

MS25-P7 New approach to phasonic Debye-Waller factor.Radoslaw Strzalka¹, Ireneusz Buganski¹, Pawel Kuczera¹, Janusz Wolny¹

1. Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Krakow, Poland

email: strzalka@fis.agh.edu.pl

The very serious concerns of scientists dealing with crystal structure refinement, including theoretical research, pertains to characteristic bias in calculated vs. measured diffraction intensities, observed particularly in weak reflections regime. We attribute it most distinctly to corrective factor for phasons, and give credible proofs of this in our presentation. The lack of consistent theory of phasons in quasicrystals manifests most spectacularly in a characteristic bias of fitted vs. observed diffraction intensities. In our presentation we show that the most commonly used exponential Debye-Waller factor for phasons fails in case of quasicrystals and propose a novel method of calculating the correction factor within a statistical approach. Our results obtained for model quasiperiodic systems show that phasonic perturbations can be successfully described. It is possible to include very weak reflections to a dataset during the structure refinement and fits of high quality are achievable.

By phonons we mean a rearrangement of atoms in the structure [1]. The calculations are performed for vertex decoration models based on 1D Fibonacci chain and 2D Penrose tiling. For such models, phasons can be introduced as flips of tiles violating matching rules. Such flips are easily recognized within statistical method based on average unit cell concept [2]. The probability distributions of atomic positions calculated against some reference lattice are sensitive to phason flips, which occur in their fragmentation as comparing to ideal shapes [3]. The level and manner of this fragmentation depends on the amount and type of flips introduced to the system. Including this in a definition of structure factor automatically solves the problem of phasons at the very basic level of calculating the diffraction pattern. Neither any multiplicative correction factor nor iterative fitting of parameters in the Gaussian's exponent is required. The only free parameter to fit would be a number of phason flips, which has a very physical grounds.

[1] de Boissieu M., Phonons, phasons and atomic dynamics in quasicrystals, Chem. Soc. Rev. 41, 6778-6786, (2012).

[2] Wolny J., The reference lattice concept and its application to the analysis of diffraction patterns, Philos. Mag. A77, 395-412, (1998).

[3] Wolny J., Buganski I., Kuczera P., Strzalka R., Pushing the limits of crystallography, submitted (2016).

Keywords: phasons, quasicrystals, correction factor

MS26 Incommensurate modulated and composite phases

Chairs: Michal Dusek, Artem Abakumov

MS26-P1 Structural complexity and O²⁻ ordering in Pr_{2-x}Sr_xNiO_{4+δ} studied by single crystal x-ray diffractionRajesh Dutta^{1,2}, Avishek Maity¹, Monica Ceretti¹, Antoine Villesuzanne², Werner Paulus¹

1. Institut Charles Gerhardt, UMR 5253, CNRS-University Montpellier, 34095 Montpellier, France

2. ICMCB, UPR 9048, University Bordeaux, 33600 Pessac, France

email: rajeshatiim@gmail.com

Ruddlesden-popper phases especially those with K₂NiF₄-type structure, are of particular interest, as they exhibit high ionic and electronic conductivity already at moderate temperatures. Among them, Pr₂NiO_{4+δ} phases have attracted much attention as promising materials, showing a rather wide range of oxygen non-stoichiometric and accommodating extra oxygen on interstitial lattice sites, suitable for membranes in next generation SOFCs. A high oxygen doping level has been shown to induce a special lattice dynamics, allowing the apical oxygen atoms to easily move to vacant interstitial sites on a shallow energy diffusion pathway [1,2].

