



S4-L5

PHASONS AND AMPLITUDONS IN INCOMMENSURATE FERROELECTRICS, MAGNETOELECTRICS, NANOTWINNED FERROELECTRICS AND RELAXORS

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Dynamical fluctuations of the modulated polarization wave in incommensurate crystals used to be a very active subject in 80's and 90's [1-3]. However, in the last two decades, the ferroelectric community has been much more oriented to studies of perovskite ferroelectrics, where incommensurate polarization occurs rather rarely. Consequently, recent studies of phasonic excitations has been mostly restricted to quasicrystals [4], charge-density wave systems [5] or to studies of analogical excitations in magnetic systems.

In this contribution, we would like to address two issues. First, we would like to overview of the concept of phason excitation and to explore phason properties in magnetoelectric materials, using the auxiliary concept of vectors and bidirectors. [6]

Secondly, we wish to draw the attention to the multisoliton limit and to argue that certain properties of relaxors and nanotwinned ferroelectric thin films could be understood in terms of phasonic excitations, and that there

is so far almost unexplored area of possible research, related to the partially disordered ferroelectric materials that could be described as modulated ferroelectrics with frozen phasonic disorder.

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PL5

A CRYSTALLOGRAPHIC EXCURSION IN THE WORLD OF APERIODIC NATURAL STRUCTURES

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We still have in memory the celebrations of hundred years of crystallography following the discovery of X-ray diffraction and the elucidation of the first crystalline structures. Indirectly, the celebrations can also be considered as a confirmation of the three dimensional periodicity of most crystalline structures. However it is interesting to realize that even before the discovery of X-ray diffraction by matter, mineralogists already did question the validity of the law of rational indices which we know now to be directly linked to the three dimensional periodicity of structures. Finally in a seminal paper published in 1931, the law of rational indices was given up on the basis of a careful analysis of Calaverite samples. Unfortunately the scientific community was not ready to accept such a verdict. It was only in

the nineteen seventies that the 3D periodicity of structures had to be generalized in order to explain the structure of another natural compound namely natrite.

Since then, the concept of aperiodic structures described in superspace is well accepted and the number of structures belonging to this new class of compounds is constantly increasing, encompassing not only natural occurring structures but covering nearly all the possible class of materials.

The aim of this presentation is to illustrate how aperiodic natural structures contributed in a significant way to the theoretical development of the superspace concept which is now fully accepted for the description of aperiodic structures.



S5-L1

DIRECT MAPPING OF SPATIALLY MODULATED OCTAHEDRAL TILTING AND COUPLED IN-PLANE STRAIN IN THE (3+2)-D MODULATED, $\text{Li}_{1/2-3x}\text{Nd}_{1/2+x}\text{TiO}_3$ SYSTEM AND ITS UNDERLYING CRYSTAL CHEMISTRY

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A remarkably complex, typically long period, (3+2)-dimensional, incommensurately modulated structure occurs in the layered perovskite, $\text{Li}_{1/2-3x}\text{Nd}_{1/2+x}\text{TiO}_3$ (LNT), $\sim 0.02 < x < \sim 0.12$, solid solution system [1-3]. The metric symmetry and typically long period of the overall structure is compositionally dependent (*i.e.* dependent upon x) with *e.g.* tetragonal metric symmetry and, on average, $\sim 27-28a_p \times \sim 27-28b_p$ basal plane, parent perovskite (subscript p) unit cell dimensions at low x ($= 0.04$) by comparison with orthorhombic metric symmetry and $\sim 20a_p \times \sim 13b_p$ repeat dimensions at high x ($= 0.095$). The overall structure at any one composition appears to result primarily from competition between $00c^+$ and $a^-a^-c^0$ tilting of TiO_6 octahedra (in Glazer notation), leading to spatially variable $a^-b^-c^+$ octahedral tilting and parent perovskite unit cell shape and size.

In this contribution, a special atomic-resolution BF-STEM imaging condition is used to quantitatively measure the spatially modulated $00c^+$ component of the oxygen octahedral tilting in LNT, parent unit cell by unit cell. A rigorous dynamical calculation is used to determine detector collection angles that filter out the heavy Nd columns and enable TiO_6 octahedra to be imaged sensitively and robustly over a large range of specimen thicknesses, up to 150 nm. Using these calculations, the image of each octahedral column can be converted to a direct measurement of the corresponding octahedral-tilt angle (see Fig.1).

In this way, the [001] octahedral-tilt angles in LNT, for $x = 0.04$ and 0.095 samples, have been quantitatively mapped and the mathematical equations in superspace describing the 2D ordered octahedral tilt pattern determined as well as the absolute magnitude of the maximum [001] octahedral-tilt angle. In this manner, it is shown that the $x = 0.04$ sample requires higher order modulation wave harmonics in order to fit the observed anharmonic octahedral tilt distributions whereas the $x = 0.095$ sample can be adequately described by only first order harmonic terms.

