

Session IV - Tuesday, September 1 - morning
PL4
NEUTRON DIFFRACTION STUDY ON SPIRAL AND SKYRMION-LATTICE PHASES IN MULTIFERROIC COMPOUNDS
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Magnetic crystals without inversion symmetry often show intriguing long-range incommensurate magnetic structures. These incommensurate structures may sometimes couple with the electric polarization, giving rise to the so-called multiferroic behaviour. In this talk, I would like to introduce our recent two neutron diffraction experiments on incommensurate magnets.

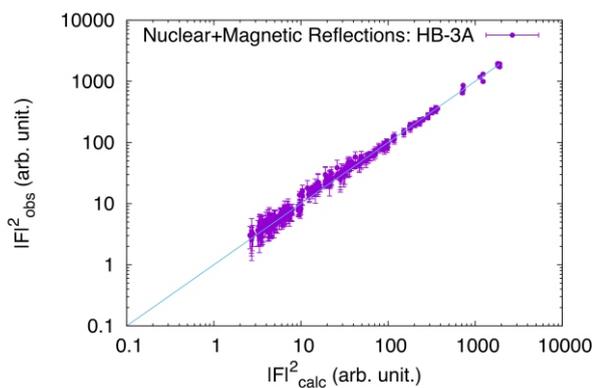


Figure 1. $|F|^2_{\text{obs}}$ vs $|F|^2_{\text{calc}}$ for the tilted cycloidal spin structure proposed for MnSb_2O_6 . Unpolarized neutron intensities are shown in the figure.

The first system is MnSb_2O_6 , which belongs to the space group of $P321$ [1, 2]. Combining unpolarized and polarized neutron diffraction, we determined the magnetic structure of the ordered phase established below $T_N = 11.6$ K (Fig. 1). The magnetic modulation vector was found to be $\mathbf{q} \sim (0, 0, 0.182)$. The spin structure is dominantly spiral with the spin-rotation plane slightly tilted from the $[210]$ - c plane towards the $[010]$ direction. As the magnetic order establishes at T_N , electric polarization \mathbf{P} becomes finite, indicating multiferroic nature of this compound. Furthermore, due to the tilting of the spiral structure, this compound shows very interesting switching behaviour of the electric polarization when the external field is rotated in the ac -plane. The switching was observed at very low magnetic field, such as $H = 0.6$ T, indicating that this switching behaviour is closely related to the switching between the two differently tilted magnetic structures. In the talk, we will report details of the magnetic structure analysis on this compound.

