論文

Layers Sequences in the Materials with Perovskite-Related Structures

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A new approach to get a qualified view on large amounts of materials data is proposed. Global understanding on the relations among chemical composition, crystal structure and properties of materials on the basis of suitable classification is a starting point of material design. The present work is focused on studying the crystal structures and structural primitives as keys for materials design based on crystallographic information, and a sequence of stacking 2-dimensional layers, implying hidden regularities in the high temperature superconducting (HTSC) materials, is selected as an additional features to generic crystallographic information.

Prerequisites for using this approach, its limitations and possibilities for database developments are discussed based on the analyses of data extracted from Inorganic Crystal Structure Database (ICSD) . In addition, possible applications of this method for classification and design of these interesting materials are proposed.

1 Introduction

The more we get the insight on the semantics of material structures, the more we can extract the rich properties from materials. And it is the first milestone to explore the new domains of materials in the process of materials design. In this paper, an approach to describe material structures beyond traditional crystallographic and metallographic approaches is proposed to have a new articulation on material structures by taking advantage of fascinating high Tc superconducting materials.

The presence of CuO_2 conduction sheets is crucial for the presence of superconductivity in copper oxide compounds. Their overall structures are usually described as stacks of 2-dimensional sheets and structural blocks along the direction perpendicular to the sheets. As all these compounds comprise similar structural units, describing their structures in a coherent manner becomes useful for clarifying their common structural features and relationships among various crystal structures. Such a structural representation also serves as a tool to devise strategies to search for new compounds that may exhibit interesting electronic and magnetic properties.

The four number classification scheme of superconducting copper oxides with very close relation to their layered structure has been proposed by Shaked[1]. However, this approach, although gives us very convenient representation of the material, can not adequately describe its crystal structure.

Tokura with his colleagues[2] has proposed another classification method for layered copper oxide compounds. Every HTSC compound possesses alternately one-to-one stack of CuO_2-sheets and "block layers", or intervening atomic layers which are composed of metal ions (mostly alkaline earth and/or rear-earth ions) and oxygen or halogens. All CuO_2-layered compounds are classified into the combination of "block layers". Moreover, the

"block layers" sequence governs fundamental physical chemical properties of the compounds, such as crystal structure (including space group), Cu-O bond lengths and prescriptions for doping by p and n type carriers.

A convenient method of expressing the (ideal) structure of superconducting copper oxides by regarding them as combinations of perovskite and rocksalt-type sheets has been proposed by Santoro et al. in 1988[3]. Although perovskite-like and related commensurate structures (like rocksalt or fluorite) were considered as layered and described as stacking layers even before the HTSC discovery[4], their work[3] was the first systematic analysis of layered structures of copper-oxide superconductors from the viewpoint of layer patterns and stoichiometry. Later the development of this approach was continued by the same authors[5][6] and also in other publications[7][8][9].

The present work at the first time considers this approach as an advanced "data mining" procedure to search for compounds with similar but different crystal structure. When we are going to find compounds with closely related structures, such as homologous series members, solid solutions, derivative structures, etc., standard principles based on space group theory cannot be very helpful. Disadvantage of such methods is that even a minor change in the position of the atom in a crystal structure can often reduce its symmetry, leading to a new mathematical description and a "new" crystal structure. Instead of principles of symmetry, rearrangement of atoms in crystal structure and structural primitives should be taken into account. Following this idea, the analysis of layered structures of copper-oxide compounds, with huge amount of repre
sentatives, can be a good example for such a procedure. In addition a special interest is paid to their superconducting properties, and this interest does not decrease during last decade. This paper discusses the problem of automation of sequence of layers building procedure for "data mining", classification and comparison of different structures, and for other purposes.

2　Methods

In the present work widely famous Inorganic Crystal Structure Database (ICSD) has been used as a data source[10][11]. CD-ROM version of the database contains about 37.5 thousands of entries of different inorganic structures.

Software programs have been written on C language (ANSI standard) with the help of SgInfo comprehensive collection of routines for handling of crystallographic space groups[12].