Simultaneously, the heavy atom positions have been imaged and measured using conventional annular dark-field (ADF) STEM, enabling us to correlate, cell-by-cell, changes in local parent perovskite lattice parameters with octahedral tilting and, in turn, with the over-

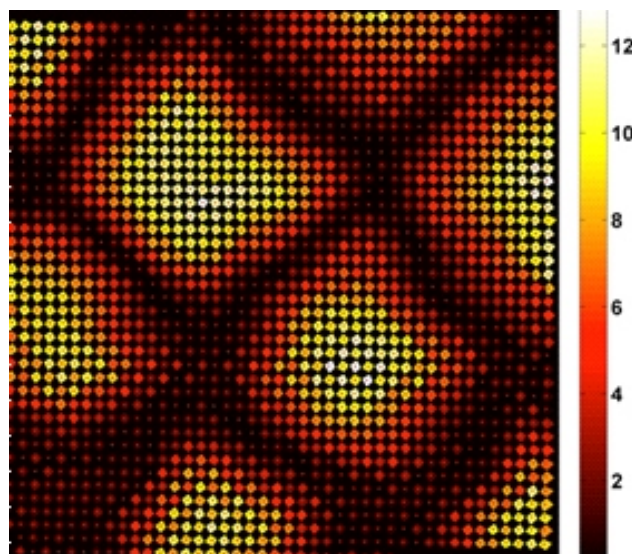


Figure 1. A quantitative mapping of the magnitude of the spatially modulated $00c^+$ octahedral tilt angle for an LNT, $x = 0.04$ sample.

all superstructure. The observed strain variation is found to be surprisingly large ($\sim 2-3\%$) and largely localised to within 2 parent unit cells of the octahedral tilt twin boundaries associated with the a^-b^- octahedral tilting.

Bond valence sum calculations were also carried out using the recently reported average and modulated crystal structures of an $x = 0.1167$ sample [3] to investigate the local crystal chemistry of LNT. Remarkably, it is found that the stabilising drop in the square of the global instability index, G_{II}^2 , associated with $a^0a^0c^+$ tilting is almost the same as it is for $a^-a^-c^0$ tilting strongly suggesting that the origin of the overall LNT modulated structure is indeed the competition between $a^0a^0c^+$ and $a^-a^-c^0$ tilting.

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S5-L2

1D COMMENSURATE COMPOSITE STRUCTURE OF THE BaVS₃, A QUASI-1D CORRELATED ELECTRON SYSTEM

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Correlated electron systems, which are among the centerpieces of condensed matter sciences, give us a remarkable chance to study relations between variable structural and electronic states. With the example of BaVS₃, which is a model quasi-1D correlated electron system, it is shown that the 1D commensurate composite approach can only explain both the newly observed XRD experimental details and the group – subgroup relationship appearing in a series of transformations in the 10 – 295 K temperature range. Using a high quality single crystal and synchrotron radiation XRD experiments, it appears that BaVS₃ exhibits a *host-guest* structure, in which the V-chains (*guest*) are lo-

cated in the hexagonal channels of a BaS₃ matrix (*host*). Space groups of the *host* and the *guest* composite substructures are different at room temperature and behave independently by decreasing the temperature down to 130 K. At $T < 130$ K, a common monoclinic symmetry appears leading to the metal-insulator transition occurring at 69 K. The 1D composite approach allows to successfully analyze the group-subgroup relations throughout the phase transitions occurring in the temperature range between 10 and 295 K. Precise structure refinements allow to find the correlation between the series of phase transformations and Jahn-Teller instability of VS₆ octahedra.

S5-L3

APERIODIC AND PERIODIC SPIN-STATE CONCENTRATION WAVES ERASED BY LIGHT

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The optical control of materials and related physical properties (electronic state, magnetic, optical...) by laser irradiation has gained tremendous interest within the emerging field of photoinduced phase transitions. Light-induced changes of molecular systems involve subtle coupling between the electronic and structural degrees of freedom, which are essential to stabilize the photo-excited state. Therefore the new experimental field of photocrystallography plays a key role. Its outreach goes far beyond simple structural analysis under laser excitation, as one can investigate new out of equilibrium physics and light-driven cooperative transformations in materials, or follow a chemical reaction in real time [1].

Here we will discuss the photo-switching process in spin-crossover materials, presenting a molecular bistability between low spin (LS) and high spin (HS) states. Ultrafast x-ray techniques allows to follow the structural dynamics and to probe how the molecular structural reorganization can trap the photoinduced electronic state. Recent studies performed on the LCLS X-FEL have shown that the structural molecular changes, with the characteristic ligand expansion, occurs within 160 fs [2].

