

for intermolecular interactions in the monoclinic paraffins. This value sharply decreases in the region of “rotator” phases existence and equals to zero in H_{rot} . A statistic and dynamic model was proposed, which provides an adequate description of the observed effect [2].

[1] Kotelnikova E. N., Filatov S. K., *Krystalokhimiya paraffins*, ed. “Neva” Zhurnal, St-Petersburg, 2002, 351. [2] Puchkovska G., Danchuk V., Kravchuk A., *J. Mol. Struct.*, 2004, **704**, 119.

Keywords: *n*-paraffins, polymorphism, X-ray - FTIR

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Structure and Properties of [4-NH₂C₅H₄NH][BiCl₄]

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The halogenoantimonates(III) and halogenobismuthates(III) of the general formula $R_aM_bX_{3b+a}$ (where R denotes organic cations, X = Cl, Br, I and M = Sb, Bi) form a large group of ferroelectric crystals [1]. The title crystal [4-NH₂C₅H₄NH][BiCl₄] (abbreviation – 4APCB) is closely related to the recently found antimonate(III) analog [4-NH₂C₅H₄NH][SbCl₄] [2], which reveals interesting ferroelectric properties with intermediate incommensurate phases. 4APCB undergoes at 252 K structural phase transition (PT) of first order. The room temperature structure (phase I) is monoclinic, space group Cc with $a = 13.229$, $b = 13.505$ $c = 7.350$ Å and $\beta = 120.31^\circ$. The structure is composed of BiCl₄⁻ ions which form infinite chains through the crystals via chloride linkages. Each bismuth lies in a distorted octahedral environment. The 4-aminopyridinium cation reveals substantial disorder. The low temperature phase (II) is monoclinic, space group P2₁/c with $a = 11.1660(7)$, $b = 13.5857(8)$, $c = 7.2750(4)$ Å and $\beta = 93.777(5)^\circ$. Over the phase II the organic cations are fully ordered. The structural analysis, calorimetric (DSC) and spectroscopic studies (IR) show that the PT is governed by the dynamics of the 4-aminopyridinium cations.

[1] Sobczyk L., Jakubas R., Zaleski J., *Pol. J. Chem.* 1997, **71**,265. [2] Jakubas R., Ciunik Z., Bator G., *Phys. Rev. B*, 2003, **67**, 024103.

Keywords: halogenobismuthate(III), disorder, phase transition

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Structure Transformations in the Saturated Hydrides ZrV₂H₄₋₆

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We have studied, by means of neutron powder diffraction, the structure transformations caused by hydrogen redistributions in the Laves saturated hydrides ZrV₂H_x, 4 < x < 6. In the range of 4 < x < 5, the uncommon order-disorder phase transition has been found [1]. Unlike the known transitions in the unsaturated hydrides, x < 4, it results in change of hydrogen surroundings when hydrogen ordering. As a result, the novel hydrogen superstructure ZrV₂H₅, with the atypical hydrogen surroundings, forms [2]. At maximum hydrogen saturation, near x=6, whatever phase transitions are eliminated. The maximum hydride ZrV₂H₆ exists only as ordered, and any attempt to disarrange the hydrogen results in hydrogen discharge down to x=5. The crystal structure of ZrV₂H₆ has been determined [3]. It is advance of the Spinel-type structure found earlier in the saturated hydrides ZrTi₂H₄ and HfTi₂H₄. The work was partly supported by the Russian Foundation for Basic Research and Russian State Program HIII-2037.2003.2.

[1] Bogdanova A.N., Andre G., *J. Alloys Comp.*, 2004, **379**, 54. [2] Bogdanova A.N., Irodova A.V., Andre G., Bourée F., *J. Alloys Comp.*, in press. [3] Bogdanova A.N., Irodova A.V., Andre G., Bourée F., *J. Alloys Comp.*, 2003,

50, 356-357.

