

Polysomatic series in the structures of complex cuprates

L. LEONYUK,^{a*} G.-J. BABONAS,^b V. MALTSEV^a AND V. RYBAKOV^c

^aDepartment of Geology, Moscow State University, Moscow 119899, Russia, ^bSemiconductor Physics Institute, Vilnius LT-2600, Lithuania, and ^cDepartment of Chemistry, Moscow State University, Moscow 119899, Russia.

E-mail: lydia@nw.math.msu.su

(Received 12 June 1998; accepted 7 December 1998)

Abstract

The modular approach was applied to analyse the structure of complex cuprates. The modular series of various types were distinguished in the family of layered cuprates making use of the classification scheme in a fragment approximation developed earlier. The polysomatic series were revealed in the groups of cuprates which were expected to possess the properties of both salt and oxide. The structure of the ladder-type cuprates was analysed in more detail. The present study has shown that the polysomatic model can be efficiently applied to the structural analysis of complex cuprates.

1. Introduction

The concept of polysomatism was firstly proposed by Thompson (1978) and developed by Veblen (1991) for the analysis of a complex structure of rock-forming silicates. In the polysomatic model, the complex structure of a polysome is considered as a regular alternation of various geometrically commensurate polysomatic slabs. Each slab corresponds to one of the end members of the series. The polysomatic approach allows one to reveal the common structural features in a family of related compounds and to correlate them with specific physical properties. At present, the polysomatic model takes into account the defects and domains of nanometric scale which can be indicated by high-resolution electron microscopy (HREM). Nanometric domains possess particular chemical composition and structure that differ from those of a host compound.

In the present work, the polysomatic approach is applied to the structural analysis of cuprates, which are treated as the class of salts similar to silicates by the principles of structure formation. The compounds in the family of complex cuprates are distinguished to reveal the generic relationship between the structures and to emphasize the characteristic features. In the present study, the polysomatic model for cuprates was developed. The structure of incommensurate-type cuprates was analysed in more detail and new possible structural types were predicted.

2. Series in the modular structures of complex compounds

In the fragment approximation (Veblen, 1991), the modular structure of a complex compound is considered as that composed of separate modules or building blocks usually stacked alternately in a particular direction. According to the structure and chemical composition, the blocks can be both identical or different. The identical blocks can form a complex compound due to the *crystallographic shear* and *chemical twinning* (Makovicky, 1997). Various combinations of different blocks can be distinguished in the compounds which are grouped into the *plesiotypic*, *merotypic*, *polytypic* or *polysomatic* series of structures (Veblen, 1991; Makovicky, 1997). The terms noted above characterize the relationship between the structures that constitute a particular series. The similarity between compounds increases in the sequence *plesiotypic* → *merotypic* → *polytypic* series. The structure is similar in the *polytypic* or *polysomatic* series. In a great variety of cuprate structures, various groups of compounds are expected to form the series of different types.

The *polytypic* series represents the compounds composed of the same set of various blocks stacked in a different order. The principal distinguishing feature of the *polysomatic* series (Thompson, 1978) is the presence of the real compounds called the end members *A* and *B*, each containing blocks of one type. The member of a polysomatic series called a polysome *AB* is the combination of the polysomatic blocks (or slabs) corresponding to the end members *A* and *B*. In the structure of the polysome, the bonds inside the blocks are usually assumed to be stronger than those between the blocks. Hence, structural distortions as well as deformations are expected (Veblen, 1991) to accumulate at the interfaces between the blocks. In considering the features of a polysome, the geometry and composition as well as the physical properties of the end members should be taken into account.

If the end members are absent in the group of related compounds composed of the same set of various blocks, the series is called *polytypic*. If each member of the series is composed of several blocks but only one block is common for all the members, the series is called

Table 1. *Structural classification of layered cuprates*

Row No.	Type of blocking layer BL [†]	Columns of constant main fragments MF					
		1	2	3	4	5	6
1	–	0201	0021	0011			
2	–		0222	0212	0223	0234	0245
3	<i>BO</i>	1201	1222	1212	1223	1234	1245
4	<i>2BO</i>	2201	2222	2212	2223	2234	2245
5	<i>C S 2S</i>	1201- <i>C</i>		1212- <i>C</i> 1212- <i>S</i> 2212- <i>S</i>	1223- <i>C</i>	1234- <i>C</i>	1245- <i>C</i>
6	<i>O 2O</i>	1201- <i>O</i>	1222- <i>O</i>	1212- <i>O</i> 3212- <i>O</i>			
7	<i>T</i>	1201- <i>T</i>	1222- <i>T</i>	1212- <i>T</i>			
8	<i>RO + ABO₃</i>	3201- <i>C</i>	3222- <i>C</i>	3212- <i>C</i>			

[†] *BO* and *2BO* are rock-salt- and double rock-salt-type units; *C*, *S*, *O* and *T* denote that the oxygen polyhedra for cations in blocking layers are lines, squares, octahedra and tetrahedra, respectively

merotypic. If the structures form a group that is built on the same overall principles, *i.e.* contain fundamental structural elements of the same general types and mutual disposition/interconnection of these elements in all groups follows the same general rules, the series is called *plesiotypic* (Makovicky, 1997).