3　Basic definitions of the layers approach

The layered structure can be described in different ways and at different levels of details. Pperovskite-like structures, despite of the great variety, allow to descrbe them with the help of small set of atomic networks perpendicular to (pseudo)-four fold axis[7]. The layer composition may be expressed by the chemical formula corresponding to the stoichiometry of the layer, for example A, AX, B_2, BX_2, etc. For the sake of simplicity, generally atomic positions are redefined as A - large size cation position, B - small or middle size cation position, X - anion position. Subscript indices are shift of cell relatively to coordinate origin with translation vector: o=(0,0); c=(1/2,1/2); x=(1/2,0); y=(0,1/2). Square brackets, using in some formulae, indicate the layers that are enclosed in one unit cell of the structure. This notation, which is more close to Cava[5], has been chosen because of its simplicity for automation. In other works notations are a little bits different. Furthermore, each pattern can be represented by a digital code. Although this code does not describe atomic arrangement, it sig-
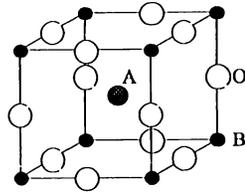
Figure 1a Schematic representation of crystal structures of perovskite

nificantly simplifies the computer analysis of the patterns.

For example, if we apply this symbolism to the structure of perovskite $CaTiO_3$ (Figure 1a), we obtain the sequence $[(BX_2)_o(AX)_c]$, where A=Ca, B=Ti and X=O; or simply - 1o5c(see Figure 2). The rocksalt structure, the second main building block in cuprates, is represented as sequence $[(AX)_o(AX)_c]$ or 5o5c. For Y123 structure (Figure 1b) the sequence will be $[(BX_2)_o(AX)_cc(BX_22)_o(A)_c(BX_2)_o(AX)_c(BX_2)_o]$ or 1o5c1o8c1o5c1o. As one can see, the perovskite block in Y123 phase can be identified easily with the help of the sequence of layers. If necessary (for example, for the analysis of formal electronic state of elements in layers), letters A, B and X can be replaced back by real symbols of the elements, as $[(TiO_2)_o(CaO)_c]$ for the perovskite structure.

4 Possibilities for automation of layers sequence building process and pattern matching

The procedure of automatic analysis of layers and building them into the sequences requires the primary definition of limiting amount of basic elements - layers patterns, which would cover majority of possible copper-oxide structures. Here the common building principles of such structures are considered in context of the possibility of revealing basic structural primitives and limiting their amounts.

The basic cell for such types of phases is a planar network of $CuO_2^{\cdot}$ composition with
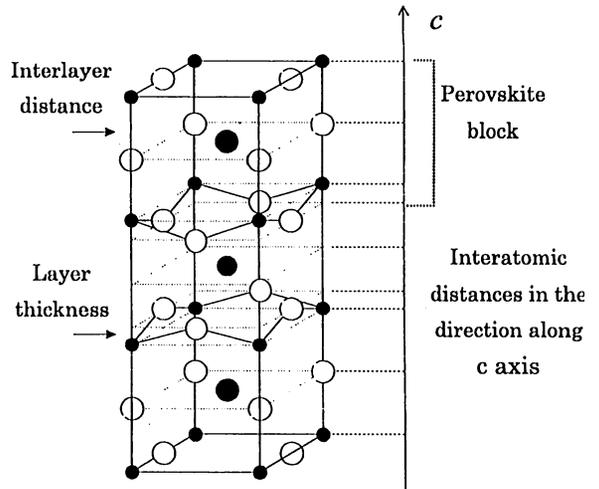

Figure1b Superconducting YBa$_2$C$_3$O$_{7-x}$ (Y123 phase) with perovskite blocks.

3.8~4.2 Å

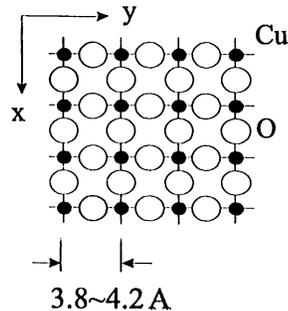Figure 1c Basic fragment of layered perovskite-like structures Cu-O network

lattice parameters a~b=3.8~4.2 Å [13]. Its sche-matic representation is shown in Figure 1c. At such short values of lattice parameters the number of possible cation-anion cells, proportionate CuO_2, is limited - only nine topologically different patterns. The networks BX and (BX)' are topologically identical, but differ by rotation by 90° in xy plane.

Figure 2 illustrates schematic representation of possible atomic networks for perovskite related compounds.

