above, the

equality of all *N_k* at *k* ≤ 5 allows one to assume that LGs are isomorphic to each other.

The program *IsoTest* provides the following two-stage analysis of the created database with the purpose of determination of a degree of topological relationship of crystal structures. In the first stage, the search for isomorphism of separate atomic subnets (LGs) in compared compounds is carried out. As will be shown below, in this case one can find a similarity between substances that seem to be crystal-chemically completely different. In the second stage, the crystal structures should be found, RGs of which (possibly modified by removing or contracting some vertices) are essentially isomorphic to each other. The search for isomorphism of RGs is carried out by determining the relation between sets of their LGs, taking into account the modification of RGs. Let us consider as an example the RGs of NaCl and NaNO₃ for crystal structures of which one can propose 5 and 31 variants of the selection of atomic sublattices, respectively. The topological characteristics of appropriate LGs are given in Table 2. As was already mentioned, in many cases the modification of a RG results in its decomposition on a set of isolated finite graphs corresponding to molecular structural groups, whose topology is trivial in terms of LGs (in particular, all *N_k* = 0 starting from some *k* value). There are 2 and 13 such variants of modification for NaCl and NaNO₃, respectively, which are not of interest for the topological analysis

(Table 2). The topology of a forbidden LG is also trivial because in this case all *N_k* = ∞. This variant is realized in the crystal structure of NaNO₃ when considering LGs of nitrogen atoms (Table 2). LGs with a nontrivial topology should be grouped before comparison according to the following rules of complementarity:

- (i) the sets of removed atoms {DA} must be identical;
- (ii) the sets of complexing atoms {CA} and of the atoms contracted to them {TA} must not be intersected;
- (iii) the union of sets {CA} ∪ {TA} ∪ {DA} must coincide with the set of chemical sorts of atoms of a crystal structure.

The complementarity of several LGs means that all of them can be obtained as a result of dividing a RG, *i.e.* they completely characterize the topology of a crystal structure at some level of its description. For example, in the RG of NaNO₃, the LGs of nitrogen atoms with contracted oxygen atoms and of sodium atoms are complementary to each other (the *group* of collections [(CA: {N}, TA: {O}, DA: {}); (CA:

{Na}, TA: {}, DA: {}]) corresponds to them). These LGs specify the topology of an appropriate RG on contracting oxygen atoms to nitrogen atoms, *i.e.* on considering NaNO_3 as a quasibinary AX compound, where $X = \text{NO}_3$. The collection (CA: {Na}, TA: {O}, DA: {N}) forms a group itself and corresponds to selecting a framework of the coordination polyhedra NaO_n in the crystal structure of NaNO_3 without taking into account their connection to nitrogen atoms of nitrate groups. Hereinafter, we shall not indicate empty sets when writing collections. A group of complementary LGs, corresponding to a nonmodified RG of a crystal structure (in it all collections contain only the sets {CA}), will be called *general*. This group characterizes the topology of a crystal structure as a whole. Other groups of LGs will be called *special* because they correspond to the crystal structure modified one way or another. The number of variants of representation of a crystal structure (or, otherwise, the number of groups of LGs) depends only on m . In particular, binary and ternary compounds can be represented in 4 and 27 different ways, respectively. For example, four variants of representation of the crystal structure of NaCl, characterized by the groups [(CA: {Na}); (CA: {Cl})], [(CA: {Na}, DA: {Cl})], [(CA: {Cl}, DA: {Na})] or [(CA: {Na, Cl})], correspond to selecting two sublattices (cationic and anionic) in the crystal structure, removing one of the sublattices or considering the cationic anionic framework as a whole.

