

metal-organic frameworks (MOFs), however, the NTE mechanism in these structurally complicated compounds still eludes in-depth understanding. Here we use X-ray diffraction techniques to elucidate the nature of the isotropic NTE mechanism in the cubic metal-organic framework  $Zn_4O(BDC)_3$  (BDC = benzenedicarboxylate), also known as MOF-5 or IRMOF-1. Variable temperature synchrotron radiation powder X-ray diffraction data reveal almost linear NTE behaviour in the measured temperature range from 80-500 K with  $\alpha = dL/dT = -11.2 \times 10^{-6} \text{ K}^{-1}$ . Variable temperature single crystal X-ray diffraction (SCXRD) measurement over a broad temperature range has been used to probe the changes in atomic coordinates and vibrational modes causing the NTE behaviour in the framework. The results suggest population of transverse vibrations, similar to the findings in the metal cyanide frameworks [2], with preferential population of vibrational modes out-of-plane of the BDC oxygen atoms and of the BDC aromatic ring.

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Keywords: negative thermal expansion, structure and property, metal-organic frameworks

## MS.74.1

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### Magnetic and crystal structure in connection with ferroelectric properties of multiferroic $RMn_2O_5$

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$RMn_2O_5$  (R=Y and rare earth) are well known multi-ferroic compounds. A colossal magnetoelectric effect is reported such that magnetic field induces an electric polarization. We found successive phase transitions of magnetic and dielectric ordering occurring simultaneously, using neutron and x-ray scattering as well as electrical measurements. The character of magnetic ordering is essentially incommensurate - commensurate and again to incommensurate phase transitions. From the magnetic and dielectric phase diagram in magnetic-field and temperature, we can easily say that the origin of colossal magnetoelectric effect is the phase transition from the magnetic incommensurate and weak ferroelectric phase to the commensurate and ferroelectric phase. We will show the magnetic structure to discuss the mechanism to introduce ferroelectric polarization. For all the compounds, the spin configuration for  $Mn^{4+}$  and  $Mn^{3+}$  ions in the commensurate magnetic phase, where spontaneous electric polarization occurs, was determined to be a transverse spiral spin structure propagating along the  $c$ -axis. By contrast, the alignment of the induced  $4f$ -moment of  $R^{3+}$  ions has a variety depending on the character of each element. The lattice modulation wavevector  $q_L$  was carefully measured, and we found the lattice modulation vector  $q_L$  is exactly twice of the magnetic propagation vector  $q_M$ ,  $q_L = 2q_M$ , in all phases. The precise structure giving the spontaneous polarization is still unclear at the moment. The structure analysis of modulation (magnetostriction pattern) in ferroelectric and magnetically commensurate phase of  $YMn_2O_5$  was successfully carried out.

Keywords: magnetic structures, ferroelastics, physical properties

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### Ferroelectricity from magnetic order

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Magnetic insulators with competing exchange interactions can give rise to strong fluctuations and qualitatively new ground states. The proximity of such systems to quantum critical points can lead to strong cross-coupling between magnetic long-range order and the nuclear lattice. Case in point is a class of multiferroic materials in which the magnetic and ferroelectric order parameters are directly coupled, and a magnetic field can suppress or switch the electric polarization [1]. Our neutron measurements reveal that ferroelectricity is induced by magnetic order and emerges only if the magnetic structure creates a polar axis [2-5]. The spin dynamics and the field-temperature phase diagram of the ordered phases provide evidence that competing ground states are essential for ferroelectricity. The origin of the magneto-electric coupling most probably arises from strain derivatives of the isotropic exchange interactions and anisotropic exchange couplings such as Dzyaloshinskii-Moriya interactions.

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Keywords: multiferroic, frustration, ferroelectricity

## MS.74.3

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### Function from frustration in modern multiferroics

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Although in conventional ferroelectrics the requirements of magnetism and ferroelectricity are chemically incompatible[1], recent investigations of spin frustrated manganite perovskites  $RMnO_3$  (where R is a rare earth ion) have shown that this chemical incompatibility can be overcome by frustration[2]. In particular spin frustrated perovskite manganites for appropriate size R-ions show a peculiar transverse spiral magnetic ordering that breaks inversion symmetry[3]. What is novel about these materials is that the direction of the ferroelectric polarization can be controlled via magnetic field. In this talk I will discuss the mechanism by which ferroelectricity can be coupled to magnetism in  $RMnO_3$  perovskites and describe the changes in the magnetic structure associated with changes in the ferroelectric polarization. The magnetic excitation spectrum that we have recently measured using cold neutron spectroscopy supports evidence that the fundamental driving mechanism behind these multiferroics is the coupling of a magnon to polar phonons, or electromagnon[4]. I will further show how the ordering of the rare earth spins couples to the Mn-spins[5] and in the case of R=Dy can enhance the ferroelectric polarization by as much as a factor of 3[6]. In collaboration with N. Aliouane, S. Landsgessel, O. Prokhenko, E. Dudzik, Ralf Feyerherm, J. Strempfer and I. Zekinoglou, M. Mostovoy and D. Senff and M. Braden.