Short interatomic distances (2.7-3.0 Å), approximately equal to $a/\sqrt{2} \approx b/\sqrt{2}$, on the other hand, seem to play a role of lower limit of cation-cation or anion-anion bonds (if compounds with chemical bonds of the corresponding types are not taken into ac-
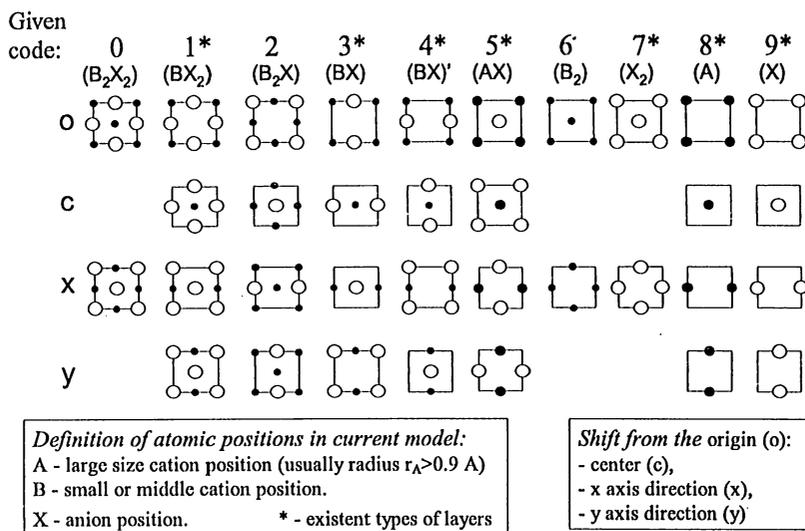
Figure 2　Possible atomic networks for perovskite related compounds

A - large size cation position; B - small or middle cation position; X - anion position. * - existent types of layers. Shift from the origin (o): c- center, x - x axis direction, y - y axis direction.

count). On the other hand, it is approximately equal to the upper boundary of the shortest lengths of cation-anion (metal-oxygen) distances. Therefore, this number specifies both the maximum distance between layers (in copper-oxide HTSC the maximum interlayer distance does not exceed 2.4 Å [7]) and certain limitations on their combination, preventing from neighboring atomic networks, identical by type and shift (with the same subscript symbol). Similar steric reasons prevent large cations from allocation in B_2X_2, BX_2, B_2X, BX, B_2 and X_2 networks, that uniquely determines X as oxygen or fluorine and ionic radius B^{n+} $r_B < 0.9$ Å. Some variants of allocation of cations with different charge in the networks cannot be realized also because of limitations of electrostatic character (improper charge balance), resulted from Pauling's electrovalence rule[14]. Summarizing the above statements, practically all the possible combinations of considered networks could be defined in advance. However, as will be shown later, most of them

do not exist or very rare in practice (Table 1). It can be claimed that the layer formalism considered with the data from Table 1, allows complete automating of the process of modeling perovskite-related structures.

However, the method of identifying individual layer in perovskite-like superconductors is not obvious, in contrast to, for example, the clearly expressed layered crystals of the type of As_2S_3, GeSe, and others. In the latter compounds the bonding of atoms within the layers has a covalent nature, and the interaction between the layers is determined by van der Waals forces.

Developing the layer pattern matching we need to solve the following problems.

- Orthorhombic distortions. Different orientations of unit cell.
- Superstructure and modulation.
- Complex anions, e.g. carbonate CO_3^{2-}.
- Deviations of atomic positions from the ideal model.
- Non-plain layers.

	B_2X_4	BX_2	B_2X	BX	BX'	AX	B_2	X_2	A	X
$(B_2X_4)_0$	X	XY	O	XY	XY	-	X	O	XY	OC
$(BX_2)_0$	X	XY	OC	XY	XY	C	X	O	CXY	OC
$(B_2X)_0$	O	OC	XY	OC	OC	O	O	X	OC	CXY
$(BX)_0$	X	XY	OC	CXY	XY	CY	X	OX	CXY	OCX
$(BX)'_0$	X	XY	OC	XY	CXY	CX	X	OX	CXY	OCY
$(AX)_0$	-	C	O	CX	CY	CXY	X	X	CXY	OXY
$(B_2)_0$	X	XY	OC	XY	XY	XY	X	OX	XY	OCXY
$(X_2)_0$	O	OC	XY	OC	OC	XY	OX	X	OCXY	XY
$(A)_0$	X	CXY	OC	CXY	CXY	CXY	X	OX	CXY	OCXY
$(X)_0$	O	OC	CXY	OCX	OCY	OXY	OX	X	OCXY	CXY

Table 1 Possible variants of layers combination, satisfying the crystal chemical rules.
Each cell represents possible variants of shift (see Figure 2) of the column layer relatively to row layer, that is in the origin. Revealed variants are shown in bold. O - origin; C - center; X - X direction; Y - Y direction.