The separation of the series reveals the generic relationship among the compounds and it is useful for a classification of the crystalline structures. In addition, common structural fragments can be correlated with the properties of real compounds, in particular, in the case of polysomatic series.

3. Structural series in the groups of complex cuprates

The structures of several cuprate groups will be considered. The polysomatic and other series types will be distinguished in order to reveal the general regularities in the structures of complex cuprates.

3.1. Layered cuprates with CuO_2 planes

The structure of layered cuprates possessing the CuO_2 plane was discussed previously in the fragment approximation (Leonyuk *et al.*, 1997a). Detailed analysis has shown that the structure of cuprates can be considered as a modular structure of tetragonal or pseudotetragonal symmetry. The structures consisted of a limited number of layered modules with identical lattice parameters in the basal plane perpendicular to the stacking direction. The modules were separated into two groups of main fragments (MF) and blocking layers (BL). The MF contained the essential fragments in layered cuprates, the Cu–O planes. A variety of cuprate structures was analysed by various combinations of the main fragments stacked alternately with the BL.

Table 1 presents the scheme of the layered cuprate structures according to Leonyuk *et al.* (1997a). In the numerical notation of the compounds, the first entry describes the number of blocking layers BL. The first number is zero for the compound consisting of only main fragments. If the BL is represented by a dumbbell,

square, tetrahedron or octahedron, then additional notations *C*, *S*, *T* and *O* are correspondingly used. The last three numbers characterize the structure of the Cu-containing main fragment MF. The second numeral denotes the number of atomic layers *RO* of a rock-salt-type structure outside the Cu–O units in the MF. Cation and oxygen atoms are assumed to be located in one plane of the *RO* unit. The third and fourth numerals characterize the MF containing Cu. The fourth numeral is the number of Cu–O planes, while the third is the number of cation layers between the Cu–O planes. The third entry is 1 for the CaCuO_2 -type fragment and 2 for the D_2O_2 fragment representing the fluorite-type unit with cations and oxygen atoms located in different planes. If the Cu-containing unit is the fragment $n\text{ACuO}_2$ (where *A* is an alkaline-earth element), then the last two numbers are equal to 12, 23, 34 and 45 for $n = 1, 2, 3$ and 4, respectively.

In the present approach, the columns in Table 1 represent the merotypic series as the corresponding compounds are composed of one common module, the main fragment MF and various blocking layers BL. In each row, the compounds contain different main fragments and the blocking layer of the same structure. However, the blocking layers can also differ owing to the isomorphic substitutions. For these reasons, the complete series of modular structures are not formed in each row.

As an example, let us consider the second row in Table 1. It presents the set of compounds (Table 2) consisting of the main fragments including the layers *RO* of the rock-salt-type structure at the ends. The part of the fragment enclosed between the Cu–O planes is different for various members of the row. The first compound 0222 contains Ce which causes the fluorite structure of the layer D_2O_2 instead of the infinite-layer type structure $\text{CuO}_2\text{--A--CuO}_2$ in the three other compounds of the set. Therefore, the set of compounds does not form a series. However, the last three members of the row can be considered as *plesiotypic* series or as *polytypic* series with isomorphic substitutions. It should be noted that the distinct boundary between these two

Table 2. Structural interpretation for a group of cuprates

Notation	Chemical formula	Structural formula
0222	(Nd, Ce, Sr) ₂ (Sr, Nd, Ce) ₂ Cu ₂ O ₈	...+RO-CuO ₂ -D ₂ O ₂ -CuO ₂ -RO+...
0212	(La, Sr, Ca) ₂ (La, Sr, Ca)Cu ₂ O ₆	...+RO-CuO ₂ -A-CuO ₂ -RO+...
0223	(Pb, Ba) ₂ (Y, Sr) ₂ Cu ₃ O ₈	...+RO-CuO ₂ -A-CuO ₂ -A-CuO ₂ -RO+...
0234	(Sr, Ca) ₂ (Sr, Ca) ₃ Cu ₄ O ₁₀	...+RO-CuO ₂ -A-CuO ₂ -A-CuO ₂ -A-CuO ₂ -RO+...

types of series is difficult to determine in the case of complex structures.