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Keywords: multiferroics, electromagnons, neutron scattering

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### Crystal and magnetic structures of frustrated antiferromagnet CuCrO<sub>2</sub>

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The crystal and magnetic structures of the frustrated antiferromagnet delafossite CuCrO<sub>2</sub> have been investigated by means of neutron powder diffraction between 1.5K and 300K. CuCrO<sub>2</sub> exhibits at 300K a highly anisotropic rhombohedral *R*-3*m* structure (*a* = *b* = 2.976(1) Å and *c* = 17.109(1) Å), in which compact CrO<sub>6</sub> layers are separated by linearly coordinated Cu<sup>+</sup> ions. Within the instrumental resolution, no crystal structure transition is observed down to 1.5K. Below T<sub>N</sub> = 27K, broad magnetic peaks appear, which can be indexed with an incommensurate propagation vector (*q*, *q*, 0), *q* ≈ 0.329. Using symmetry analysis [1], we found several possible models for the magnetic structure, some of them compatible with magnetoelectricity. It is noteworthy that, chromium species being distributed on a triangular lattice, the total spin on each triangle is roughly Σ<sub>i</sub> S<sub>i</sub> = 0, as expected for a frustrated antiferromagnet. Second order magnetic exchange between CrO<sub>6</sub> layers is probably responsible for the 3D ordering. The shape of the magnetic peaks can be well described by a model of magnetic platelets 200Å thick randomly stacked along *c* [2], which suggests that long-range order is finite in the *c* direction but well established in the *a*-*b* planes, in agreement with previous results [3]. Effects of various Cr-site substitutions on the magnetic ordering will also be presented.

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Keywords: neutron powder diffraction, delafossite, magnetic structures

## MS.74.5

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### Frustration of magnetic and ferroelectric long-range order in Bi<sub>2</sub>Mn<sub>4/3</sub>Ni<sub>2/3</sub>O<sub>6</sub>

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Attempts to design a multifunctional material that can be made under ambient conditions, yielded Bi<sub>2</sub>Mn<sub>4/3</sub>Ni<sub>2/3</sub>O<sub>6</sub>. The material adopts a perovskite related structure with Bi on the A-site and a

random of 67% Mn and 33% Ni on the B-site. X-ray and neutron powder diffraction data appear to give an orthorhombic cell of 2<sup>1/2</sup>*a*<sub>p</sub>, 2x2<sup>1/2</sup>*a*<sub>p</sub> and 4*a*<sub>p</sub> (*a*<sub>p</sub> ~ 3.88Å) and the polar Pn2<sub>1</sub>m space group. More detailed analysis of the room temperature phase showed that it is incommensurate and a more detailed description of the structure and properties is presented. Synchrotron x-ray diffraction and constant wavelength neutron diffraction on powder samples were analyzed using the superspace group *Ibmm*(0-β0,α00)gm.ss (*a* = 5.5729(1) Å, *b* = 7.7686(2)Å, *c* = 5.5091(2)Å, α = 0.4930(3), β = 0.4210(7)). This (3+2)D description is more consistent with the observed physical properties and the apparent low polarization, and shows that some Mn/Ni order is present. Impedance spectroscopy shows an anomaly in the dielectric constant between 150 and 240°C. Which temperature dependent neutron powder diffraction data confirmed is associated with a structural transition to a GdFeO<sub>3</sub> type structure, though weak modulation peaks are observed at high temperature neutron diffraction consistent with either short range order or cation order. Magnetic measurements show spin-glass like behavior below 35K. Variable temperature neutron diffraction confirms the absence of long-range magnetic order, though there is an anomaly in the temperature dependence of the sub-cell parameters at the spin glass transition temperature.

Keywords: incommensurate structures, magnetic oxides, ferroelectric oxides

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### Electron localization phenomena in complex carbides of rare earth and transition metals

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The nature of chemical bonding in the complex carbides Sc<sub>3</sub>[TM(C<sub>2</sub>)<sub>2</sub>] (TM = Mn, Fe, Co, Ni) has been explored by combined experimental and theoretical charge density studies.<sup>[1]</sup> The structures of these organometallic carbides contain one-dimensional infinite TC<sub>4</sub> ribbons embedded in a scandium matrix. The bonding in these carbides were studied experimentally by multipolar refinements based on high resolution X-ray data and compared to scalar-relativistic electronic structure calculations using the augmented spherical wave (ASW) method. Besides substantial covalent T-C bonding within the TC<sub>4</sub> ribbons one observes also discrete Sc-C bonds of noticeable covalent character. Furthermore, our study highlights that even tiny differences in the electronic band structure of solids might be faithfully recovered in the properties of the Laplacian of the experimental electron density. In our case, the lifting of the Fermi level in the Co(d<sup>9</sup>) carbide 1 relative its isotypic Fe(d<sup>8</sup>) species 2 is reflected in the charge density picture by a significant change in the polarization pattern displayed by valence shell charge concentrations of the transition metal centers in the TC<sub>4</sub> units (T = Fe, Co). Hence, precise high-resolution X-ray diffraction data provide a reliable tool to discriminate and analyze the local electronic structures of isotypic solids even in the presence of a severe coloring problem (Z(Fe)/Z(Co) = 26/27). Funding from the DFG priority program (SPP 1188) is gratefully acknowledged.

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