Then in the program *IsoTest*, the groups of LGs generated for various compounds are compared with each other. Two compounds are assumed to be topologically close if a bijective relation between at least two special groups of complementary LGs belonging to the compounds can be found on the basis of essential isomorphism of LGs. For this, it is necessary to take into account the method of modification of the RG of a crystal structure for each special LG. If the relation can be found for general groups of LGs, we shall combine such compounds into the same topological type. In particular, the analysis of the data of Table 2 shows that two relations can be established between special groups of LGs of NaCl and NaNO_3 . Namely, the special group of LGs of NaNO_3 [(CA: {N}, TA: {O}); (CA: {Na})] and the general group of LGs of NaCl [(CA: {Na}); (CA: {Cl})], and also the special group of NaNO_3 [(CA: {Na}, TA: {O}, DA: {N})] and another general group of NaCl [(CA: {Na, Cl})] are essentially isomorphic. Thus, the crystal structure of NaCl is topologically close to the cationic–anionic subnet in the crystal structure of NaNO_3 (if nitrate ions are considered as quasimonoatomic groups) and also to the framework of coordination polyhedra of sodium atoms without taking into account nitrogen atoms. Nevertheless, these compounds cannot be related to the same topological type because the crystal structure of NaNO_3 should be modified before comparison in the two cases.

Generally speaking, within the framework of the proposed scheme of crystal-chemical classification, one can discern three levels of topological relationship for a pair of compared groups of compounds:

(i) an essential isomorphism of only one or several pairs of, generally speaking, noncomplementary atomic sublattices;

(ii) an interrelation within one or several pairs of special groups of LGs, indicating the topological similarity of crystal structures of considered compounds;

(iii) an interrelation within a pair of general groups of LGs, showing the complete topological equality of compared structures and their belonging to the same topological type (topological isotypism).

Hereinafter, we shall call the compounds having a topological relationship of the second level topologically *partially isotypic* to emphasize that the similarity of the topology of their crystal structures can be found only after an appropriate modification. Those are the crystal structures of NaCl and NaNO_3 . The first level of topological relationship indicates the topological isotypism of separate atomic subnets and rather weak resemblance of crystal structures of considered substances.

4. Examples of the use of the program *IsoTest*

As an example of application of the described technique, let us consider the results of the analysis of topological similarity of crystal structures of simple sulfates, oxo-sulfates with the general composition $M_xO_y(\text{SO}_4)_z$ or double anhydrous sulfates $M1_xM2_y(\text{SO}_4)_z$, where M , $M1$, $M2$ are metal atoms, and of binary compounds A_yX_z . For the study, the database containing the information on crystal structures of 2486 A_yX_z compounds, and 76 simple and 52 double sulfates was created by means of the program package *TOPOS*. The calculation of the topological characteristics of LGs within the first three coordination spheres for all variants of modification of RGs of these compounds with the program *IsoTest* required about a day of machine time of a Pentium 200 MHz. Then the complementary LGs were grouped for each compound from the database and the groups of LGs obtained for sulfates were compared with LGs corresponding to binary compounds by means of the program *IsoTest* according to the conditions mentioned above.

4.1. Topological analysis of simple sulfates

A typical example of a topological relationship of the first level detected for the majority of sulfates is an essential isomorphism between LGs of two types: (i) a LG specified by the collection (CA: {M}, TA: {O}; DA: {S}) and corresponding to a sublattice of metal atoms; and (ii) LGs (CA: {A, X}) or (CA: {A}); (CA: {X}) conforming to the lattice of A_yX_z as a whole or to separate sublattices consisting of the atoms A or X . For example, in the crystal structure of high-temperature α - BaSO_4 (Sawada & Takeuchi, 1987), for the LGs of this type the N_k values are equal to 12, 42, 92 at $k = 1, 2, 3$ (N_{1-3}), respectively, which is typical for a f.c.c. lattice (Table 1). In particular, the same N_{1-3} values describe the topology of LGs for atomic subnets in the crystal structures of substances belonging to the sphalerite type or for the crystal structure of uranium silicide U_3Si (Kimmel, 1975), in which uranium and silicon atoms together form a distorted close packing. In the

Table 3

Examples of the topological relationship of the second level between crystal structures of the sulfates $M_3(\text{SO}_4)_z$ and binary compounds A_yX_z according to the scheme $M \leftrightarrow A$; $\text{SO}_4 \leftrightarrow X$.