The compounds in rows 3 and 4 and columns 3 to 6 (Table 1) with the main fragments ($RO + nACuO_2 + RO$) (where $n = 1, 2, 3, 4$) form the *polytypic* series for Tl-Ba cuprates. This set does not correspond to the polysomatic series because the rock-salt-type structure is not characteristic of Tl oxide: the fluorite-type and Sc_2O_3 -type structures are typical of Tl_2O and Tl_2O_3 (Wells, 1986), respectively. If the Tl-Ba compound from the first column with the main fragment ($RO + CuO_2 + RO$) is taken into account, the set represents the *merotypic* series with a common block $ACuO_2$.

Using the present approximation, it is interesting to analyse the group of compounds described by the formula $M - m2(n - 1)n$ (Yamauchi *et al.*, 1996), where m denotes the 'charge reservoir' block with m atomic planes like Bi_2O_2 , Tl_2O_2 , TiO , HgO_8 *etc.* for each cation M and n is the number of CuO_2 planes. A homologous series can be formed by the compounds with the same charge-reservoir block and with different n values. However, from the viewpoint of modern modular crystallography (Ferraris, 1997), the series with a constant M member can be called *merotypic* because of the presence of one constant member M or *polytypic* as being composed of identical units but differing in their number and stacking sequence.

It should be noted that the well known tetragonal Y-123-type structure can be treated (Wu *et al.*, 1994) as isomorphous to the $n = 2$ member of the series $Cu-12(n - 1)n$. As a whole, the Ba-Ca-Cu-O system can be considered as a *polytypic* series, into which $Y(Ca)Ba_2Cu_3O_x$ can be included taking into account a possible substitution $Y \leftrightarrow Ca$.

The structure of Bi compounds is known to be strongly dependent on doping. In the case of Pb-doped Bi-2212-type compounds, the Bi-O layers are characterized by the rock-salt-type structure and the regularities are similar to those described above for Tl compounds. Our recent studies have shown (Maltsev *et al.*, 1997) that the Bi-O layer of the rock-salt structure can be formed only at high Pb concentration on the Bi sites or making use of a special technological regime of the crystal growth with multiple melting and quenching. However, in the major cases of non-doped Bi-2212 compounds, the structure of the Bi-O layer is close to defect fluorite and to the structure of Bi_2O_3 (Leonyuk *et al.*, 1997a; Maltsev *et al.*, 1997). Therefore, the Bi-2212-type compound can be regarded as the polysome

AB of chemical composition $(Bi_2O_{3-x})(Sr_2CaCu_2O_6)$ in the *polysomatic* series with the end members $(Sr, Ca)_2(Sr, Ca)Cu_2O_6$ (A) and Bi_2O_3 (B). On the basis of the polysomatic model, the monoclinic distortion as well as the solid-phase reactions at the interface boundaries between the corresponding polysomatic slabs can be expected. The corresponding structural features of Bi-2212-type compounds were indicated experimentally as a particular habit of the single-crystalline samples.

The Bi-2212 phase can be considered as the polysome in another polysomatic series with the end members $CaCuO_2$ (the infinite layer structure) and $Sr_{1+x}Bi_{1-x}O_3$ (perovskite with monoclinic distortion). The structure of the latter phase was determined experimentally (Kazakov *et al.*, 1997).

A consideration of the Bi-2212-type phases as the members of a polysomatic series allows one to assume that the anomalously high T_c values observed experimentally (Maltsev *et al.*, 1997) can be related to the local lattice deformations and the solid-state reactions at the block boundaries. Such a possibility proposed earlier (Geballe, 1993) can be justified by the model described above.

The compounds in row 5 (Table 1) form the *merotypic* series with a common blocking layer of the Cu, O dumbbells. The compounds 1212-S ($YBa_2Cu_3O_7$) and 2212-S ($Cu_2Ba_2YCu_2O_8$) in column 3 with the main fragment ($RO + ACuO_2 + RO$) contain a similar blocking layer composed of the chains of the Cu, O squares. The whole set represents the *plesiotypic* series because the blocking layers are only similar but not the same.

The analysis presented illustrates that all known series of the modular structures can be distinguished in the family of layered cuprates. All high- T_c cuprates can obviously be attributed to one merotypic series in which the common fragment is the part of the infinite layer structure $CaCuO_2$ taking into account the isomorphic substitution of Y for Ca. The charge reservoir is represented by the blocking layer, the composition and structure of which vary in a wide range.

The identification of polysomatic series is most important for understanding the physical properties and their correlation with the structural features. For example, the end members A and B of the polysomatic series denoted above for the Bi-2212 phase differ not only by the symmetry. The end member A is oxide and the end member B is cuprate, *i.e.* the salt of the hypo-

thetical 'copper-acid' (Leonyuk, Babonas, Pushcharovskii & Maltsev, 1998). Therefore, cuprates that can be treated as polysomes in the polysomatic series are expected to manifest the features of both oxide and salt.

