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Local atomic order in apparently disordered crystals: What we can learn from Pair Distribution Function.

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Many metallic alloys, intermetallic compounds and metal hydrides show disordered crystal structure (partly or mixed occupied and/or split or close atomic sites) when Bragg scattering is analyzed by the Rietveld method. If the crystal appears from Bragg scattering as disordered, it does not mean that it cannot be ordered locally. Significant, and often sufficient, information about the local order can be gleaned from the analysis of the atomic Pair Distribution Function (PDF) obtained from the Total Scattering which samples Bragg and diffuse scattering data of a polycrystalline sample simultaneously. The local ordering in apparently disordered crystal is of high importance in determining the materials property, and helps to understand the chemical bonding in the crystal. We will show on two examples what is possible to learn from the PDF obtained from a powder sample:

The crystal structure of $YCu_{6.576}$, a substitution variant of the $CaCu_5$- type, was shown to contain Cu_2-dumbbells replacing Y-atoms in a fraction s=0.19 in the formula $Y_{1-s}Cu_{5+2s}$. The structure type $TbCu_7$ is assigned to the disordered structure. The local order in the vicinity of the Cu_2-dumbbells has been derived from the PDF obtained from the X-ray powder data [1]. The coordinating Cu_6-hexagon around the dumbbell site shows a shrinkage of 0.33(1) Å *w.r.t.* the equivalent environment of the Y-atom. No adjacent Y-atoms are substituted but a hexagonal arrangement of Cu_2-dumbbells exists in layers perpendicular to **c**. The stacking along [001] is random and can be modeled locally from the PDF data consistent with both *ab*- and *abc*-type stacking. Therefore, the local order is comparable to that in $Ni_{17}Th_2$- and Th_2Zn_{17}- structure types, ordered variants of $TbCu_7$. These results agree with the recent atomistic simulations based on interatomic pair potentials extracted from *ab-initio* calculated total energy curves by adopting modified Möbius inversion method [2].

Deuterium local order in cubic Laves phase deuteride $YFe_2D_{4.2}$ was studied by neutron (*ToF*) powder diffraction experiments and PDF modeling [3]. The minimal D-D distance in a metal hydride of 2.1 Å (Switendick rule) has been experimentally proved in the HT-disordered phase. The distribution of deuterium atoms around the iron is not random, and cannot be explained only by applying the Switendick rule. The local order of deuterium atoms within the first iron coordination sphere in the HT-disordered phase above 343 K is similar to the iron coordination in the LT-ordered phase. Same composition of the coordination polyhedra FeD_5 and FeD_4 was found in both phases by Reversed Monte Carlo modeling of the PDF. The exact shape of the FeD_5 and FeD_4 coordination polyhedra in the HT-disordered phase cannot be, however, unambiguously revealed by the PDF analysis.

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α-"NaLuF$_4$": A crystal with Twining, Modulation and Diffuse Scattering.

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$NaLnF_4$ (Ln=Y,La-Lu) crystallizes in two predominant forms. The low temperature, stable hexagonal β-form, doped with various Ln^{3+} ions shows efficient light upconversion properties. Understanding these properties requires a knowledge of the local structure; the average structure of β-$NaLaF_4$ has occupational disorder within columns of mixed Na^+/La^{3+} sites and Na^+/vacancies; an examination of strong diffuse scattering allowed the relative alignments of the columns to be deduced [1]. We are studying the structure of α-$NaLuF_4$ (high temperature phase) with likely composition $Na_5Lu_9F_{32}$, and have recorded the full scattering using synchrotron radiation. Reconstructed reciprocal lattice layers reveal a rich, apparently cubic diffraction pattern with very strong main reflections, weaker satellites and strong diffuse scattering. Stronger main reflections in reciprocal lattice rows are not collinear and at higher angles splitting of these reflections were observed. Therefore, the highest possible symmetry is

tetragonal and 6-fold twinning accounts for the apparent cubic symmetry. If the satellites are treated as Bragg peaks, one can derive an orthorhombic cell with space group *Cmmm*. The structure could be solved in the 5-fold supercell using Superflip[2] which reveals two distinct commensurately modulated parallel columns of cations: one with varying Na^+/La^{3+} occupancy and one with positional displacements of the ions from the average structure positions.
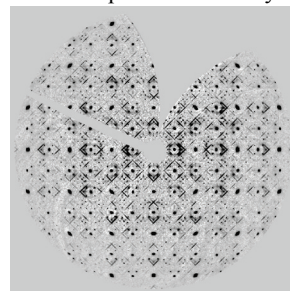
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Diffuse x-ray scattering from correlated dislocations in epitaxial layers.

