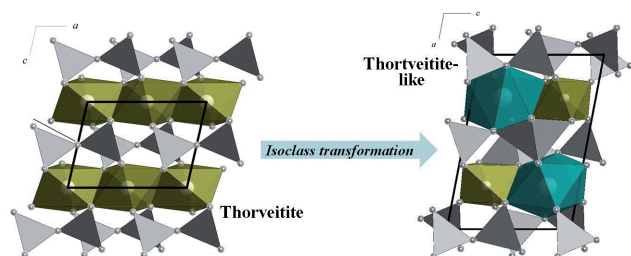


of this work was to determinate the structural relations between the space groups of the basic structure of layered thortveitite (S.G. $C12/m1$) and its derivative structure named thortveitite-like (S.G. $P12_1/m1$) when iron is partially substituted by yttrium in the layered thortveitite $FeInGe_2O_7$. The symmetry reduction promoted by the incorporation of yttrium in the formula $Y_xIn_{1-x}FeGe_2O_7$ ($x = 0, 0.25, 0.50, 0.75, 0.90$ and 1.0), is explained by mean of the crystallographic group-subgroup relationships.



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Keywords: symmetry relations, klassengleiche subgroups, thortveitite

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Using Lee-Richards Surfaces to calculate close contacts and complex interfaces

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The calculation of geometric interactions among macromolecular fragments, such as the identification of close contacts and complex interface regions, normally involves atom-by-atom comparisons of coordinates. In a brute-force calculation distance search involving molecular fragment A with N_A atoms and fragment B with N_B , $O(N_A N_B)$ distances need to be computed. A calculation using Levinthal cubing, Voronoi diagrams, NearTrees or other partitioning schemes can reduce this time to

$$O(\min(N_A \log(N_A) + N_B \log(N_A), N_B \log(N_B) + N_A \log(N_B))) \\ = O((N_A + N_B)(\log(\min(N_A, N_B))))$$

which is excellent for fragments of very different sizes but problematic for fragments of similar sizes. It is difficult to reduce the time further with any atom-by-atom based scheme. An alternative is to base the analysis of an interface on the electron density or a pseudo-density, which should display significant excess density in an interface, or on a molecular surface, which should tend to bridge an interface. Use of the Pseudo-Gaussian Approximation to Lee-Richards Surfaces (PGALRS) algorithm [2] to compute Lee-Richards surfaces [3] combined with use of a NearTree [1] to partition space allows generation of a molecular surface in linear time and identification of atoms forming a surface ($L RSA()$) in linear time. The atoms in the interface are then

$$(L RSA(A) \cup L RSA(B)) \cap (\neg L RSA(A \cup B))$$

which can be computed in $O(N_A + N_B)$ time. This calculation is sufficient for identification of close contacts and an efficient first approximation for interface identification. We are looking at using atom pairs for

more accurate interface identification. Use of only the atoms in A and B within a reasonable distance of $(L RSA(A) \cup L RSA(B)) \cap (\neg L RSA(A \cup B))$ would help to pre-prune the search tree for these calculations.

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Keywords: complex_interface, molecular_surface, contact

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Odd n-fatty acids $C_nH_{2n}O_2$ and their alloys on the X-ray powder diffraction data

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Saturated fatty acids $C_nH_{2n}O_2$ play important role in the life of plants and animals. Some even ones (even number n) were specified in the literature including our works. We refined X-ray characteristics of six even acids ($n = 12, 14, 16, 18, 20$, and 22) [1]; determined thermal deformations and polymorphic transformations of three acids ($n = 12, 14$ and 16); synthesized double alloys $C_{12}H_{24}O_2-C_{14}H_{28}O_2$ and $C_{14}H_{28}O_2-C_{16}H_{32}O_2$ as well as quaternary one $C_{12}H_{24}O_2-C_{14}H_{28}O_2-C_{16}H_{32}O_2$ in relative binary and ternary systems; and revealed rather limited isomorphism in these mixtures [1, 2].

Oppositely, odd fatty acids (odd n) have a weak state of knowledge because of their less spread in the nature [3]. For example, information about odd acids missed in the ICDD bank [4]. In this work we present results of X-ray powder diffraction study of odd fatty acids.

X-ray characteristics (crystal system, polymorph modification, indices hkl , elementary cell parameters, space group, etc.) of four odd fatty acids with $n = 13, 15, 17$, and 19 (homological purity 98–99 %) were obtained for the first time. In particular it was found that odd acids could crystallize at room temperature in monoclinic polymorphs of single and double layers.

Limits of solid solutions were established for two binary systems of odd components: $C_{13}H_{26}O_2-C_{15}H_{30}O_2$ (studied compositions, mol. % $C_{15}H_{30}O_2$: 10, 33, 50, 67, and 90) and $C_{15}H_{30}O_2-C_{17}H_{34}O_2$ (studied compositions, mol. % $C_{17}H_{34}O_2$: 10, 25, 33, 50, 67, 75, and 90). Our experiments showed rather limited isomorphism too, like in binary systems of even components [1, 2]. Thus, rather limited isomorphism specifies n-fatty acids even in systems of one parity. This differs principally n-fatty acids from n-paraffins, which molecules mix together in wide ranges forming solid solutions easily [5].

The diffractograms of the majority of melted binary mixtures of odd n-fatty acids displayed peaks of binary acid compound. Remarkable, the binary compounds are the new acids. They are presented by dimers combined of two molecules of different lengths. Herewith, we identified on these diffractograms also peaks of solid solutions, which compositions are nearly close to those of the excess components.

