P.22.01.1

Structure of LaSrCuO$_{3.5}$

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The oxygen deficient La$_{1.07}$Sr$_{0.93}$Cu$_{0.92}$O$_{3.52}$ has been synthesized and the structure has been determined using a combination of transmission electron microscopy, X-ray diffraction and neutron diffraction.

X-ray diffraction showed a basic K$_2$NiF$_4$ type structure of a=3.7583(3) Å and c=13.005(3) Å in space group *I4/mmm*. However some reflections remained unexplained. Therefore electron diffraction was performed which showed the presence of an incommensurate modulation and allowed the determination of the superspacegroup and modulation vectors as *I4/mmm(αα0, α-α0)00mg*, q_1=0.22a* + 0.22b* and q_2=0.22a*-0.22b*. Following these observations neutron diffraction was used to determine the origin of these modulations.

The five-dimensional model obtained using the super space formalism shows oxygen-vacancy ordering, implying three different environments present for the copper in the structure: octahedral, pyramidal and square plane coordination. Significant displacements in the (a,b) plane occur for all atoms, no displacement is observed along the c-axis.

High resolution electron microscopy images support the model.

Keywords: incommensurate structures, copper oxides, structural determination

P.22.01.2

HMT-Resorcinol: An Example of Modulated Structure in Substituted HMT Adducts

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Hexamethylenetetramine (HMT) has a tendency to create modulated structures when forming adducts with hydroxyl moieties. Many examples have been reported recently [1], [2], [3], [4], [5]. We report here a model of the incommensurately modulated structure of HMT-Resorcinol solved at room temperature, in the superspacegroup Xmcm(0b0)s0s (where the X centering corresponds h+k+m=2n). The model consists mainly in an occupation modulation of the Resorcinol, which can adopt two different positions related by a mirror plane. This compound undergoes a lock-in phase transition of second order at about 278K yielding a commensurate structure. X-ray diffraction data have been collected at 120K, with LT cell parameters related to the room temperature ones by (a_{LT}=a_{RT}, b_{LT}=2b_{RT}, c_{LT}=4c_{RT}). A comparison of the supercell model and a commensurate model derived from the superspace formalism will be presented. .

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Keywords: superspace refinement, incommensurate structures, modulated structure

P.22.01.3

The Way of Crystal of [cpMe$_4$SiMe$_2$N(t-Bu)]TiCl$_2$ from Disorder thru Modulation to Twinning

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Constrained geometry catalysts based on *ansa*-{(*tert*-butylamido-κN)dimethyl(η^5-2,3,4,5-tetramethylcyclopentadienyl)silane} dichloro-titanium (IV) (**1**) allowed for a large scale production of new polymers and copolymers of specific properties [1] The structure of compound **1**

was investigated by X-ray diffraction a [2,3], however the geometrical parameters were not published in full.

From our reinvestigation [4] follows that the *tert*-butyl moiety is disordered in two positions over mirror operation of Pnma space group at room temperature. The new measurement of **1** at low temperatures revealed two phase transitions by reordering t-Bu moiety. The results of first one can be described in supercel 4**a**,**b**,**c** (**1b**), and space group Pna2$_1$, the second one (**1c**) as 3**a**,**b**,**c** and P2$_1$/n11 pseudomeroedricaly twinned into the lattice symmetry mmm. Whole pathway can be unified by applying the modulation concept, superspace group Pnma(a00)0s0 with two q-vectors (1/4,0,0) and (1/3,0,0) for **1b** and **1c**, respectively, affording unique opportunity to test various models (commensurate versus incommensurate etc.).

[1] McKnight A.L., Waymouth R.M., *Chem. Rev.*, 1998, **98**, 2587. [2] a) Stevens J.C., *Stud. Surf. Sci. Cat.*, 1994, **89**, 277. [3] Carpenetti D.W., Kloppenburg L., Kupec J.T., Petersen J. L., *Organometallics*, 1996, **15**, 1572. [4] Zemanek et al., *Coll. Czech. Chem. Commun.*, 2001, **66**, 2397.