Sulfate	Type of packing [†]	A_yX_z [‡]	Composition of LG	CN	N_1	N_2	N_3
$\text{Zr}(\text{SO}_4)_2$ [§]	H.c.p. (Zr)	PbCl_2	Zr, Pb	7	12	44	96
			SO_4, Cl	3	21	81	186
				4	15	77	172
$M_2(\text{SO}_4)_3$ ($M = \text{Al, Ga, In, Fe, Cr}$)	H.c.p.	<u>$\alpha\text{-Al}_2\text{O}_3$</u>	M, A	6	13	46	101
			SO_4, X	4	16	66	150
$M_2(\text{SO}_4)_3$ ($M = \text{In, Fe, Er}$)	–	$\text{Rh}_2\text{O}_3; \text{Rh}_2\text{S}_3$	M, A	6	14	50	110
			SO_4, X	4	16	70	163
				4	17	72	162
PdSO_4 [§]	F.c.c. (Pd)	PtS, CuO	Pd, A	4	10	42	92
MSO_4 [§] ($M = \text{Be, Zn}$)	F.c.c.	<u>ZnS (sphalerite)</u>	SO_4, X	4	10	42	90
			M, A, SO_4, X	4	12	42	92
MSO_4 ($M = \text{Pb, Sr, Ba}$)	H.c.p. (M)	<u>CoB</u>	M, A	7	22	90	198
MSO_4 ($M = \text{Hg, Ca, Sr, Ba}$)	F.c.c.	<u>NaCl</u>	SO_4, X	7	24	90	200
			M, A, SO_4, X	6	18	66	146
MSO_4 ($M = \text{Zn, Cu, Fe, Co, Ni, Mg, Mn, Cd}$)	H.c.p.	<u>FeS</u>	M, A	6	20	74	164
			SO_4, X	6	18	74	162
Ag_2SO_4	F.c.c. (Ag)	TiSi_2	Ag, Si	5	30	128	288
			SO_4, Ti	10	18	66	146
Li_2SO_4	F.c.c.	<u>CaF_2</u>	Li, X	4	22	82	182
			SO_4, A	8	12	42	92
SnSO_4 [§]	F.c.c.	<u>SnS</u>	$\text{Sn, A, SO}_4, X$	3	6	12	18
$\text{As}_2\text{O}_2\text{SO}_4$	F.c.c.	<u>$\beta\text{-HgI}_2$</u>	As, I	2	6	16	24
			SO_4, Hg	4	4	8	12

[†] The types of close packings of ions, determined by an analysis of appropriate incomplete RGs, are given. By default, close packing consists of sulfate ions, in other cases the atoms of close packing are specified in brackets. [‡] The representatives of structure types for a great number of compounds are underlined. In other cases, all found topologically isotopic binary compounds are indicated. [§] In crystal structures of these compounds, the correspondences $\text{MO}_n \leftrightarrow A$; $\text{S} \leftrightarrow X$ are also observed.

crystal structure of $\gamma\text{-CaSO}_4$ (Bezou *et al.*, 1995), the LG (CA: {Ca}, TA: {O}; DA: {S}) is characterized by $N_{1-3} = 4, 12, 30$, which indicates the topological similarity of the subnet of calcium atoms with the crystal structure of $\alpha\text{-HgS}$ (Auvray & Genet, 1973) or with the subnet of silicon atoms in quartz, having the same values of N_{1-3} . It is of interest that the subnets of zirconium atoms in $\text{Zr}_3\text{O}_5\text{SO}_4$ (Li *et al.*, 1988) and of silver or iodine atoms in a four-layer polytypic modification of AgI (Johnson & Schock, 1976) are topologically similar. For these subnets, $N_{1-3} = 9, 21, 33$. Similarly, one can find the correspondence between the pairs HgSO_4 and CsCl (26, 56, 98) or CaSO_4 (anhydrite) and NaCl (18, 38, 66) (in brackets the values N_{1-3} are indicated for LGs of metal atoms). For some sulfates, removing sulfur atoms from the graph of a crystal structure [the appropriate group of LG comprises the collections (CA: {M}, DA: {S}) and (CA: {O}, DA: {S})] results in a decrease of its dimensionality. For example, in the crystal structures of TiOSO_4 (Grey & Stranger, 1992) and VOSO_4 (Boghossian *et al.*, 1995), one can select the chains MO_5 , which are topologically similar to the complex groups in such compounds as PtF_5 or UF_5 . The subsequent contraction of oxygen atoms, resulting in the LG (CA: {M}, TA: {O}; DA: {S}), gives a simple chain, which consists of connected metal atoms ($\dots - M - M - M - \dots$) and is topologically equivalent to LGs of binary compounds containing similar chains, for example, AuCl or Sn . Note that for every considered sulfate one can find the binary compound, which is topologically isotopic to it at a level of at least some atomic subnet.