3.2. Layered cuprates with Cu_2O_3 planes (ladder-type structures)

From the viewpoint of crystallography, the structure of cuprates with various cuprate-forming cations is analogous to groups of silicates with small and large silicate-forming cations. The structural units, such as chains, ribbons, layers and frames, composed of single SiO_4 tetrahedra sharing apexes are typical of silicates with small cations like Mg, Fe *etc.* Similar structural units composed of doubled tetrahedra Si_2O_7 are distinguished in silicates with large cations like Ca, Sr *etc.* (Bokii, 1971). By analogy, the structural units in cuprates are composed of the single Cu, O squares sharing corners and the doubled Cu, O squares sharing edges in the case of relatively small (Ca) and large (Sr) cations, respectively. Therefore, the structure of the Ca-row compounds $[\text{Ca}_2\text{CuO}_3\text{-CaCuO}_2\text{-(Y)123}]$ is characterized by the chain CuO_3 or the plane CuO_2 while the double chain Cu_2O_4 and the so-called ladder-type plane Cu_2O_3 are typical of the Sr-row compounds. This scheme includes only some of the cuprates. However, the scheme is important for a comparison of the ladder-type compounds with well studied cuprates possessing the CuO_2 planes.

Recently, cuprates containing Cu_2O_3 planes were widely investigated. These compounds were predicted to be superconducting (Rice *et al.*, 1993). So far, two structural types with the Cu_2O_3 planes have been distinguished: SrCu_2O_3 (Takano, 1994) and $[\text{MCu}_2\text{O}_3]_m[\text{M}_{m/n}\text{CuO}_2]_n$. The latter structure was usually represented by the formula $\text{M}_{14}\text{Cu}_{24}\text{O}_{41}$, *i.e.*

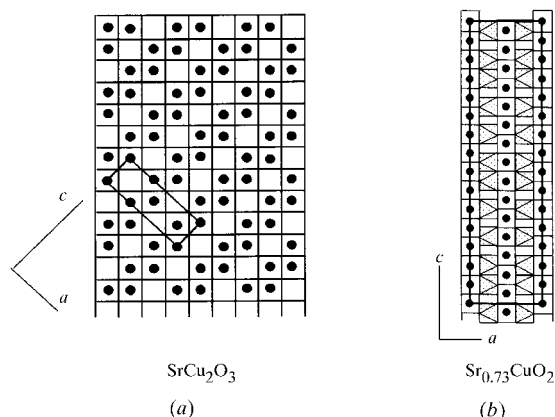


Fig. 1. The cross section parallel to the (ac) plane and perpendicular to the stacking b axis in the structures of SrCu_2O_3 (a) and $\text{Sr}_{0.73}\text{CuO}_2$ (b). The full circles denote Cu atoms in square coordination with oxygen. In (b), the projection of cation polyhedra is shown by the dotted planes. The unit cells are marked by thick lines.

$[\text{MCu}_2\text{O}_3]_m[\text{M}_{m/n}\text{CuO}_2]_n$, where $m/n = 7/10$. The $[\text{MCu}_2\text{O}_3]_m[\text{M}_{m/n}\text{CuO}_2]_n$ -type compound is called an incommensurate phase and can be represented as the polysome (Leonyuk, Babonas, Maltsev, Shvanskaya & Dapkus, 1998) in the polysomatic series with end members SrCu_2O_3 and $\text{M}_{1-x}\text{CuO}_2$ (Karpinski *et al.*, 1997). Both end members are not stable and are grown at high pressures. However, the incommensurate-type compound $[\text{MCu}_2\text{O}_3]_m[\text{M}_{m/n}\text{CuO}_2]_n$ is stable at ambient pressures. Our recent investigations have shown (Leonyuk, Babonas, Rybakov, Sokolova, Szymczak, Szymczak *et al.*, 1998) that $[\text{M}_2\text{Cu}_2\text{O}_3][\text{Cu}_{1+\delta}\text{O}_{2+\gamma}]$ of the 'Cu-deficient ladder-type structure' can be attributed to the group of ladder-type compounds. In the growth at ambient pressure, the Cu-deficient ladder-type structure is formed instead of the MCu_2O_3 type. The $[\text{M}_2\text{Cu}_2\text{O}_3][\text{Cu}_{1+\delta}\text{O}_{2+\gamma}]$ -type structure can be considered as a stacking of the ladder-type planes in which each second ladder plane is rotated by 45° and about 1/3 of Cu atoms are absent.