In binary systems of mixed parity, binary compounds of fatty acids do not apparently form after melting. For example, the diffractogram of the melted mixture (mol.) $C_{18}H_{36}O_2 : C_{19}H_{38}O_2 = 1:1$ represents peaks of only the original components. In our opinion, the limitation of the isomorphous miscibility should be caused by the dimeric nature of fatty acid molecules.

Apart from this, structural (thermal) deformations and polymorphic transitions of stearic acid $C_{18}H_{36}O_2$ were studied in view of the variety its polymorphic modifications; high temperature X-ray powder diffraction method was used.

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Keywords: organic, acid, isomorphism

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Structural deformations and phase transitions of normal paraffins

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Rotation of particles (atoms or molecules) around a point or an axis is a specificity of rotator crystals. Normal paraffins $n\text{-C}_n\text{H}_{2n+2}$ are classical representatives of rotator substances. This makes available to take them as examples for investigation of the rotator-crystal state, which is among the less investigated phase states of the matter. Transformation of a substance into a rotator-crystal state can be caused for instance by a heating and related to a change of the type of thermal movement of particles (atoms, molecules) due to the loss of the fixed orientation in the structure. In the case of n-paraffins, chain molecules acquire an ability of oscillator-rotator thermal motions around their axes.

Structural deformations and polymorph transitions were investigated with using of high temperature X-ray powder diffraction method (the temperature step is 0.1–0.5°C) for odd n-paraffins (*orthorhombic*) and even ones (*triclinic* and *monoclinic*) in the range of $n = 17\text{--}36$ (homological purity 97–99 %).

All the n-paraffins except of $n = 18$ transform into the low-temperature rotator-crystal state $rot.1$. Short-chain n-paraffins ($n = 17\text{--}28$) transform into the orthorhombic rotator-crystal phase $Or_{rot.1}$ [1, 2] and long-chain n-paraffins ($n = 29\text{--}36$) transform into the triclinic rotator-crystal phase $Tc_{rot.1}$ [3, 4]. The transformations of long-chain n-paraffins of $n = 27$ and 30 into the phases $Or_{rot.1}$ and $Tc_{rot.1}$ respectively run through the intermediate monoclinic rotator-crystal phase $M_{rot.1}$. The transformation of n-paraffins of $n = 33\text{--}36$ into the phase $Tc_{rot.1}$ runs through the intermediate triclinic crystal phase Tc_{cryst} . Only the “middle” (triclinic and orthorhombic) members of the n-paraffin homological members ($n = 22\text{--}26$) transform into high-temperature rotator-crystal state $rot.2$ (hexagonal phase $H_{rot.2}$). Cooling melts displayed the temperature reversibility and unreversibility of short-chain ($n = 17\text{--}28$) and long-chain ($n = 29\text{--}36$) n-paraffin transformations respectively.

The variety of the rotator crystal types (rotator-crystal states) increases owing to the crystal lattice shows the signs of both dynamic and static models as well as due to different molecules possess different character of thermal movement [1]. High temperature phase transition in long-chain n-paraffins are accompanied by lowering of crystal structure symmetry: $Or_{cryst} \rightarrow M_{rot.1}$ ($n = 27$), $Or_{cryst} \rightarrow Tc_{rot.1}$ ($n = 29$ and 31), $M_{cryst} \rightarrow Tc_{rot.1}$ ($n = 32$), $Or_{cryst} \rightarrow Tc_{cryst} \rightarrow Tc_{rot.1}$ ($n = 33$ and 35), and $M_{cryst} \rightarrow Tc_{cryst} \rightarrow Tc_{rot.1}$ ($n = 34$ and 36). The symmetry lowering proceeds due to a re-packing molecules in the n-paraffin structure. Under certain conditions, less symmetric but more dense packing can be formed.

Rotator phases possess some physical features, which are not typical for crystal substances. They are of a pronounced plasticity, which is the most important operating characteristic of n-paraffins. Eight binary

phase diagrams were plotted using data for mixtures of n-paraffins.

The work is supported by Russian Fund for Basic Research (project 10-05-00891).

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Ab initio direct solution from powder data lower than atomic resolution

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Direct methods work best when large numbers of well-determined reflection intensities have been collected to atomic resolution (better than 1.2Å). For a powder diffraction experiment, this situation is rarely the case. Powder diffraction patterns generally contain contributions from many overlapped reflections meaning that the condition of ‘well determined’ reflection intensities is not met. For moderately sized crystal structures, even with powder diffractometers of the highest angular resolution, it is impossible to obtain individual integrated intensities at atomic structural resolution.

The dual-space-based *Shake-and-Bake* procedure is one of the most successful direct methods for phasing single crystal diffraction data. A new method, termed Powder *Shake-and-Bake* [1] and implemented in the computer program *PowSnB*, addresses the handling of multiply overlapped reflections and the extension of powder diffraction data to atomic resolution via empirical estimation of the integrated intensities. *PowSnB* performs in each cycle of *SnB* iteration (i) a re-partitioning of overlapped-reflections (via partial structural information from the previous cycle), (ii) a reciprocal-space phase refinement (via the reduction of the values of a statistical minimal function), and (iii) a real-space density modification (via peak picking).

Successful *PowSnB* applications to experimental powder diffraction data lower than atomic resolution have demonstrated the power of the powder *Shake-and-Bake* method. This research was partially supported by a Knowledge Building grant from ExxonMobil Research and Engineering.

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Waste-free synthesis of the metallodrug bismuth subsalicylate

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