The second level of topological relationship can be detected if one considers the oxygen-containing complex groups in the

crystal structure of sulfates as quasimonoatomic. The consideration of the sulfate ion as such a group is the most essential crystal chemically because the bonds $\text{S}-\text{O}$ are stronger than the bonds $M-\text{O}$, as a rule. In this case, the group of LGs will include the collections (CA: {S}, TA: {O}) and (CA: {M}). At the same time, the consideration of the group [(CA: {M}, TA: {O}); (CA: {S})] is also possible, which corresponds to the variant of RG modification by means of contraction of oxygen atoms to metal atoms, *i.e.* to division of the crystal structure of a sulfate into sulfur atoms and quasimonoatomic MO_n groups. The examples of topological partial isotypism of binary compounds and sulfates in this kind of representation of their crystal structures found with the program *IsoTest* are given in Table 3. In addition to coordination sequences, the values of coordination numbers (CN) of atoms in an appropriate modified RG are also indicated in Table 3. In particular, the CN of a metal atom in the crystal structure of a sulfate is equal to the number of sulfate groups connected to it.

The third level of topological relationship for considered groups of compounds is found rarely. In this case, its implementation means that a sulfate may be considered as a quasibinary compound if one does not differentiate atoms of different chemical sorts. Thus, for the crystal structure of BeSO_4 (Grund, 1955) and two variants of the high-temperature modification of ZnSO_4 (Spiess & Gruen, 1978), the combination of metal and sulfur atoms into one sublattice enables one to establish their similarity with the crystal structure of cristobalite [their LGs (CA: {M, S}) and (CA: {O}) correspond to the LGs (CA: {Si}) and (CA: {O}) of cristobalite]. It should be noted that the relationship between the

Table 4

Examples of a topological relationship of the second level between crystal structures of the sulfates $M1_xM2_y(SO_4)_z$ and binary compounds A_yX_z according to the scheme $M1, M2 \leftrightarrow A; SO_4 \leftrightarrow X$.

See also Tables 2 and 3 for details.