Let us consider the polysomatic model of incommensurate-type phases $[\text{MCu}_2\text{O}_3]_m[\text{M}_{m/n}\text{CuO}_2]_n$ in more detail. Fig. 1 presents the (ac) plane cross section of the structure of the end members perpendicular to the stacking b axis. The polysome AB is formed when two slabs A and B are combined. The incommensurate parameters in the slabs A and B along the c direction perpendicular to the stacking b axis leads to the formation of modulated structures $[\text{M}_2\text{Cu}_2\text{O}_3]_m[\text{CuO}_2]_n$ (Fig. 2).

The treatment of the incommensurate phases in the polysomatic approach means that the $[\text{M}_2\text{Cu}_2\text{O}_3]_m[\text{CuO}_2]_n$ -type phase can be considered as the polysome $[\text{MCu}_2\text{O}_3]_m[\text{M}_{m/n}\text{CuO}_2]_n$ (AB) (Fig. 2). Each member of the polysomatic series represents the phase with different coefficients m/n . The m/n values indicate the period of the structural modulations along the c axis and ensure the resulting commensurate matching of the sublattices which correspond to the end members. The most stable structure is realized in the

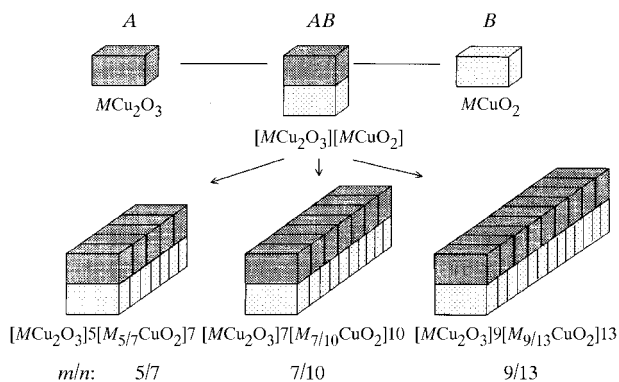


Fig. 2. The construction of polysomes $[\text{MCu}_2\text{O}_3]_m[\text{M}_{m/n}\text{CuO}_2]_n$ in the series of incommensurate ladder-type cuprates.

case of $m/n = 7/10$. In the latter compound, the interatomic Cu—O distances are close to the average values in the whole family of cuprates. The deviation of the m/n ratio from $7/10$ indicates (Leonyuk, Babonas, Rybakov, Sokolova, Szymczak, Szymczak *et al.*, 1998) the phase metastability, which according to Matthias (1973) can lead to high values of the temperatures at which the transition to the superconducting state occurs.

3.3. Polysomatic series in the structures of doped Ca, Sr cuprates

The scheme of polysomatic series in the structures of alkaline-earth cuprates is shown in Fig. 3. The scheme allows one to predict the formation of new structural types in the group of doped Ca, Sr cuprates. The apexes correspond to the end members and the points on the lines joining apexes represent the polysomes in the polysomatic series. The compounds known so far are denoted as full circles while the open circles are for predicted compounds. On the apices of the central triangle, three compounds SrCu_2O_3 , CaCuO_2 and $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ are located. These compounds are considered as the end members of the polysomatic series with the characteristic two-dimensional modules: the ladder-type Cu_2O_3 plane, the ordinary CuO_2 plane and the Cu_3O_4 plane with crossed Cu—O ribbons (Müller-Buschbaum, 1977), respectively. The single polysomatic compound known so far is $\text{Sr}_{n-1}\text{Cu}_{n+1}\text{O}_{2n}$ ($n = 3, 5, 7$) (Takano, 1994). The ladder-type planes in $\text{Sr}_{n-1}\text{Cu}_{n+1}\text{O}_{2n}$ compounds with various numbers of legs can be considered as the combination of the slabs typical of the end members SrCuO_2 and CaCuO_2 . The middle point corresponds to the complex cuprate with a three-leg ladder plane. An increase in the number of legs will shift the point towards the end member CaCuO_2 . The principal aspect is that the two-dimensional modules are combined *in the plane* while the structure of the poly-

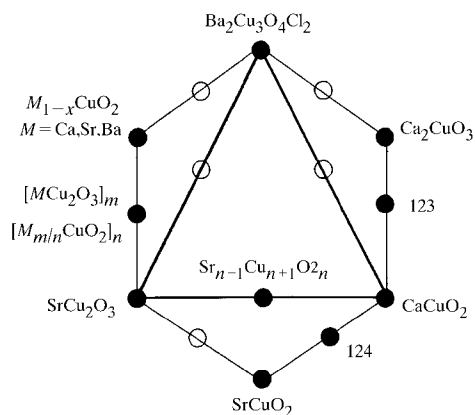


Fig. 3. Polysomatic series in the structures of alkaline-earth cuprates. Full and open circles denote known and predicted polysomatic compounds, respectively.

some can be represented as the alternating stacking of identical modules.