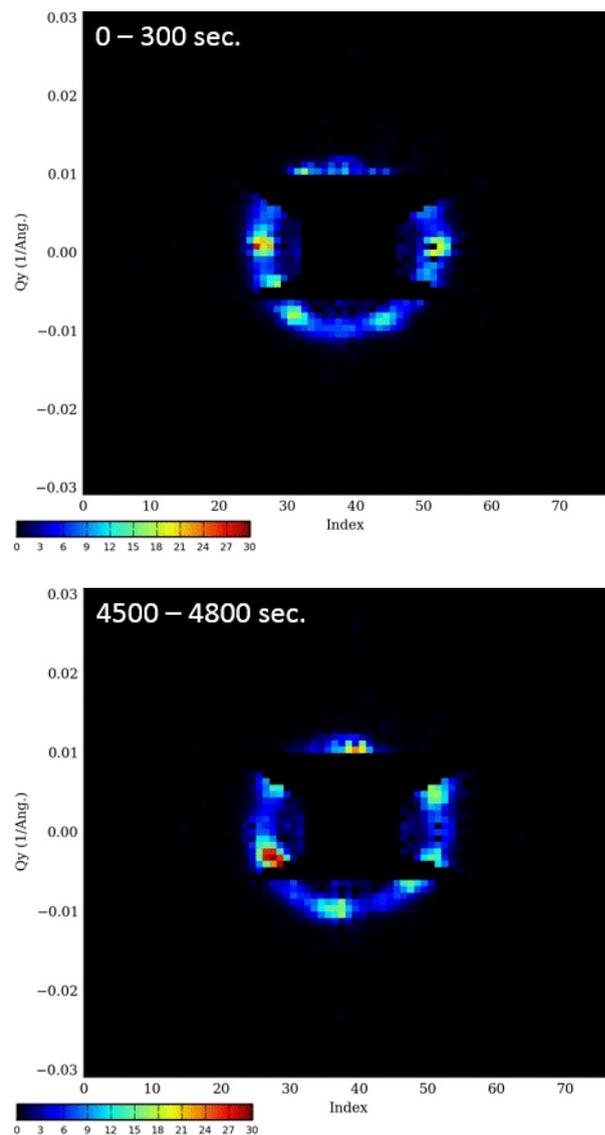


Figure 2. SANS patterns observed at $T = 54.1$ K and $H = 160$ Oe. (Left) SANS pattern observed immediately after applying $E = 3$ kV along $[001]$; (Right) SANS pattern observed 4500 sec after applying E . Complete switching (i.e. 30 degree rotation) of skyrmion-lattices was confirmed after one hour of soaking time. Dark regions in $1/4, 3/4, 5/4, 7/4$ are due to missing detectors.

The second system we will report is Cu_2OSeO_3 , which belongs to $P2_13$. At zero external magnetic field, this com-



pound shows incommensurate helical magnetic order below $T_c \sim 58$ K. Recent small angle neutron scattering (SANS) study shows that under weak magnetic field of $H \sim 200$ Oe, a skyrmion-lattice phase was stabilized at a narrow temperature range just below T_c [3]. Using the SANS technique, we investigated response of the skyrmion-lattice phase to the external electric field. In contrast to the weak rotation of the skyrmion-lattice under external electric field reported earlier [4], we observed complete switching of the two skyrmion-lattice phases with gigantic rotation angle of 30 degrees under the moderate electric field of $E = 3$ kV along the [001] direction. The time-dependence measurement shows that such switching requires quite long time (in a time scale of an hour), compared to the formation of the skyrmion-lattice phase itself under zero electric field. In the talk, we will report details of the time dependence of the skyrmion-lattice dynamics.

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This work has been performed in collaboration with Y. Nambu, D. Okuyama, D. Higashi, T. Hong, M. Matsuda, H. Cao, K. Ohishi, S. Takata, J. Suzuki, M. Kinoshita, S. Seki, S. Ishiwata, and Y. Tokura.

S4-L1

MAGNETIC AND NUCLEAR SUPERSTRUCTURES OF CrOCl—THE ROLE OF MAGNETIC SUPERSPACE GROUPS

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Isostructural compounds $MOCl$ ($M = Ti, V, Cr, Fe$) are magnetic compounds with different numbers of unpaired $3d$ electrons on the trivalent metal atoms: $3d^1$ for Ti^{3+} ($S = 1/2$), $3d^2$ for V^{3+} ($S = 1$), $3d^3$ for Cr^{3+} ($S = 3/2$) and $3d^5$ for Fe^{3+} ($S = 5/2$). They crystallize in a layered structure with orthorhombic symmetry $Pmmn$. Magnetic interactions are geometrically frustrated on these layers, while they are weak or absent between magnetic atoms of different layers. Together with orbital order of the different numbers of unpaired electrons, this is responsible for different magnetic phase diagrams of $MOCl$. Orbital order of the single $3d$ electron of $TiOCl$ makes this compound a one-dimensional (1D) magnetic system, which transforms into a spin-Peierls state at low temperatures [1,2]. The other compounds feature two-dimensional (2D) magnetic systems on the layers. They develop antiferromagnetic (AFM) order at low temperatures, with various incommensurate and commensurate magnetic superstructures [3-5]. Special to $MOCl$ is the strong magnetoelastic coupling, for example expressed by monoclinic lattice distortions, which develop at the Néel temperatures of the AFM transition [6-9].