Keywords: hydrides, neutron powder diffraction, phase transitions and structure

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Structure and Phase Transitions of Some Crystals Containing [(CH₃)₃NH₂]⁺ and MeCl₄

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Results of our investigation of crystal structure and phase transitions of some crystals containing a bivalent metal, chlorine anion, and dimethylammonium (DMA) cations are reported. Studies of the crystals are of great interest, since data of the crystal structure of this compound are very scarce and mechanisms of phase transitions in them are not available. It was established that the crystal were grown from solution with copper chlorides have the composition [(CH₃)₂NH₂]₂CuCl₄[(CH₃)₂NH₂]Cl and, in room temperature are describes by orthorhombic space group *Pna*2₁. The structure of the crystals is built of CuCl₄ tetrahedral, three structure nonequivalent DMA groups, and individual chloride ions, which are links via an extended hydrogen bond system into three-dimensional framework. The unit cell parameters are measure as function of temperature. The crystals undergo jump-wise phase transition into incommensurate modulated phase at 279 K and commensurate modulated phase at 253 K, respectively. The result of our studies demonstrated that the crystals obtained from solution containing cadmium were grown in orthorhombic system [(CH₃)₂NH₂]₅Cd₃Cl₁₁ as well as monoclinic system [(CH₃)₂NH₂]₂CdCl₄. The temperature curves of unit cell parameter and the vicinity of phase transition are reported. At room temperature [(CH₃)₂NH₂]₂CoCl₄ belong to the *P2*₁/*c* space group and have ferroelectric properties in the temperature range 227-260 K. The crystals of this family has complicated system of hydrogen bonds and are a great interest because of ordering of hydrogen bonds and changes in cation dynamics pay an important role in the processes of phase transitions.

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Keywords: crystal structure, phase transition, ferroic

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Striking Effect of Pressure and Temperature on PdSe₂ Allotropes

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Under ambient conditions, PdSe₂ adopts the PdS₂-type structure (o-PdSe₂). Its crystal structure at high pressure (up to 30 GPa) was investigated at 20°C and at 300°C by X-ray energy-dispersive diffraction. Le Bail refinements and ab initio calculations evidenced a solid-solid phase transition to the pyrite-type structure (c-PdSe₂), strongly related to the o-PdS₂. Using the experimental data obtained at 20°C and 300°C, we examined the order of the PdSe₂ phase transition and its dependence on temperature. For this purpose, we calculated and analyzed the thermodynamical potential and the entropy generation by numerically calculating the equation of state.

We also found that the cell volume of c-PdSe₂ was smaller at 300°C than at 20°C by nearly 40%. Such a dramatic decrease in the unit cell volume meant a strong reorganization of the bonding and was suggestive of an incoming phase transition. This possibility has been experimentally confirmed by fledgling high pressure experiments at ESRF. We surprisingly found that the new allotropic phase was a 2D CdI₂-type structure. It probed that all MSE₂ (M=transition metal) structures are linked. We evidenced the interconversion path between

the 3 allotropes, explaining their relative stabilities on the basis of a thermodynamic and electronic structure study.

Keywords: phase transitions in solids, thermodynamics, X-ray synchrotron powder diffraction

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Diffusion Path Formation for Cu⁺ Ions in Superionic Cu₆PS₅I Single Crystal

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The knowledge of structural transformations to phases characterized by high ionic conductivity remains still very important in understanding the mechanisms and structural conditions supporting high mobility of ions in solids.

Trying to understand the mechanism for superionic conductivity of Cu⁺ ions in Cu₆PS₅I argyrodite compound the detailed structure analysis based on single-crystal X-ray diffraction was performed. The main interest was focused on a new cubic superstructure F-43c, stable from 140K to 275K. In the range of this phase ordering of copper ions occurs. The final structure model is given including the detailed temperature evolution of site occupation factors of copper ions. Possible diffusion paths for the copper Cu⁺ ions are represented by means of the atomic displacement factors and split model. Ordering process of Cu⁺ ions with temperature lowering is found to be similar with ordering of copper in β-Cu₇PSe₆ [1].

Comparison of the structural data with non-Arrhenius behavior of conductivity [2] indicates significant change in conduction mechanism with temperature increasing: from hopping to liquid like behavior.

[1] Gaudin E., et al., *Acta Cryst.*, 2000, B56, 402-408. [2] Beeken R.B., et al., *Journal of Physic and Chemistry of Solids*, 2003, 64, 1261-1264.