Keywords: modulated crystal structures, phase transitions, catalyst structure

P.22.01.4

Structure of the Pseudodecagonal Al-Co-Ni Approximant PD4

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The similarity of crystalline approximants to the quasicrystals in terms of their compositions, densities and diffraction patterns, makes them very important for determining the structures of quasicrystals. Several crystal structures of these approximants were determined [1–2].

Several periodic pseudodecagonal (PD) structures were found in the Al-Ni-Co system. They are named PD1, PD2 etc. and exhibit diffraction patterns with almost perfect tenfold symmetry and quasiperiodic reflection arrangements [3].

X-ray diffraction data (0.85 Å resolution) from a single crystal of PD4-phase was collected using Oxford XcaliburTM 3 diffractometer. The unit cell parameters for this structure are a = 101.302(9) Å, b = 32.102(2) Å, c = 4.1803(4) Å.

The phase problem for the approximant PD4 was solved by direct methods in the non-centrosymmetric space group *Bbm*2. The refinement of the structure using the deduced model is in progress.

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Keywords: quasicrystal crystallography, direct methods, structure simulation

P.22.02.1

Diffuse Scattering from Composite Crystals Containing Stacking Faults

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The compound (Ca$_2$CoO$_3$)$_{0.62}$CoO$_2$, a potential candidate for a thermoelectric material, has been revealed to be a misfit-layered compound, which consists of two interpenetrating monoclinic subsystems, CoO$_2$-part of CdI$_2$-type sandwiches and Ca$_2$CoO$_3$-part of ordered three-atom-thick NaCl-type blocks [1]. Sometimes reflections with specific indices showed rather large line-widths in powder diffraction patterns of the compound. They suggested occurrence of stacking disorder in one subsystem or in two subsystems. In some powder patterns of misfit-layered sulfides such as (PbS)$_{1.12}$VS$_2$, composed of VS$_2$ sandwiches and two-atom-thick NaCl-type PbS

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layers [2], selective broadening of the reflections was observed and occurrence of stacking faults was suggested.

An expression for intensity distribution in powder diffraction from a sample containing stacking faults [3] has been modified in consideration the misfit between two-dimensional lattices of the subsystems, and applied to stacking disorder in composite crystals. The analyses have been made for neutron and X-ray powder patterns of faulted $(Ca_2CoO_3)_{0.62}CoO_2$, and X-ray powder patterns of faulted $(PbS)_{1.12}VS_2$. The experimental results have been interpreted satisfactorily on the basis of stacking disorder model.

[1] Miyazaki Y., Onoda M., Oku T., Kikuchi M., Ishii Y., Ono Y., Morii Y., Kajitani T., *J. Phys. Soc. Japan*, 2002, **71**, 491. [2] Onoda M., Kato K., Gotoh Y., Oosawa Y., *Acta. Cryst.*, 1990, **B46**, 487. [3] Onoda M., Saeki M., Kawada I., *Acta. Cryst.*, 1980, **A36**, 952.
Keywords: composite crystals, stacking faults, diffuse scattering

P.22.02.2
5-D Modeling of the Co-rich decagonal Al-Co-Ni Quasicrystal
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Even twenty years after the discovery of quasicrystals, not a single structure is known with the accuracy and reliability commonly expected for regular periodic structures [1]. One way leading towards understanding the structure of quasicrystals, is given by the examination of approximants.

The main interest of this work is to investigate the complete stability field of decagonal Al-Co-Ni by 5-D modeling, starting from the W-phase [2]. The latter is of particular interest, as it is the only known approximant in this system, containing the complete atomic cluster [3]. The focus will be on order, disorder and phase transformations of the decagonal Al-Co-Ni.

First 5-D modeling results of the Co-rich decagonal phase will be discussed. Via embedding the W-phase, models of the decagonal phase are rendered and phasonic modes are being applied.