In the superconducting structures, copper-oxide layers tend to be either planar or relatively thin. Other layers such as LaO or BaO are ordinarily much thicker, generally to such an extent that it seems more reasonable to consider the cations and oxygen atoms as forming separate layers. This may cause a situation that we cannot separate each layer from others without a certain ambiguity even if we have a layered structure due to the possibility of intersection of layers. To show the real layered character of cuprates structures, interatomic distances in them along characteristic direction (axis c) have been calculated, that will be described later.

5 Developed programs

As a result of the present work, a set of computer programs for data mining, building crystal lattice and layer sequencing have been developed:

I. Crystal Unit Cell Builder - program to generate all atoms within unit cell from the basic atomic position table. C routine library SgInfo[12] has been used for handling symmetry operation and transition matrices. The program also checks, whether new position located too close to another position, that may be results of atomic deviations and partial occupancy.

II. Layer Sequencer - program for creating the sequence of layers in crystal structure and for 2-dimensional representation of layers in ASCII graphics. This program is under development and the present version treats only structures with parameters a~b~3.8 Å. It isolates layers along axis with maximum length and matches them with the patterns given in advance. If the separation of layers or pattern recognition is ambiguous, the program puts question marks in the sequence and allows user to make decision.

III. ICSD to Table Converter - utility to convert output data from ICSD database to a tab delimited text file, which is used to upload the data to database table.

IV. Reference Extraction - utility to extract reference information from ICSD database and convert it to *MedLine format which can be used by any reference*

Figure 3　Distribution of compounds extracted from ICSD by element composition

manager program.

6　Preliminary analysis of data extracted from ICSD

A search query is started by identifying chemical components on the basis of knowledge about similarities in superconducting and related cuprates:

(Cu and O) and (Ca or Sr or Ba) and (Y or La or LAN or Hg or Tl or Pb or Bi)

As a result, with the help of build-in RE-TREIVE v.2.0 software, 1333 cuprates have been extracted from ICSD in this work.

To have a clear view and to show a big picture of the using array of data, distribution analyses of elemental compositions and structural properties have been done as shown in Figures 3, 4 and 5. As it can be seen in Figure 3, close-packing principles in perovskite-like compounds result in very limited set of possible atoms in these structures. Last two figures clearly show that there are not so much varieties in the distribution of these compounds by structural properties: orthorhombic and tetragonal structures are dominant, and only four space groups prevail. This is due to the very strict limitations which CuO_2 network imposes to the crystal structure of these compounds.

As for the space group appearance, it is im-

Figure 4　Crystal symmetry population pattern for inorganic materials extracted from ICSD.

Figure 5　Distribution of cuprates by space groups in copper oxides (totally 59 groups)

portant to bear in mind that the symmetry of the system depends on the dimension of the subgroup of translations, which may be equal to the dimension of space, but can also be less. In general case when there is a lowering of the space dimension and of the dimension of the translation subgroup, the symmetry of the corresponding object will be described by one of the groups, which have been summarized by Zallen[16]. According to him, layers are systems with two-dimensional translation symmetry and three-dimensional point symmetry, and their space symmetry can be described by one of the 80 three-dimensional doubly periodic (layer) groups. In our case in total only 59 space groups have been found, and 80 % cases are described by 4 main groups: Pmmm, P4/mmm, I4/mmm and Ammm. That can be explained by additional limitations of perovskite structure. Looking the big picture, it should be noted that the structures, for which sequences of layers have been resolved, are described by only 10 space groups, while above mentioned 4 space groups appear in 98 % cases.

As it has been emphasized before, the above structural layers are not ideally plain, but they may have some thickness. In the considered case the interatomic distance means a distance between two neighboring points, produces by projection of atoms to c axis (z coordinates) as shown in Figure 1b. The layer thickness in this context is a distance between the minimum and the maximum z coordinates of atoms of the same layer. The interlayer distance in its turn is defined as a distance between two neighboring layers, exactly between the maximum z coordinate of lower layer and the minimum z coordinate of upper layer. Results of calculation are displayed in Figure 6.

On this histogram each column relates to the number of those layers (in this case ideal plain layers are considered) which fall into a specific range of interatomic distances. It is clear to see two separated areas on this graph responsible for layers thickness and real in-

terlayer distances. Thus, it can be concluded that in the majority of cases there is no ambiguity to separate atoms into two-dimensional layers by using this characteristic interatomic distances.