Keywords: ionic conductors, phase transition and structure, copper ions

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Tensor Distinction of Domain States in Ferroic Phase Transitions
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Distinction of domain states in ferroic phase transitions by their tensor properties is of importance in domain engineering. This is simple if the ferroic group is a halving subgroup of the parent group. In such cases there are two domains which differ only by the sign of primary transition parameter. However, even in these cases we may run into complications if the transition parameter is not a cartesian tensor components but a linear combination of such components as in cases of parent groups of tetragonal and higher symmetries. For ferroic transitions associated with two- and three-dimensional *R-ireps* we meet even more complicated relations which are a consequence of the fact that symmetry allowed tensor forms are invariants of the symmetry groups while their cartesian components are generally not invariant. The use of the ordinary transformation formulae is awkward and error inviting in these cases.

Transition parameters are generally expressed as components of tensorial covariants [1]. To find changes of cartesian components at the ferroic transition we proposed a method consisting of "labelling of covariants" followed by "conversion equations" This method facilitates the description of individual domain states in terms of cartesian tensor components and hence also their distinction.

[1] Kopský V., *Phase Transitions*, 2001, 73, No.1-2, 1-422.

Keywords: domain states, labelling of covariants, conversion equations

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Maximal Symmetry Transition Paths for Reconstructive Phase Transitions

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The transition path of a phase transition with no group-subgroup relation between their phases (as reconstructive phase transitions) can be defined as the set of atomic displacements, and strains that should occur at a local level during the transformation. The maximal symmetry transition paths are characterized by intermediate structural configurations with symmetries given by maximal common subgroups of the space groups of the two end phases. Additional symmetry constraints follow from the compatibility conditions of the occupied atomic positions at both ends of the path. By definition, the symmetry of any possible transition path must be among those maximal symmetry paths, or their subgroups. Recently, we have developed a systematic procedure for the determination of the full set of possible maximal transition paths between two structure types with no group-subgroup relations between their symmetries. A computer program has been implemented at the Bilbao Crystallographic Server (<http://www.cryst.ehu.es>) [1].

Here we present the results of our search of maximal symmetry transition-paths for some typical cases of reconstructive phase transitions (*e.g.* wurtzite to rocksalt, wurtzite to zinblende or zinblende to rocksalt structure types, *etc.*) [2].

[1] Kroumova E., Perez-Mato J.M., Aroyo M.I., Kirov A., Capillas C., Ivantchev S., Wondratschek H., *Phase Transitions*, 2003, 76, 155-170. [2] Perez-Mato J.M., Aroyo M.I., Capillas C., Blaha P., Schwarz, *Phys. Rev. Lett.*, 2003, 90, 4, 049603.

Keywords: reconstructive transitions, maximal transition paths, Bilbao crystallographic server

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Melting and Freezing of Bi Nanoclusters Embedded in Glass

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Bi-glass nanocomposites were obtained by quenching homogeneous Bi-doped soda-borate melts followed by an annealing at $T = T_a$. This process induces the formation of spherical Bi nanoclusters embedded in a glass matrix [1]. Since $T_a \neq T_{mb}$, T_{mb} being the melting temperature of bulk Bi, we have in fact obtained liquid Bi droplets that, after cooling, became spherical nanocrystals. The nanocrystal-to-liquid transition was investigated using simultaneously the SAXS and WAXS techniques [2]. The melting temperature T_m decreases for decreasing radius and is a linear function of $1/R$, $T_m = T_{mb} - a/R$, a being a positive constant related to surface energy parameters. For Bi nanocrystals with $R = 1.5$ nm, the magnitude of the melting temperature reduction is about 200 K. An additional study of the liquid-to-crystal transition was performed. The freezing temperature of bulk Bi, T_{cb} , is much lower than T_{mb} , ($T_{mb} - T_{cb} = 150$ K). We have established that the freezing temperature also decreases linearly for increasing values of $(1/R)$, but at a rate lower than the melting temperature, in such a way that the magnitude of the overcooling is progressively reduced for nanodroplets with decreasing radius. The overcooling vanishes for droplets with radius close to 2 nm. The linear nature of T_c vs. $1/R$ is explained by using a simple thermodynamic model of heterogeneous crystal nucleation at the liquid-glass interfaces.

[1] Kellermann G., Craievich A. F., *Phys. Rev. B*, 2003, 67, 085405. [2] Kellermann G., Craievich A. F., *Phys. Rev. B*, 2002, 65, 134204.

Keywords: nanocrystals, melting, SAXS WAXS