Sulfate	DA	Type of packing	A_yX_z	Composition of LG†	CN	N_1	N_2	N_3
$M1_2M2_2(SO_4)_3$ ($M1 = K, Tl$; $M2 = Mg, Mn, Co, Cd, Zn$)	–	–	<u>Th₃P₄</u>	$M1+M2, X$ SO_4, A	6 8	26 20	113 86	293 224
	Li	–	$Rh_2O_3; Rh_2S_3$	Mg, Rh S(1)O ₄ , X(1) S(2)O ₄ , X(2)	6 4 4	14 17 16	50 72 70	110 162 163
$M1_3M2(SO_4)_3$ ($M1 = Na, Cs; M2 = V, Yb$)	M1	H.c.p.	<u>β-TiCl₃</u> (chains)	$M2, A$ SO_4, X	6 2	2 8	2 6	2 6
	$M1M2(SO_4)_2$ ($M1 = Na, K, Cs; M2 = Al, V, Fe$)	$M1(M2)$	H.c.p.	<u>CdI₂</u> (layers)	$M2(M1), A$ SO_4, X	6 3	6 12	12 24
$M1LiSO_4$ ($M1 = K, Rb, Cs$)	–	–	<u>FeS</u>	$M1+M2, A$ SO_4, X	6 6	20 18	74 74	164 162
	M1	H.c.p.	<u>ZnS</u> (wurtzite)	Li, A, SO ₄ , X	4	12	44	96
KPr(SO ₄) ₂	Li	–	<u>FeS</u>	M1, A SO ₄ , X	6 6	20 18	74 74	164 162
	–	H.c.p. (K+Pr)	CoB	K+Pr, A SO ₄ , X	7 7	22 24	90 90	198 200
LiPr(SO ₄) ₂	Pr	F.c.c.	SnO, PbO (layers)	Li, SO ₄ , A, O	4	8	16	24
LiEu(SO ₄) ₂	Li	–	<u>TiO₂</u> (rutile)	Eu, A SO ₄ , X	6 3	10 14	34 62	74 144
β -LiNaSO ₄	Li	–	ϵ -TaN	Na, N S(1)O ₄ , Ta(1)	5 3	16 12	66 56	156 140
	K ₃ Er(SO ₄) ₃	K	F.c.c.	<u>AF₃</u> (A = V, Nb, Bi, U) (chains)	S(2, 3)O ₄ , Ta(2, 3) Er(1), A	6 1	2 5	2 10
KEr(SO ₄) ₂	–	–	<u>SrX₂</u> (X = Br, I)	S(5)O ₄ , F(1) Er, Sr	2 7	10 10	10 36	10 78
	K	H.c.p. (Er)		S(2)O ₄ , X(1) S(1)O ₄ , X(2)	4 3	19 15	70 62	152 148
Cs ₂ Ce(SO ₄) ₃	Cs	F.c.c.	<u>β-BiBr₃</u> (layers)	Ce, A SO ₄ , X	6 2	3 9	6 16	9 28
	–	F.c.c.	<u>NaCl</u> <u>MgCl₂</u> (layers)	$M1+M2, A, SO_4, X$ $M2(M1), A$	6 6	18 6	66 12	146 18
$M1M2(SO_4)_2$ ($M1 = K, Rb; M2 = V, Tl$)	$M1(M2)$	–	<u>MgCl₂</u> (layers)	SO_4, X Rb, A	3 4	12 2	24 2	36 2
	RbLu(SO ₄) ₂	Lu	F.c.c.	<u>BeCl₂</u> (chains)	SO ₄ , X Lu, A	2 6	5 6	4 12
RbDy(SO ₄) ₂ ; K ₂ Pb(SO ₄) ₂ ; CsLa(SO ₄) ₂	–	–	<u>MgCl₂</u> (layers)	SO ₄ , X SO ₄ , X	3 3	12 12	24 24	36 36
	K(Rb, Cs)	H.c.p.	<u>CdI₂</u> (layers)	Pb(Dy, La), A SO ₄ , X	6 3	6 12	12 24	18 36
RbEu(SO ₄) ₂	Eu	F.c.c.	<u>CaF₂</u>	Rb, A SO ₄ , X	8 4	12 22	42 82	92 182
	Rb	–	<u>MgCl₂</u> (layers)	Eu, A SO ₄ , X	6 3	6 12	12 24	18 36
Na ₆ Mg(SO ₄) ₄	–	–	<u>AF₄</u> (A = Sn, Pb, V, Nb) (layers)	Mg, A S(1)O ₄ , F(1)	6 2	4 10	8 28	12 44
	Na	–		S(2)O ₄ , F(2) Pr, A	1 6	5 6	20 12	36 18
CsPr(SO ₄) ₂	Cs	–	<u>CdI₂</u> (layers)	SO ₄ , X Cs, A	3 6	12 6	24 12	36 18
	Pr	–	<u>MoS₂</u> (layers)	SO ₄ , X SO ₄ , X	3 3	13 19	24 72	36 163
–	–	4-layer h.c.p. (Cs+Pr)	TiP, TiAs, ZrAs	Pr, X(1) Cs, X(2)	6 6	18 18	74 66	162 162

† The records 'M1+M2' and 'M1(M2)' mean 'M1 and M2' and 'M1 or M2', respectively. The ordinal numbers of nonequivalent atoms [for instance, S(1)] are given according to original papers.

crystal structures of cristobalite and BeSO₄ was specified by Grund (1955). Under these conditions, the layer structures of (IO)₂SO₄ (Furuseth *et al.*, 1974) and β -HgI₂ (Delgado *et al.*, 1987), and also of SnSO₄ (Donaldson & Puxley, 1972) and As₂O₄ (Jones *et al.*, 1980) appear to be similar. It is of interest that arsenic oxo-sulfate As₂O₂SO₄ (Mercier & Douglade,

1982), whose composition is similar to (IO)₂SO₄, is also topologically related to β -HgI₂, however, only at the second level (Table 3). On the whole, 36 and 5 considered sulfates and some binary compounds have the topological relationship of the second and third level, respectively, and 4 of those 5 sulfates [not (IO)₂SO₄] are contained in both indicated groups.