Hole doping in Pr₂NiO₄, either by substituting Pr with Sr cations or by O²⁻ ion intercalation on interstitial lattice sites modifies the structural (ordering of O²⁻ ions) and electronic ordering in Pr_{2-x}Sr_xNiO_{4+δ}. We investigated the structural evolution of the complex electronic and structural ordering as a function of x and δ by scanning the whole reciprocal space using single crystal x-ray diffraction. The average structure changes from orthorhombic *Fmmm* (x = 0 and 0.125) to tetragonal *P4/2ncm* (x = 0.25 and 0.5) in Pr_{2-x}Sr_xNiO_{4+δ}. Due to oxygen intercalation δ up to 0.25 and long-range ordering of those O²⁻ ions, Pr₂NiO_{4+δ} forms complex superstructures with 2D-incommensurate modulation ($q_{1,2} = \pm 0.83a^* - 0.49b^*$) in the (*hkn*, *n=integer*) reciprocal plane (Fig. 1), still present in the doped crystal (x = 0.125). More complex and different modulation exists in (*hkn*+1/2, *n=integer*) plane due to ordering along *c*-direction which as contrary disappears in doped crystal with x = 0.125. Four twin individuals are present in the as grown Pr₂NiO_{4+δ} single crystal which also makes the incommensurate modulation more complex whereas this modulation disappear gradually and new p-type superstructure reflections appear when entering to the tetragonal phase of Pr_{2-x}Sr_xNiO_{4+δ} (x=0.25 and 0.5) with no modulated incommensurate superstructure.

Reference:

[1] M. Ceretti, O. Wahyudi, A. Cousson, A. Villesuzanne, M. Meven, B. Pedersen, J. M. Bassat and W. Paulus, *J. Mater. Chem. A*, 2015, 3 (42), 21140-21148.

[2] O. Wahyudi, M. Ceretti, I. Weill, A. Cousson, F. Weill, M. Meven, M. Guerre, A. Villesuzanne, J.-M. Bassat and W. Paulus, *CrystEngComm*, 2015 17, 6278-6285.

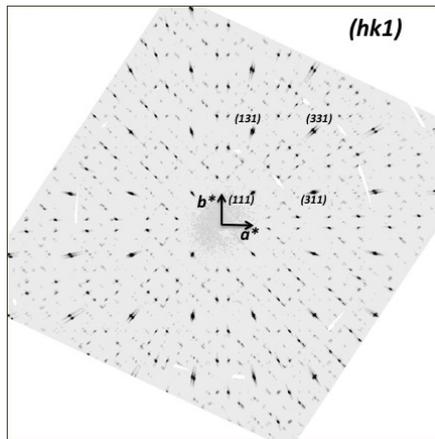


Figure 1. (hk1) reciprocal plane of $\text{Pr}_2\text{NiO}_{4.25}$ containing incommensurate superstructure reflections* along with main reflections @RT reconstructed from X-ray single crystal diffraction data obtained on a STOE STADIVARI diffractometer (Mo K α μ -focus) equipped with a 2D Pilatus detector.

Keywords: Hole doped, Incommensurate modulation, Oxygen/charge ordering

MS26-P2 The mystery of the AuIn 1:1 phase

Laura C. Folkers¹, Sven Lidin¹

¹. Centre for Analysis and Synthesis, Lund University, Naturvetarvägen 14, 223 62 Lund, Sweden

email: laura.folkers@chem.lu.se

Recently, the Gold Indium system has regained interest due to its importance for applications in soldering and nanowire growth. For these applications knowledge of the occurring components in the phase diagram is important. Earlier studies of this alloy were able to uncover most currently known compounds along with their crystal structures. Only the structure of the seemingly most straight-forward one, AuIn 1:1, has not been elucidated. Its lattice parameters are known from earlier experiments [1], but growth of single crystals has proved difficult.

The powder diffraction pattern contains unindexed peaks that cannot be explained by any known Au-In binary or by any known oxide or nitride. The problem is exacerbated by the tendency of the compound to amorphisize on grinding. Subsequent annealing at low temperature (400°C) however restores full crystallinity.

Differential thermal analysis (DTA conf. Fig. 1) reveals further surprises. On heating, a small endothermic peak appears at 440°C while a second endotherm at 515°C corresponds well with the reported melting point of AuIn ($T_M = 510^\circ\text{C}$ [2]). On cooling only one exothermic peak can be observed, which, in position, corresponds to the low temperature exotherm at 440°C, but in size it corresponds to the high temperature endotherm at 515°C.

An electron diffraction study reveals weak satellites in AuIn, indicating that the structure may be incommensurately modulated [3].

In this study we will discuss structure models for AuIn and possible explanations for the thermal behaviour.

[1] K. Schubert, U. Rösler, M. Kluge, K. Anderko, L. Härle, *Naturwissenschaften*, **40**, (1953), pp.437

[2] I. Ansara, J.-Ph. Nabot, *CALPHAD*, **16**, (1992), pp. 13-18

[3] Wilder Carillo-Cabrera, unpublished work, (2014)