[1] Steurer W., *Z. Kristallogr.*, 2004, **219**, 391. [2] Hiraga K., Ohsuna T., Nishimura S., *J. Alloy Comp.*, 2001, **325**, 145-150. [3] Sugiyama K., Nishimura S., Hiraga K., *J. Alloy Comp.*, 2002, **342**, 65-71.
Keywords: quasicrystal, 5-D modeling, W-phase

P.22.02.3
Modulated Structure of [FeCl(DMPE)$_2$(NCC$_6$H$_4$NO$_2$)][PF$_6$] a Material for Use in NLO
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It is well known the recent interest in the nonlinear optical (NLO) properties of organometallic complexes [1,2]. Most efficient NLO-active complexes have a dipolar composition, with an electron-donating group linked by a π-conjugated bridge to an electron-accepting group. Our studies on complexes with this composition have been focused on metal σ-nitriles, for which the second-order NLO responses have been determined [3,4]. Since, it is also of interest to assess the importance of co-ligands in the donor metal coordination sphere, our attention has turned to an alternative coordinated Fe(II) system, namely trans-chloro(diphosphine)iron nitriles. In the solid state our main interest is to align the molecules and avoid centrosymmetric space groups. When trying to solve the structure of the title complex we had several difficulties and the structure proved to be modulated. Refinements are being done using JANA and final results will be presented in this work.

[1] Whittall I.R., et al, *Adv. Organomet. Chem.*,1999, **43**, 349. [2] Goovaerts E., et al, *Handbook of Advanced Electronic and Photonic Materials*, Ed. H.S. Nalwa, 2001, **9**, Ch. 3, 127. [3] Wenseleers W. et al, *J. Mater.Chem.*, 1998, **8**, 925. [4] Garcia M.H., Robalo M.P., Teixeira A.P.S., Piedade M.F.M., Duarte M.T., Dias A.R., *J. Organomet. Chem.*, 2001, **632**, 145.

Keywords: NLO, organometallic compound, modulated structure

P.22.02.4
Dislocation Dynamics in a Dodecagonal Quasiperiodic System
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We have developed a set of numerical tools for the quantitative analysis of defect dynamics in quasiperiodic structures, with the intention of addressing some of the open questions regarding the dynamics of dislocations in quasicrystals. We are applying these tools to study dislocation motion in the dynamical equation of Lifshitz and Petrich [1] whose steady state solutions are quasiperiodic, exhibiting dodecagonal symmetry.

Here we demonstrate - by showing real-time computer simulations - our ability to inject an arbitrary set of dislocations, parameterized by the homotopy group of the D-torus, and quantitatively follow the positions of these dislocations as the equation evolves in real time. We measure and analyze the dislocation velocity as a function of applied stress and shear, as well as the phonon and phason strains that accompany this motion as the system evolves in time. These results display intriguing differences with respect to the behavior of dislocations in periodic solutions of the dynamical equation.

[1] Lifshitz R., Petrich D.M., *Phys. Rev. Lett.*, 1997, **79**, 1261.
Keywords: dislocation dynamics, quasicrystals, computer simulation

P.22.03.1
Ab initio Simulations on the W-phase of the Al-Co-Ni System
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The W-phase [1] is the highest stable approximant of the decagonal quasicrystal known in the system Al-Co-Ni. Its structure contains the so-called "20 Å-cluster", which is a characteristic building unit of decagonal Al-Co-Ni.

The Co/Ni ratio determines which modification of decagonal $Al_{72}Co_{28-x}Ni_x$ ($8 \leq x \leq 20$) is formed. Therefore, we studied the influence of the Co/Ni ratio on the structure of the W-phase, starting from binary compositions Al-Co and Al-Ni with idealized positions. From these results a realistic ternary model was derived.

The structure models were optimized using the VASP code [2,3]. Our calculations are based on the generalized gradient approximation and utilized PAW potentials [4] supplied with VASP. The band structure, electron density districution and electron localization function were calculated.

These calculations help to get insight into the factors governing formation and stability of this kind of complex intermetallic alloy. They also corroborate the results of the single-crystal X-ray structure analysis, from which a significantly distorted and disordered structure model was obtained.

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Keywords: quasicrystals, ab initio calculations, clusters

P.22.03.2
Interaction and Phase Transitions in a Potototype Self-assemblied Supramolecular Aperiodic Crystal
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This contribution reports on very new structural and physical