39 of 76 investigated sulfates have no topologically isotopic analogs among the compounds A_yX_z .

4.2. Topological analysis of double sulfates

In the analysis of the topology of the crystal structure of a double sulfate $M1_xM2_y(SO_4)_z$ ($m = 4$), there are already 161 variants of selection of atomic sublattices. In this connection, we shall deal with only such variants of the description of a crystal structure in which the sulfate ion is represented as a quasimonoatomic group. In other words, we shall take into account only the groups of LGs that comprise such collections as (CA: {S}, TA: {O}, DA: {}, {M1} or {M2}) and one of the collections (CA: {M1, M2}); (CA: {M1}, DA: {M2}) or (CA: {M2}, DA: {M1}). Accordingly, all the variants of the topological relationship of double sulfates with binary compounds given in Table 4 can be combined into two groups:

(i) a subnet of metal atoms in the crystal structure of a double sulfate is considered as a whole, (CA: {M1, M2}, DA: {});

(ii) one of the metal atoms is removed from the RG of a double sulfate (DA: {M1} or DA: {M2}), which is equivalent to the separation of a subnet, corresponding to simple sulfates $M1_x(SO_4)_z$ or $M2_y(SO_4)_z$.

In the first case, a subnet composed from metal atoms of two sorts ($M1 + M2$) is put in correspondence with a monoatomic subnet of the atoms A or X . In four of five detected examples of topological isotypism in this group (Table 4), the stoichiometric composition of sulfates and appropriate binary compounds is similar [$M1M2(SO_4)_2$ and AX], however, the topology of crystal structure differs in the type of packing of sulfate ions and/or of metal atoms. The interesting variant of structural correspondence is found for sulfates which are described by the ratio $(x + y):z = 4:3$ and stoichiometrically similar to chalcogenides, phosphides and antimonides of f elements, belonging to the structure type of Th_3P_4 . In this case, sulfate ions form a distorted two-layer h.c.p. and metal atoms of two types are situated in octahedral holes of this packing.

Examples of topological relationships of the second type are more manifold. Although a double sulfate can be formally considered as a simple sulfate without taking into account one of the metal atoms, the cases of similarity of their topology are not numerous. Apparently, this is due to a decrease in the dimensionality of the structural groups $M1_x(SO_4)_z$ or $M2_y(SO_4)_z$, which is frequently caused by removing a metal atom from the crystal structure of a double sulfate. Only in the crystal structures of $Li_2Mg_2(SO_4)_3$ (Touboul *et al.*, 1988) and $RbEu(SO_4)_2$ (Sarukhanyan *et al.*, 1983) are the subnets $Mg_2(SO_4)_3$ and $Rb(SO_4)_2$ structurally similar to the sulfates $M_2(SO_4)_3$ ($M = In, Fe, Er$) and Li_2SO_4 , respectively (Tables 3, 4). Note that at the primary comparison of the LG topology of non-three-dimensional structural groups the type of their mutual packing is not taken into account because for this purpose the additional analysis of 'incomplete' RGs of a crystal structure should be fulfilled, as was mentioned above. For example, the layer complex groups $Cs(SO_4)_2$ and $Pr(SO_4)_2$ in the crystal structure of $CsPr(SO_4)_2$ (Bukovec *et al.*, 1978)

Table 5

Pairs of compounds that are not topologically similar but have close topological characteristics.

Compound	Composition of LG†	Composition					
		CN	N_1	N_2	N_3	N_4	N_5
$Zr(SO_4)_2$	Zr	7	12	44	96	170	264
	S(1)O ₄	3	15	77	172	316	505
	S(2)O ₄	4	21	81	186	334	519
ZrO_2 [$T = 30$ K (Kisi <i>et al.</i> , 1989)]	Zr	7	12	42	92	162	252
	O(1)	3	17	72	175	304	491
	O(2)	4	19	82	175	322	491
PdSO ₄	Pd	4	10	42	92	162	252
	SO ₄	4	10	42	90	162	250
PdO	Pd, O	4	12	42	92	162	252
BeSO ₄	Be, SO ₄	4	12	42	92	162	252
β -BeO	Be, O	4	11	41	90	157	247
MSO ₄	M	6	20	74	164	290	452
	SO ₄	6	18	74	162	290	450
MO ($M = Be, Cu, Mg, Mn, Cd$)	M, O	6	18	66	146	258	402

† The ordinal numbers of nonequivalent atoms are given according to original papers.

are topologically similar to the layers MoS_2 and CdI_2 in appropriate binary compounds, however, unlike them the distorted close packing in $CsPr(SO_4)_2$ is formed by cations, not by anions (Table 4).