7 Results of the layers sequence building and their analysis

The first two programs described above have been used to calculate the sequences of layers for 1333 copper oxide compounds extracted from ICSD. About 19 % (261) of the compounds have been rejected because of large lattice parameters (the cell reduction procedure is not implemented yet), or imperfect initial data (positions of some atoms have not been defined), or high degree of disordering. The sequences of main representatives of perovskite-related materials are shown in Table 2.

Layers sequences are given in two-character system, where the first digit represents a pattern defined in advance, and the second character describes a shift of the pattern from the origin position. More details have been given in Figure 2.

Figure 7 shows the revealed layer patterns and the number of extracted compounds, where these patterns have been found. Pattern 1-(BX_2) (CuO_2) is the basic building network, determining the most common structural features of superconducting and related copper oxides. Pattern 5-(AX) (metal-oxygen) layers take place in building perovskite blocks and play a very important role in the local charge distribution as shown in the next chapter. Layers 8-(A) (more often Y or Ca atoms) is a separator of perovskite blocks. Copper-oxygen chains, also playing an important role in the superconductivity in 123 phases, are represented by patterns 3 or 4. Patterns 3 and 4 (BO) differ from the pattern 1 (BO_2) only by oxygen vacancies in one of the edge and they together represent the Cu-O layers. As one can see in Figure 7, at
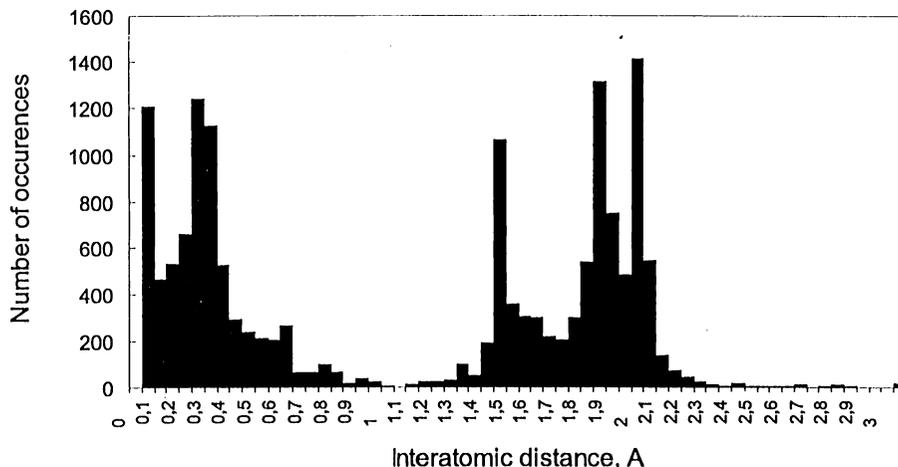
Figure 6　Distribution of interatomic distances along [001] direction (c axis) in cuprates.

N	Compound	Layers sequence	T_c, K
1	$(La,Ba)_2CuO_4$	1o 5c 5o 1c 5o 5c	38
2	$(Nd,Ce)_2CuO_4$	1o 8c 7c 8o 1c 8o 7c 8c	24
3	$(Nd,Ce,Sr)_2CuO_4$	1o 8c 7c 8o 1c 5o 5c	35
4	$YBa_2Cu_3O_7$	1o 8c 1o 5c 4o 5c	92
5	$YBa_2Cu_3O_6$	1o 8c 1o 5c 8o 5c	-
6	$YBa_2Cu_4O_8$	1o 5c 4o 4x 5y 1x 8y 1x 5y 4x 4o 5c 1o 8c	80
7	$Y_2Ba_4Cu_7O_{14}$	1o 8c 1o 5c 4o 4x 5y 1x 8y 1x 5y 8x 5y	95
		1x 8y 1x 5y 4x 4o 5c 1o 8c 1o 5c 8o 5c	
8	$TlBa_2CuO_5$	1o 5c 5o 5c	-
9	$TlBa_2CaCu_2O_7$	1o 8c 1o 5c 5o 5c	40
10	$TlBa_2Ca_2Cu_3O_9$	1o 8c 1o 8c 1o 5c 5o 5c	123
11	$Tl_2Ba_2CuO_6$	1o 5c 5o 5c 5o 1c 5o 5c 5o	95
12	$Tl_2Ba_2CaCu_2O_8$	1o 8c 1o 5c 5o 5c 5o 1c 8o 1c 5o 5c 5o 5c	118
13	$Pb_2Sr_2YCu_3O_8$	1o 5c 5o 8c 5o 5c 1o 8c	70
14	$HgBa_2CaCu_2O_{6.26}$	5o 5c 1o 8c 1o 5c 5o	134