Three apexes outside the central triangle (Fig. 3) represent Ca_2CuO_3 , SrCuO_2 and $M_{1-x}\text{CuO}_2$ with characteristic one-dimensional beam modules (Leonyuk *et al.*, 1997b) composed correspondingly of the single and double chains of Cu—O squares sharing corners and the Cu—O ribbon of Cu—O squares sharing edges. The combination of the end members with different dimensions of the characteristic modules leads to the formation of the layered-type polysomes in which different slabs are stacked along a particular direction. In this case, the one-dimensional modules are polymerized to form the two-dimensional module (Leonyuk *et al.*, 1997b). In this scheme, the well known superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$ (123) is treated as a polysome with the end members of the structural types CaCuO_2 and Ca_2CuO_3 . Another superconducting cuprate $\text{YBa}_2\text{Cu}_4\text{O}_8$ (124) is the polysome in the series with the end members of the structural types SrCuO_2 and CaCuO_2 . As noted above, the incommensurate-type compounds $[\text{MCu}_2\text{O}_3]_m[\text{M}_{m/n}\text{CuO}_2]_n$ can also be considered as the polysomes. The polysome with the end members SrCuO_2 and SrCu_2O_3 is assumed to be analogous to the Y-124-type compound.

Two other polysomes on the main triangle can be predicted. A simple scheme in Fig. 4 illustrates a possible combination of the ladder-type Cu_2O_3 and ordinary CuO_2 -type planes with the fragments of the plane of the crossed Cu—O ribbons characteristic of $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$. In the first case (Fig. 4a), the corresponding polysome can be realized with cuprate-forming cations Ba and Sr distributed randomly. In the second case (Fig. 4b), a large difference in ionic radii for Ba and Ca should be noticed. Therefore, possible cation ordering can be predicted or a high pressure during the growth must be used to preserve the random cation distribution in a realization of the polysome.

Similar difficulties can be foreseen in a realization of polysomes with a combination of a two-dimen-

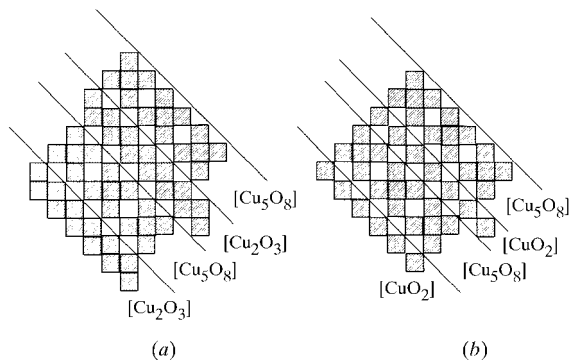


Fig. 4. A possible combination of the slabs in the polysomes of the series with the end members $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ – SrCu_2O_3 (a) and $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ – CaCuO_2 (b).

sional module of crossed Cu—O ribbons (a fragment of $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$) with one-dimensional modules $M_{1-x}\text{CuO}_2$ and Ca_2CuO_3 . Taking into account the relative concentration of M cations in the end members, the M -cation radius r_M is expected to be larger than r_{Ba} in the series with the end member $M_{1-x}\text{CuO}_2$. In another series with the end member Ca_2CuO_3 , the condition $r_{\text{Sr}} \approx r_M < r_{\text{Ba}}$ can be predicted for a realization of the polysome. However, in the latter case the predicted complex cuprate should possess the incommensurate-type structure as the parameters of two sublattices are caused by the edge and diagonal of the Cu—O square. The realization of a polysome in the series with the end member of $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ -type structure is highly probable in the group of Ba-containing composite materials.

The structures of SrCuO_2 and SrCu_2O_3 are very similar. They can be constructed by the same modules with a different relative location. Therefore, the realization of the polysome in the series with the end members SrCuO_2 and SrCu_2O_3 can be modelled as an intergrowth caused by structural defects of one structure. It is reasonable to assume that the transformation of the ladder planes in SrCu_2O_3 to the isolated 'ladder chains' in SrCuO_2 can be caused by a relative increase of the concentration of a cuprate-forming cation. In addition, the structure of SrCuO_2 can be analysed as being composed of the blocks (Fig. 5) of one structural type A , the complexity of the structure originating from the chemical shift. As the different polysomatic slabs are assumed to possess different chemical composition, the structural metastability is highly probable at the interfaces. It should be noted that the superconductivity in the crystals of the SrCuO_2 -type structure was indicated *only* in the nonhomogeneous samples (Leonyuk, Babonas, Rybakov, Sokolova, Szymczak, Maltsev & Shvanskaya, 1998). The superconductivity in $(\text{Sr}, \text{Ca})_{1-x}\text{CuO}_2$ of the SrCuO_2 -type structure can be assumed to be due to the local ordering of cations as in the $(\text{Sr}, \text{Ca})\text{CuO}_2$ compounds of an infinite layer structure (Adachi *et al.*, 1993). As a result of cation ordering in Ca, Sr cuprates, the formation of polysomes of nanometric scale can be assumed. The polysomatic features of the structures under consideration favour the occurrence of new structural types owing to a localization of defects along the boundaries of the slabs.