Some of these materials present long-range order of molecules in LS and HS states, giving rise to spin-state concentration wave (SSCW). These can be of periodic [3] or aperiodic nature, as evidenced by structural refinement in superspace [4]. Light excitation can selectively switch molecules from LS to HS states and is therefore a new parameter for controlling waves in materials. Ultrafast x-ray diffraction studies reveal that the high symmetry phase is reached few ms after light excitation. Photocrystallography studies at low temperature on aperiodic SSCW demonstrated that light can switch the crystal:

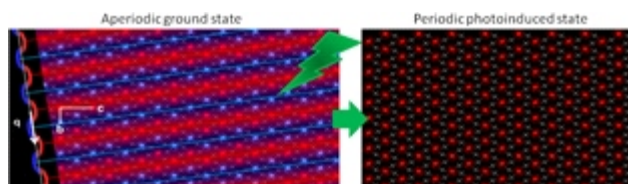


Figure 1. Aperiodic spin state concentration of LS (blue) and HS (red) states erased in the photoinduced state.



- from an incommensurately modulated HS/LS structure with a 4D superspace group $P211(0)$ to a 3D periodic $P22_12_1$ HS structure

By crossing the borders between aperiodicity, multistability, and photoinduced phenomena, new perspectives appear for switching between different regimes of periodicity and for exploring new phases of matter related to function, such as photochromism and photomagnetism.

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S5-L4

LaNb_{1-x}W_xO_{4+d}: AN INCOMMENSURATELY MODULATED STRUCTURE AND CONDUCTIVITY PROPERTIES

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Rare earth ortho-niobates (with the general formula ReNbO₄ (Re = lanthanide)) have been widely investigated as potential ionic conductors based on interstitial conducting mechanism. For instance, it has been reported that the ionic conductivity of CeNbO₄, which readily absorbs oxygen on heating due to the partial oxidation of Ce³⁺ to Ce⁴⁺, reaches 0.01 S cm⁻¹ at 800 °C. An alternative composition, namely the LaNb_{1-x}W_xO_{4+d} series were proposed to eliminate the undesirable electronic conduction in CeNbO_{4+d} and a total ionic conductivity of 0.003 S cm⁻¹ at 800 °C has been reported for LaNb_{0.92}W_{0.08}O_{4+d}. However due to the complexity of the structure, previous report provide little information on the structural features of these materials, which is key to understanding the ionic transport properties. Current study therefore aims to gain more insight of this modulated fergusonite-type structure, by employing various diffraction techniques.

The structure is modulated with a wide range of dopant level, ranging from 8 at% to 18 at% on the B site. Exemplified in Fig. 1a, the structure under investigation is 3+2D modulated in nature, with modulation vectors $q_1 = \sim 0.3a^* + \sim 0.1c^*$ and $q_2 = \sim 0.1a^* + 0.3c^*$. Structure refine-

ment was attempted with the composition LaNb_{0.88}W_{0.12}O_{4+d} using powder diffraction data gathered at Alba Synchrotron, Spain. The main feature is the partial ordering of Nb/W on the B site, accompanied by displacive modulation (Fig.1b). Most modulated fergusonite/scheelite report to date has occupation modulation on A site whereas the high valence B site polyhedron appears to be stable with little variation in bond distance. However, in the LaNb_{1-x}W_xO_{4+d} the refined displacive modulation waves suggest a significant distortion of the Nb-O polyhedron.

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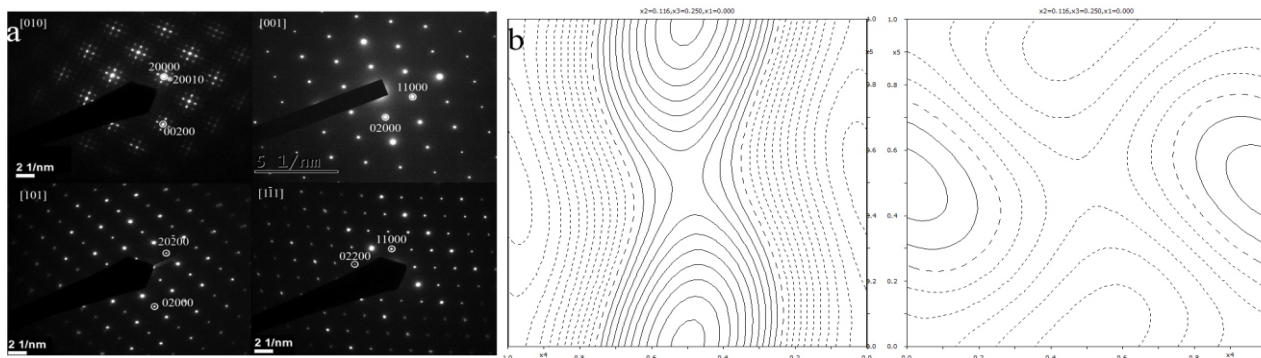