In our opinion, the numerous examples of topological relationships of simple sulfates, of subnets with similar composition in the crystal structure of double sulfates and of binary compounds containing the same metal atom requires attention. Thus, $M_2(SO_4)_3$ and M_2S_3 ($M = In$) or M_2O_3 ($M = Al, Ga, In, Fe, Cr$); MSO_4 and MS ($M = Zn, Ca, Sr, Ba, Fe, Co, Ni, Sn$) or MO ($M = Zn, Hg, Ca, Sr, Ba$); Li_2SO_4 and Li_2S or Li_2O have similar structures. In a number of cases, such compounds, not being topologically related, nevertheless have close topological characteristics (Table 5). The similarity can be found either for arbitrarily large fragments of crystal structures (in this case, the N_k values for the appropriate LGs are close at any k , for example, as for the pair PdSO₄, PdO) or only for several nearest coordination spheres [in particular, for the group of sulfates MSO_4 ($M = Be, Cu, Mg, Mn, Cd$) constructed according to a h.c.p. lattice and appropriate oxides with f.c.c. packing]. It should also be noted that in most cases the crystal structure of a sulfate can be described as a distorted close packing of structural units of one or several types with the distribution of other atomic groups in the holes of this packing (Tables 3, 4). A close packing is more often formed by sulfate ions and less often by large cations of alkali, alkaline-earth or rare-earth metals, however, there are also compounds in which some different atomic groups are arranged according to one of the close packings. Such a striking instance is $RbEu(SO_4)_2$ (Sarukhanyan *et al.*, 1983), each of the three structural units of which (Rb^+ , Eu^{3+} and SO_4^{2-}) form a strongly distorted f.c.c. packing. The authors of the original structural investigations, as a rule, do not indicate these structural regularities, except for compounds with high space symmetry and simple stereochemistry of complexing atoms (for instance, BeSO₄). Thus, the traditional crystal-chemical analysis based on the geometrical analysis of the first coordi-

nation sphere of atoms does not allow one to find numerous structural relations, which can be hidden by a strong distortion of a crystal structure, which is quite usual for compounds with complex chemical composition.

5. Conclusions

The given examples demonstrate the efficiency of the proposed method of the search for topological isotypism of crystal structures and for the relationship in the structures of substances with essentially different chemical and stoichiometric composition. At the same time, the available data do not allow one to reach unambiguous conclusions about the reasons and degree of generality of the found correspondences. Therefore, we plan to study interrelations of topology of crystal structures for other groups of binary, ternary and quaternary compounds.

This study was carried out with financial support of the Russian Fund of Fundamental Investigations (project 97-03-33218).