Table 2　Layers sequences of representatives for main classes of perovskite-related materials

least one type of these layers presents in all extracted compounds, that is the main common feature of copper-oxide perovskite related structures. Although the pattern 1' (B) geometrically is similar to 8 (A), it is more closely related to the pattern 1, where all oxygen positions are vacant. Such layers occur in tetragonal.123-O_6 related phases. The another most commonly occurring pattern is 5 (AO), which represents metal-oxygen layers, where the metal usually is an alkaline earth or transition element. Only 2 compounds are found without such types of layers nonetheless they contain the combina-tion 8o9c $(A)_o(O)_c$, which is equivalent to 5o and arises from its too large distance between metal and oxygen layers.

Copper-oxide superconducting structures are mostly often described by 3-dimensional primitives: perovskite and intermediate blocks, and coordination polyhedra. They provide convenient structural representations and also play an important role in several theoretical models. At the same time layers have close relations with 3D primitives. The latter can be easy obtained from sequences of layers. Table 3 shows some examples of such relation between layers and 3D primitives in
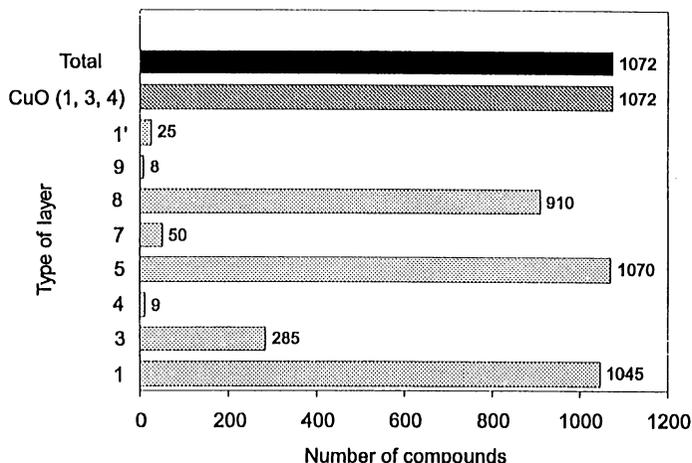
Figure 7　Presence of layers with different patterns in copper-oxide structures extracted from ICSD
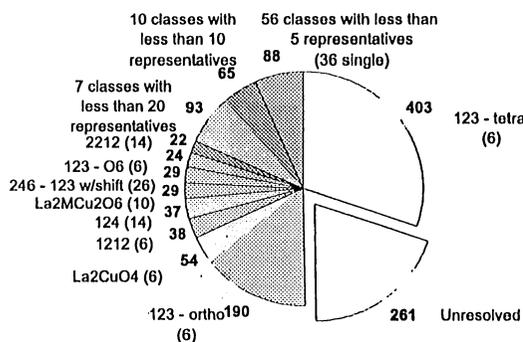

Figure 8　The most representative classes of extracted materials combined by their sequences of layers. Number of representatives is given in bold. For accentuated classes number of layers per unit cell (the sequence length) are shown in brackets.

cuprate structures and emergences of several 3D primitives in the extracted compounds.

All resulting sequences have been sorted as character strings and 82 different classes have been revealed. Diagram on Figure 8 separates the most representative 10 classes (with more than 20 representatives), others are shown in the groups with less than 20, 10 and 5 representatives.

Among compounds in the last group 36 compounds do not have analogs with the same layer sequence. Several reasons can cause this situation:

· Very rare structure.
· Sequences have not been standardized. Structure may be equivalent, but shifted relatively each other in some direction. For example, sequences $1o5c1o8c1o5c1o^{(1)}$, $1c5o1c8o1c5o1c^{(2)}$ and $8o1c5o1c5o1c8o^{(3)}$. Structure (2) shifted relatively (1) in the layer plane to the center (x+1/2, y+1/2); whereas sequence (3) shifted in the direction perpendicular to the layer plane. To eliminate separation of these structures, a normalizing procedure is necessary.
· Layers separation due to large constituent elements, as in case of 5o=8o+9c.
· Various kinds of errors in database. Unfortunately, as any man-made product, ICSD is uninsured from some errors, although, all data go through serious procedure of quality check. However, for example, 5 of the extracted compounds have interlayer distances more than 5 Å that seems to be impossible. They are displayed in Figure 9 by cross sign (×) and have been discarded from
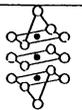
Sequence fragments	5o5c	5o1c5o	8o1c5o	8o1c8o	5o3(4)c5o	5o1?fc5o	1o8c(1o 8c)$_n$1o
3D primitives	Rocksalt shift	Cu-O octahedron, Perovskite block	Cu-O square pyramid, defective perovskite	Cu-O square	Cu-O square chains	Cu-O chains	alternate Cu-O layers
Number of compounds	298	614	904	45	208	24	877

Table 3　3D structural primitives as fragments of layers sequence.

the analysis. In several cases a wrongly assigned space group or atomic coordinates cause a distance between two atoms to be significantly smaller than the sum of their ionic radius. Thus the proposed procedure can serve as an additional tool for data quality control.

By the same reason as presented above programs are also imperfect and can result in an error in some unusual situations. To eliminate them wherever possible, sequences have been analyzed by several criteria:

· symmetry of layers relatively center of sequence;

· combinations of neighboring layers following Table 1 (revealed variants are shown there in bold);

· average distances between layers calculated from c parameter of unit cell and number of layers per unit cell and comparing them with Figure 9.

Last criteria, average interlayer distance d_l, seems to be very important for describing and understanding similarities in layered structures. Consequently, such an analysis has been performed in a systematic way and is discussed here.

To know the influence of the number of layers on unit cell size, the dependence between parameter c and number of layers per unit cell has been illustrated. (Actually the parameter c in this context does not mean the lattice parameter c assigned in the database, but the maximum axis, which represents the direction of layers stacking.) The result is shown in Figure 9. It proves a linear character of their relation for all analyzed structures. Data points can be approximated by a trend line y=1.95x at R-squared value R^2=0.98 and under a condition of fixed intersection of the origin of coordinates. (Under this approximation the thickness of layers is not taken into account, thus at N_l=0 c=0.) Coefficient 1.95 is nothing but the average interlayer distance D_l in angstroms among all analyzing compounds. The upper and lower boundary assuming average interlayer distance ($\pm$0.5 Å are shown as dashed lines. The average interlayer distance is obtained by another way, by averaging ratio d_l=c/N_l for each compounds. In this case D_l equal to 1.96, that is very close to previous result. These data also are consistent with the results obtained by calculation of interatomic distances in the direction perpendicular to the layer plane, although in that case the thickness of layers has been taken into account.

As one of the most important topics on these superconducting and related materials is to find a guideline to improve such properties as Tc, Jc, Hc, it seems to be worthwhile to test whether there is any correlation between structural parameters and critical tem-
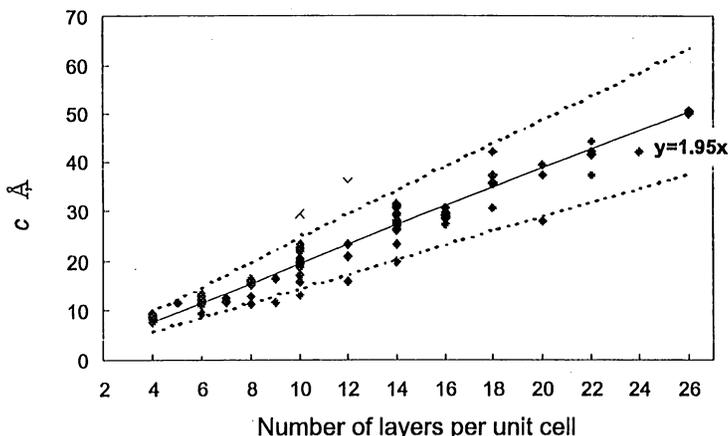
Figure 9　Lattice parameter c via number of layers per unit cell in copper-oxide compounds extracted from ICSD

perature of superconducting transition Tc or not. As a trial example, Tc via average interlayer distance (c/N_l ratio) are displayed in Figure 10.

As has been emphasized before ICSD database does not contain any physical properties including superconducting ones. The Tc data have been obtained from papers cited in ICSD. Therefore, these data has been obtained by various techniques, on different samples, by different researchers and in non-standardized experiment conditions. Thus they can be used in such study only with a great caution.