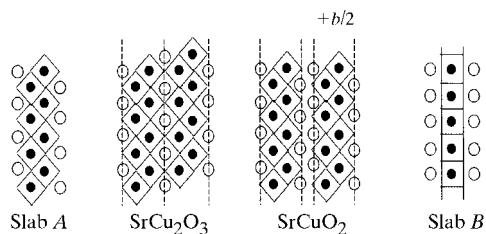


Fig. 5. The structure of slabs in ladder-type cuprates.

A similar effect of the formation of secondary phase at the decomposition of a solid solution was also observed in the rare-earth-doped Bi-2212-type structures (Leonyuk *et al.*, 1995). However, in the latter case, the decomposition of the solid solution occurred in the region of one structural type and the resulting isostructural phases differed by the concentration of the rare-earth atoms. The decomposition of solid solution and the local redistribution of cations can be considered as a manifestation of an extreme metastability of the host structure. This phenomenon can be related to an increase in the concentration of free carriers, which can lead to the occurrence of superconductivity (Matthias, 1973).

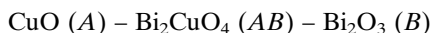
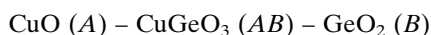
In Fig. 3, the polysomatic series between the end members located on the opposite sides of the central triangle are not shown but should be taken into account. The two-dimensional module characteristic of SrCu_2O_3 (ladder-type plane) can be combined with the one-dimensional modules Ca_2CuO_3 (single ordinary chain of Cu—O squares sharing corners). The resulting structure would be analogous to Y-123-type with the ordinary CuO_2 plane replaced by the ladder-type plane. The possibility of realizing this structure follows from the experimental observations of the intergrowth between the phases $[\text{MCu}_2\text{O}_3]_m[\text{M}_{m/n}\text{CuO}_2]_n$ and Ca_2CuO_3 .

The polysome in the series with end members CaCuO_2 and $M_{1-x}\text{CuO}_2$ can be considered as the analogue of the compounds of incommensurate-type structure, in which the ladder-type plane is replaced by the ordinary plane of Cu—O squares sharing the corners. Taking into account the structure of $\text{Ca}_{0.84}\text{CuO}_2$ (Meijer *et al.*, 1998), it is reasonable to assume that in this structural type the average cation radius should be close to that for Ca and $m/n \approx 0.84$. However, two factors preventing the formation of the structure should be mentioned. The first factor is that the structure should be incommensurate in two directions: along the c axis, as in the $[\text{M}_2\text{Cu}_2\text{O}_3]_m[\text{CuO}_2]_n$ -type phases, and along the a axis. The second factor is that the structural type CaCuO_2 is more stable than $\text{Ca}_{0.84}\text{CuO}_2$. Therefore, it is highly probable that the phase of CaCuO_2 type will be realized instead of the incommensurate structure of a new type. Nevertheless, this structural type can be obtained at high oxygen pressure from a primarily synthesized mixture of CaCuO_2 , CaO and CuO.

The scheme presented in Fig. 3 can be extended in order to take into account another polysomatic series of complex cuprates. As a whole, the scheme illustrating the relationship between the polysomatic series in alkaline-earth cuprates is quite common and can be compared with that for biopyrroboles (Thompson, 1978). The oxides of the rock-salt (SrO , CaO , BaO), defect-fluorite (Bi_2O_3) and perovskite (ABO_3 , where $A = \text{La}$, $B = \text{Cu}$, Sn , Ti *etc.*) structural types can also be considered as the end members in addition to cuprates.

3.4. Structures of CuGeO_3 and Bi_2CuO_4

These two structures can be attributed to the group of cuprates because they contain the structural units with fourfold coordinated copper (Leonyuk, Babonas, Pushcharovskii & Maltsev, 1998). The structures can be described as the members of the following polysomatic series:



It should be noted that the end members of these series are oxides of amphoteric elements which are able to manifest both acid and basic properties. Therefore, germanium and bismuth cuprates can also be called copper germanate and bismuthate, respectively, with their structures composed of equivalent modules. The structures can be compared with Ba cuprate BaCuO_2 , a typical salt, in which the oxygen atoms are bonded only to the Cu–O structural units. In the latter case, the structural units are the Cu–O ribbons composed of the edge-sharing CuO rectangles. The resulting structural units Ba–O in BaCuO_2 differ from those in the structure of Ba oxide.