Figure 1(a). Electron diffraction patterns of LaNb_{0.84}W_{0.16}O_{4+d} along various zone axis, the modulation vectors are $q_1 = 0.294a^* + 0.116c^*$ and $q_2 = -0.1047a^* + 0.3058c^*$ (b) residual electron density around Nb/W with middle: only the displacive modulation refined and right: with additional occupational modulation. The contour is 0.5 eV.

S5-L5

CRYSTAL STRUCTURE AND THERMOELECTRIC PROPERTIES OF INCOMMENSURATE HIGHER MANGANESE SILICIDES

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Higher Manganese Silicide (HMS) consists of two tetragonal subsystems of [Mn] and [Si] with an irrational c -axis ratio $= c_{\text{Mn}}/c_{\text{Si}}$, forming an incommensurate Nowotny chimney-ladder (NCL) structure as shown in Fig. 1. The [Mn] subsystem has less displacive modulation and 3d electrons of Mn are responsible for the electronic conduction of this compound. In contrast, significant displacive modulation of Si in the [Si] subsystem effectively blocks the propagation of phonons and hence to reduce lattice thermal conductivity. A good thermoelectric (TE) material must have a high Seebeck coefficient and electrical conductivity as well as a low thermal conductivity and HMS is thus regarded as a potential TE material to be used at a mid-temperature range. Using χ , the structure formula of HMSs is represented as MnSi_x ($x \sim 1.73$) [1]. To comprehend the electronic structure of such a complicated composite crystal and its solid solutions, we adopted the concept of valence electron counts, VEC. Based on the VEC concept, we have successfully prepared V-, Cr- and Fe-substituted HMS solid solutions $(\text{Mn}_{1-x}\text{M}_x)\text{Si}$ ($M = \text{V}, \text{Cr}$ and Fe).

Polycrystalline samples were prepared in an arc-melting furnace under an Ar atmosphere. A Rietveld refinement was performed for the X-ray diffraction (XRD) data using the superspace group of $I4_1/amd(00)\gamma_00s_s$ by means of a JANA2006 software package. [2] A VEC value was determined by the valence electron numbers Z of Mn, V, Cr, Fe and Si and refined χ values as $\text{VEC} = Z_{\text{Mn}}(1-x) + Z_M x + Z_{\text{Si}}$. Samples for TE measurements were densified by the spark plasma sintering (SPS) at 1223 K. The Seebeck coefficient and electrical conductivity were simultaneously measured above 300 K. The thermal conductivity was measured using a standard laser flash thermal constant analyser.

Solubility limit was confirmed to be $x = 0.10, 0.20$ and 0.35 for $M = \text{V}, \text{Cr}$ and Fe , respectively. Due to the irrational nature, the VEC value of the parent compound (13.93) is slightly less than 14, responsible to realise good p-type performance. Temperature dependence of the Seebeck coefficient S and electrical conductivity σ of the Cr-system exhibited metallic behaviour up to around 900 K. However, the increase in σ was relatively larger than the decrease in S . As a result, a substantial increase in TE power factor $S^2 \sigma$ was achieved; the $x = 0.04$ sample exhibited the maximum power factor of $S^2 \sigma = 2.01 \text{ mW/K}^2\text{m}$ compared with that of Cr-free sample of $1.48 \text{ mW/K}^2\text{m}$ at 760 K.

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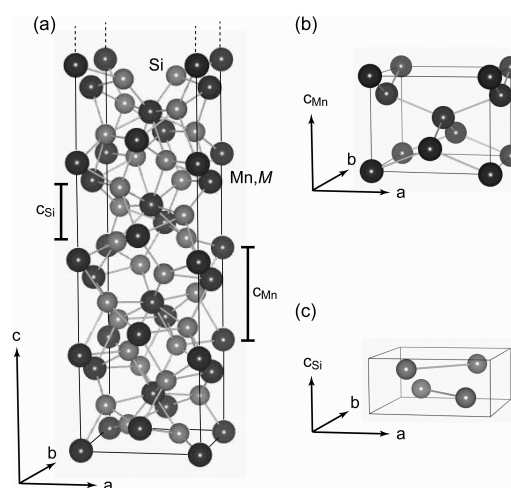


Figure 1. Incommensurate crystal structure of MnSi (a). The unit cell of the [Mn] subsystem (b) and that of the [Si] subsystem.