Unfortunately in this case even without any mathematical treatment the lack of any correlation between these properties can be concluded. It implies we need additional parameters to find some correlation in another direction or possibly in the aggregation with other dimensions. Nevertheless the study of such dependencies and search for reliable structural parameters should be continued. Several perspective·directions can be proposed. For example, thickness of layers (both average and in specific layers), distances between characteristic layers, size of structural blocks and so on. These and other features are planned to be implemented in the future versions of this developed software.

8　Search for compounds with isomorphic structure

There is also a problem now to be able to state any structure as a model and search for isomorphic structures. It is not a trivial task. Similar structures may appear in different space groups or with a different formula making it difficult to prescreen. Relation between isomorphic compounds often can be missed without prior chemical knowledge. On the other hand sometimes it is difficult to separate non-isomorphic structures with similar elemental composition. For example, lets consider 3 compounds from the ICSD:

All of them have very complex elemental compositions with element deficiency and substitution. Is it possible to find some relations between them without 3D representation? Somebody may find that elemental ratio of these phases is very close to 123 ($YBa_2Cu_3O_{7-\delta}$), compound 4 in Table 3:

1. $PrBa_2(Cu_{2.83}Al_{0.17})O_{6.55}$
2. $(Ca_{0.70}La_{0.30})(BaLa_{0.56}Ca_{0.44})$
   $[(Cu_{0.95}Zn_{0.05})_2Cu_{0.78}]O_{6.52}$
3. $(Y_{0.63}Ca_{0.53})Ba_2(Hg_{0.63}Cu_{2.21})O_{6.6}$

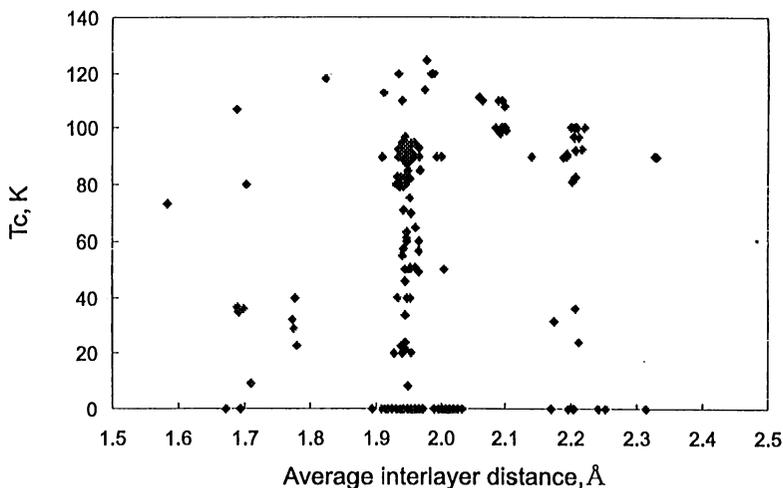However, layers sequences for these compounds:

Figure 10　Critical temperature of superconducting transition via average interlayer distance in copper-oxide compounds extracted from ICSD

N	Formula	Space group	a, Å
1	$Ba_2PrCu_2(Cu_{0.83}Al_{0.17})O_{6.55}$	P4/mmm	3.906
2	$(Cu_{0.95}Zn_{0.05})_2(BaLa_{0.56}Ca_{0.44})$ $(Ca_{0.70}La_{0.30})Cu_{0.78}O_{6.52}$	Pmmm	3.877
3	$(Y_{0.63}Ca_{0.53})Ba_2Hg_{0.63}Cu_{2.21}O_{6.6}$	P4/mmm	3.87

1. 1o 5c 1o 8c 1o 5c 1o
2. 1o 5c 1o 8c 1o 5c 1o
3. 5o 5c 1o 8o 1o 5c 5o

give us more close answer. First two compounds have identical sequences of layers and belong to 123 class, whereas third one is Hg-1212 phase.

It seems possible to conclude that this approach to description of layered compounds is very useful for comparing structures to one another, for analysis of their geometrical relationship and for understanding the atomic configuration of complex structures.

9　Conclusions

In this work the example of definition and isolation of structural primitives for the case of copper-oxide high temperature superconducting and related materials has been de-scribed. Similar approach can be applied for other classes of materials by revealing off their common structural features, structure primitives and rules of their organization. As was shown the layer-by-layer model help us not only to retrieve useful information about key elements in crystal structures of currently known superconductors, but also to find relations between different structures even with different structural types and space groups.

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