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Diffuse x-ray scattering from straight misfit and threading dislocations in epitaxial layers has been simulated using numerical Monte-Carlo method, which makes it possible to include a correlation of dislocation positions. The simulations yielded reciprocal-space distributions of diffusely scattered intensity both in coplanar and non-coplanar scattering geometry (grazing-incidence diffraction). From the results it

follows that the width of the diffraction maximum in reciprocal space is proportional to the square root of the dislocation density, however the shape of the maximum strongly depends on the correlation of dislocation positions. The results were compared with dislocation curves obtained from the standard algorithm [1] using an upper cut-off radius. It has been demonstrated that for some of the correlation types (dislocation bunching and anti-bunching), similar results of the standard algorithm can be found for a suitably chosen cut-off radius, however the shape of the diffraction maximum for dislocations in subgrain boundaries cannot be approximated by the standard method.

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Keywords: diffuse x-ray scattering, dislocations, Monte-Carlo simulation

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Phase Transitions in the lead-free mixed perovskite piezoelectrics. Maxim Korablev-Dyson[a], Sergey Vakhrushev[b], Dmitry Chernyshov[c]. [a]*Saint-Petersburg State Polytechnical University, Russia.* [b]*Ioffe Physico-Technical Institute, Russia.* [c]*SNBL/ESRF,France.*
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Most of the high-performance piezoelectric materials, which are widely used in sensors, actuators and other electronic devices, are based on the lead containing perovskites (e.g. PZT – lead zirconate-titanate). High electromechanical properties of these compounds are usually attributed to the existence of so-called morphotropic phase boundary (MPB), i.e. nearly vertical phase boundary at the composition-temperature phase diagram. In the vicinity of this MPB the phase state is easily changed by small external action. Recently the efforts of the specialists all over the world got attracted to the development of the environmental friendly lead-free piezoelectrics with the electromechanical coupling close to that in PZT and related compounds. The Li doped mixed potassium-sodium niobates $Lix(K_{0.5}Na_{0.5})_{1-x}NbO_3$ (KNN:Li) are now considered as the most prospective systems for practical applications [1]. These materials demonstrate the MPB but the origin of this "easy" phase boundary remains unclear.
One of the reasons of the absence of the data on the lattice dynamics of KNN and doped KNN is difficulty of crystal growing. Recently our German collaborators have succeeded to grow high quality single crystals of KNN and Li-doped KNN. First results of the study of these single crystals were published in Ref.[2].We have performed the 3-d study of the diffuse scattering in the $Li_{0.02}(K_{0.5}Na_{0.5})_{0.98}NbO_3$. We have followed the temperature evolution of the 3-d scattering pattern on cubic-tetragonal-orthorhombic phase transformation. Due to the high luminosity of the instrument we have succeeded to do the measurements with the single domain (both in T and O phases) crystal. In cubic phases 3 "shining plane" in the diffuse scattering are seen corresponding to 3 ionic chain displacements in real space. On C-T phase transition one corresponding plane disappears. On T-O phase transition (MPB region) two remaining "shining plane" in the diffuse scattering disappear and C-T plane reappears (it is evident from evaluation of additionally performed IXS-measurements). It means that in the close vicinity of the transition point the crystal is effectively cubic again and its symmetry can be easily altered by weak external

action. IXS data demonstrated that the phenomenon is dynamic in nature.

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Keywords: piezoelectrics, X-ray diffuse scattering, X-ray inelastic scattering

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Local order and diffuse scattering in ferroelectric oxides. M. Paściak, D. Goossens, R. Whitfield, R. Withers, T. R. Welberry. *Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia.*
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Ferroelectric materials are nowadays broadly employed as capacitors and transducers of different types, e.g. actuators. It is well known that important properties of a given material are the derivative of the degree of its structural order. It has been also known for decades, that local structure of ferroelectrics, can be studied via measurement of structured diffuse scattering [1]. The interpretation of the experiments has been disputed over the years, but there has been a recent revival of intrest due to the broad range of evidence of diffuse scattering for ferroelectric relaxors [2].
In this work we show recent experimental data for a number of ferroelectric materials acquired with different scattering methods: x-rays, neutrons and electrons. Some common features of the diffuse scattering patterns have been extracted and explained with the help of various atomistic simulation techniques [3]. These include Monte Carlo simulations, molecular dynamics and *ab-initio* techniques. The results are discussed in the context of (local) structure – property relationships with a special emphasis on mechanisms leading to the occurrence of a dielectric constant anomaly.

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Keywords: diffuse scattering, ferroelectrics, atomistic simulations

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Diffuse neutron scattering in high-temperature phase of relaxor $PbMg_{1/3}Nb_{2/3}O_3$. Roman Burkovsky[a], Sergey Vakhrushev[b], Kazuma Hirota[c], Masato Matsuura[c]. [a]*St-Petersburg State Polytechnical University, Russia* [b]*Ioffe Physical-Technical Institute, Russia.* [c]*Osaka University, Japan.*
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Relaxor ferroelectrics [1] are perovskite-like mixed crystals with random occupations of equivalent lattice positions by nonisovalent ions. These compounds have unusual and very promising dielectric and piezoelectric characteristics and present a challenge in interpreting of their properties from the point of view of microscopic structure and lattice dynamics. Below the characteristic Burns temperature T_d relaxors show strong butterfly-shaped temperature dependent diffuse scattering (DS) associated with formation of local polar