4. Conclusions

The separation of the structural series, in particular polysomatic ones, provides additional insights into the generic relationship between the compounds of a complex structure. The structures of complex cuprates were analysed in the scheme of a modularity and the series of different types were distinguished. The series in the modular approach were revealed in the classification scheme of layered cuprates based on the fragment approximation applied previously for the analysis of the structure of complex cuprates.

The polysomatic model is shown to be useful in the interpretation of the structure of new complex cuprates, a prediction of new compounds and analysis of the experimental data. The correlation between the structure and physical properties can be analysed in the polysomatic approach based on the relationship discussed.

This work was supported in part by the Russian National Program on Superconductivity (project No.

98/007) and the Lithuanian Science Foundation (project No. 327).

References

- Adachi, S., Yamauchi, H., Tanaka, S. & Mori, N. (1993). *Physica (Utrecht)*, **C212**, 164–168.
- Bokii, G. B. (1971). *Crystal Chemistry*. Moscow: Nauka. (In Russian.)
- Ferraris, G. (1997). 17th European Crystallographic Meeting, Lisbon, Portugal. Abstracts, p. 39.
- Geballe, T. H. (1993). Preprint, Department of Applied Physics, Stanford University, Stanford, CA 94305, USA.
- Karpinski, J., Schwer, H., Keijer, G. I., Conder, K., Kopnin, E. M. & Rossel, C. (1997). *Physica (Utrecht)*, **C274**, 99–106.
- Kazakov, S. M., Chaillout, C., Bordet, P., Nunez-Regueiro, M., Rysak, A., Tholence, J. L., Radaelli, P. G., Putilin, S. N. & Antipov, E. V. (1997). *Nature (London)*, **390**, 148–150.
- Leonyuk, L., Babonas, G.-J. & Maltsev, V. (1997a). *Int. J. Appl. Electromagn. Mech.* **8**, 229–242.
- Leonyuk, L., Babonas, G.-J. & Maltsev, V. (1997b). *Physica (Utrecht)*, **C282–287**, 749–750.
- Leonyuk, L., Babonas, G.-J., Maltsev, V., Shvanskaya, L. & Dapkus, L. (1998). *J. Cryst. Growth*, **187**, 65–71.
- Leonyuk, L., Babonas, G.-J., Maltsev, V. & Vetkin, A. (1995). *Supercond. Sci. Technol.* **8**, 53–59.
- Leonyuk, L., Babonas, G.-J., Pushcharovskii, D. Yu. & Maltsev, V. V. (1998). *Crystallogr. Rep.* **43**, 256–270.
- Leonyuk, L., Babonas, G.-J., Rybakov, V., Sokolova, E., Szymczak, R., Maltsev, V. & Shvanskaya, L. (1998). *J. Phys. Chem. Solids*, **59**, 1591–1595.
- Leonyuk, L., Babonas, G.-J., Rybakov, V., Sokolova, E., Szymczak, R., Szymczak, H., Baran, M., Maltsev, V. & Shvanskaya, L. (1998). *Z. Kristallogr.* **213**, 406–410.
- Makovicky, E. (1997). *EMU Notes in Mineralogy*, Vol. 1, ch. 5, pp. 315–343. Eötvös University Press.
- Maltsev, V., Leonyuk, L., Babonas, G.-J. & Reza, A. (1997). Proceedings of the 3rd Summer School on High Temperature Superconductivity, Eger, Hungary, pp. 1–4.
- Matthias, B. T. (1973). *Physica (Utrecht)*, **69**, 54–56.
- Meijer, G. I., Rossel, C., Kopnin, E., Willemin, M., Karpinski, J., Schwer, H., Conder, C. & Wachter, P. (1998). *Europhys. Lett.* **42**, 339–344.
- Müller-Buschbaum, H. (1977). *Angew. Chem.* **89**, 704–717.
- Rice, T. M., Gopalan, S. & Sigrist M. (1993). *Europhys. Lett.* **23**, 445.
- Takano, M. (1994). *J. Supercond.* **7**, 49–54.
- Thompson, J. B. (1978). *Am. Mineral.* **63**, 239–249.
- Veblen, D. R. (1991). *Am. Mineral.* **76**, 801–826.
- Wells, A. F. (1986). *Structural Inorganic Chemistry*. Oxford University Press.
- Wu, X.-J., Adachi, S., Jin, C.-Q., Yamauchi, H. & Tanaka, S. (1994). *Physica (Utrecht)*, **C223**, 243–248.
- Yamauchi, H., Karppinen, M. & Tanaka, S. (1996). *Physica (Utrecht)*, **C263**, 146–150.