Here we will discuss the magnetic and structural phase diagrams of $MOCl$. In particular, we will present a unified superspace approach to the combined magnetic and nuclear superstructures of $CrOCl$.

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Single crystals have been grown by A. Suttner at the Laboratory of Crystallography. Financial support has been obtained from the German Science Foundation (DFG) under project No. sm55/15-2. We thank M. Tolkieln for assistance with single-crystal x-ray diffraction experiments at beamline D3 of Hasylab at DESY in Hamburg (Germany). Neutron powder diffraction was measured at beamline SPODI of FRM II in Garching (Germany).

S4-L2

MAGNETIC ORDERING IN Ho-Dy-Y-Gd-Tb HEXAGONAL HIGH-ENTROPY ALLOY**J. Lužnik¹, P. Koželj¹, A. Jelen¹, Z. Jagličič², M. Feuerbacher³, J. Dolinšek¹**¹*J. Stefan Institute and University of Ljubljana, Faculty of Mathematics and Physics, Jamova 39, SI-1000 Ljubljana, Slovenia*²*Institute of Mathematics, Physics and Mechanics and University of Ljubljana, Faculty of Civil and Geodetic Engineering, Jadranska 19, SI-1000 Ljubljana, Slovenia*³*Institut für Mikrostrukturforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany
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Within the past several years, a new approach to alloy design with multiple principal elements in equimolar or near-equimolar ratios, termed high-entropy alloys (HEAs), has been proposed [1]. According to this concept, high entropy of mixing can stabilize disordered solid solution phases with simple structures like a body-centered cubic (bcc), a face-centered cubic (fcc) and a hexagonal close-packed (hcp) lattice and prevent formation of intermetallic phases during solidification. In order to achieve high entropy of mixing, the alloys must be composed typically of five or more (up to thirteen) major elements in similar concentrations, ranging from 5 to 35 at. % for each element, but do not contain any element whose concentration exceeds 50 at. %. HEAs with bcc and fcc structures were derived within the systems Al-Si-Co-Cr-Cu-Fe-Mn-Ni-Ti, W-Nb-Mo-Ta-V, and Ta-Nb-Hf-Zr-Ti, whereas the first hexagonal HEA Ho-Dy-Y-Gd-Tb was discovered recently in the lanthanide series of elements [2]. While the pure elements Tb, Dy and Ho in the metallic state all exhibit a regular sequence of phase transitions upon lowering the temperature in zero magnetic field (from paramagnetic to helical antiferromagnetic (AFM) to

ferromagnetic (FM)), whereas the s-state element Gd undergoes a direct transition from the paramagnetic to the FM phase (and Y is nonmagnetic), the Ho-Dy-Y-Gd-Tb alloy with equimolar concentration of the elements exhibits different behavior. Magnetic susceptibility measurements show that the material undergoes a transition to a helical AFM phase at 180 K (corresponding almost exactly to the same kind of transition in pure Dy), but at lower temperatures, no transition to the FM state could be observed from the magnetic susceptibility and from the specific heat (that only shows a lambda-type AFM phase transition at 180 K). It seems that the FM phase at low temperatures is absent in the hexagonal Ho-Dy-Y-Gd-Tb, in contrast to the pure constituent elements (except Y). The Ho-Dy-Y-Gd-Tb material shows a rich and complicated phase diagram in the magnetic field involving helical AFM phases with incommensurable and commensurable wave vectors, a FM phase and a spin-glass-like phase at low temperatures.