References

- Aslanov, L. A. (1988). *Acta Cryst.* **B44**, 449–458.
- Atlas of Zeolite Structure Types* (1996). Edited by W. M. Meier, D. H. Olson & C. Baerlocher, 4th ed. Amsterdam: Elsevier.
- Auvray, P. & Genet, F. (1973). *Bull. Soc. Fr. Minéral. Cristallogr.* **96**, 218–219.
- Belsky, V. K., Zorkaya, O. N. & Zorky, P. M. (1995). *Acta Cryst.* **A51**, 473–481.
- Bezou, C., Nonat, A., Mutin, J.-C., Christensen, A. N. & Lehmann, M. S. (1995). *J. Solid State Chem.* **117**, 165–176.
- Blatov, V. A., Shevchenko, A. P. & Serezhkin, V. N. (1999). *J. Appl. Cryst.* **32**, 377.
- Boghosian, S., Eriksen, K. M., Fehrmann, R. & Nielsen, K. (1995). *Acta Chem. Scand.* **49**, 703–708.
- Borisov, S. V. & Podberyozskaya, N. V. (1984). *Stable Cationic Frameworks in Structures of Fluorides and Oxides*. Novosibirsk: Nauka. (In Russian.)
- Brunner, G. O. & Laves, F. (1971). *Wiss. Z. Tech. Univ. Dresden*, **20**, 387–390.
- Bukovec, N., Golic, L., Bukovec, P. & Siftar, J. (1978). *Monatsch. Chem. Teil Wiss.* **109**, 1305–1310.
- Chung, S. J., Hahn, Th. & Klee, W. E. (1984). *Acta Cryst.* **A40**, 42–50.
- Conway, J. H. & Sloane, N. J. A. (1997). *Proc. R. Soc. London*, **453**, 2369–2389.
- Delgado, J. M., McMullan, R. K. & Wuensch, B. J. (1987). *Trans. Am. Crystallogr. Assoc.* **23**, 93–95.
- Donaldson, J. D. & Puxley, D. C. (1972). *Acta Cryst.* **B28**, 864–867.
- Furuseth, S., Selte, K., Hope, H. & Kjekshus, A. (1974). *Acta Chem. Scand.* **28**, 71–76.
- Grey, I. E. & Stranger, R. (1992). *J. Solid State Chem.* **101**, 331–339.
- Grosse-Kunstleve, R. W., Brunner, G. O. & Sloane, N. J. A. (1996). *Acta Cryst.* **A52**, 879–889.
- Grund, A. (1955). *Tschermaks Mineral. Petrogr. Mitt.* **5**, 227–230.
- Johnson, Q. & Schock, R. N. (1976). *Acta Cryst.* **B32**, 1304.
- Jones, P. G., Beesk, W., Sheldrick, G. M. & Schwarzmann, E. (1980). *Acta Cryst.* **B36**, 439–440.
- Kimmel, G. (1975). *Acta Cryst.* **B31**, 1351–1353.
- Kisi, E. H., Howard, C. J. & Hill, R. J. (1989). *J. Am. Ceram. Soc.* **72**, 1757–1760.
- Klee, W. E. (1987). *Z. Kristallogr.* **179**, 67–76.
- Konnert, J. H. & Appleman, D. E. (1978). *Acta Cryst.* **B34**, 391–403.
- Li, C., Daimon, K., Murase, Y. & Kato, E. (1988). *Nip. Ser. Yok. Gak. Ron.* **96**, 980–984.
- Liebau, F. (1985). *Structural Chemistry of Silicates*. Berlin: Springer.
- Lima-de-Faria, J., Hellner, E., Liebau, F., Makovicky, E. & Parthé, E. (1990). *Acta Cryst.* **A46**, 1–11.
- Malinovskii, Yu. A., Burzlaff, H. & Rothammel, W. (1998). *Crystallogr. Rep.* **43**, 241–255.
- Mercier, R. & Douglade, J. (1982). *Acta Cryst.* **B38**, 896–898.
- O’Keeffe, M. (1995). *Z. Kristallogr.* **210**, 905–908.
- Pearson, W. (1972). *The Crystal Chemistry and Physics of Metals and Alloys*. New York: Wiley-Interscience.
- Sarukhanyan, N. L., Iskhakova, L. D. & Trunov, V. K. (1983). *Kristallografiya*, **28**, 452–456.
- Sawada, H. & Takeuchi, Y. (1987). *Z. Kristallogr.* **181**, 179–186.
- Serezhkin, V. N. (1986). *The Problems of Crystal Chemistry*, pp. 148–179. Moscow: Nauka. (In Russian.)
- Serezhkin, V. N., Mikhailov, Yu. N. & Buslaev, Yu. A. (1997). *Russ. J. Inorg. Chem.* **42**, 1871–1910.
- Spiess, M. & Gruen, R. (1978). *Naturwissenschaften*, **65**, 594.
- Touboul, M., Quarton, M., Lokaj, J. & Kettmann, V. (1988). *Acta Cryst.* **C44**, 1887–1889.
- Wells, A. F. (1977). *Three-Dimensional Nets and Polyhedra*. New York: Academic Press.
- Wells, A. F. (1986). *Structural Inorganic Chemistry*. Oxford: Clarendon Press.