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S4-L3

LONG-RANGE MAGNETIC ORDERING IN QUASICRYSTAL APPROXIMANT Au-Si-Tb**T. Hiroto^{1*}, T. Sato², H. Cao³, K. Tokiwa⁴, and R. Tamura¹**¹*Department of Materials Science and Technology, Tokyo University of Science, 125-8585, Japan*²*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 980-8577, Japan*³*Quantum Condensed Matter Division, Oak Ridge National Laboratory, 37831, USA*⁴*Department of Applied Electronics, Tokyo University of Science, 125-8585, Japan*

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Search for long-range magnetic ordering in quasiperiodic materials is one of the main subject for condensed matter physics. It takes after three decades for discovery of icosahedral Quasicrystals (i-QCs), however, there are no experimental evidences for magnetic ordering, without exception. On the other hand, in approximant crystals, various magnetic ordering is observed at Cd₆R (Antiferromagnetic orderings) [1] and Au-SM-R (SM = Si, Ge, Sn / R = rare-earths) (Ferromagnetic orderings) [2, 3] crystals by means of bulk (susceptibility and specific heat) and X-ray scattering measurements [4].

In this study we focus on the magnetic properties and magnetic structures of Au-Si-R approximant. The crystal structure is explained by the bcc packing of Tsai-type icosahedral cluster [5]. Susceptibility and magnetization measurements exhibit the ferromagnetic transitions at low temperature. Furthermore, the magnetization behaviour of Au-Si-(Tb, Dy and Ho) are significant difference for that of Au-Si-Gd system: For Au-Si-Gd, the magnetization saturate under 1 T, whereas, for Au-Si-(Tb, Dy, and Ho), the magnetization does not saturate even up to 9 T [3].

To determine the magnetic structure of Au-Si-Tb approximant ($T_c = 11.5$ K), we performed the single crystal



neutron diffraction measurement at Oak Ridge National laboratory (Beam line: HB-3A). Magnetic Bragg reflections appear only $H + K + L = \text{even}$ condition, which demonstrate the bcc condition of magnetic structure. Whole magnetic structure is determined to be orthogonal Ising model with the net magnetic moment is parallel to $[1\ 1\ 1]$ direction. This magnetic model is explained by strong magnetic anisotropy along $[1\ 0\ 0]$ direction rather than the magnetic RKKY interactions. Strong magnetic anisotropy will explain the unsaturated magnetization behaviour of Au-Si-(Tb, Dy, and Ho). Moreover, this result speculate the existence of (local) orthogonal Ising spin structure in other Tsai-type approximants as well as i -QCs, because they also have rare-earth icosahedral cluster.

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S4-L4

LONG RANGE ORDERED MAGNETIC AND ATOMIC STRUCTURES OF THE QUASICRYSTAL APPROXIMANT IN THE RE-Au-Si (RE = Tb AND Ho) SYSTEMS

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Tsai-type 1/1 approximant crystals in the RE(13.64 to 15.29)Au(69.47 to 70.08)Si(14.63 to 16.9) systems (RE = Tb and Ho) have been synthesized using various approaches of high temperature solid state synthesis techniques. Few millimeters sizes of faceted crystals were grown using Au(79)Si(21) binary alloy as a flux [1]. The atomic structures of the compounds have been determined using X-ray and neutron diffraction data [2]. The approximants are essentially iso-structural and their atomic structures are described with concentric polyhedral cluster units made up of disordered tetrahedron, dodecahedron, icosahedron, icosi-dodecahedron and (defected) triacontahedron, respectively from the inside to out. Moreover, it is observed that an additional RE atom could partially or fully replace the inner most disordered tetrahedron. The relative ratio of the central RE atom to the disordered tetrahedron have been controlled during the syntheses and consequently 1/1 approximants with different occupancy of the central RE atom have been synthesized. The magnetic

properties of the compounds have been studied using magnetization, specific heat and neutron diffraction measurements on polycrystalline and/or single-domain-crystal specimens. The measurements revealed that the compounds order magnetically at low temperatures; the ordering temperature and the magnetic behaviors depend on both the chemical nature of the RE atom and the occupancy of the central RE atomic position. It is observed that the presence of the central RE atom at the cluster center shifts the magnetic transition temperature to lower temperature values for approximants which have the same chemical components [1]. The macroscopic magnetic property measurements have been further confirmed by determining the magnetic structures of some of the compounds by using neutron diffraction measurements [2].

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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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Session V - Tuesday, September 1 - afternoon

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.