Analysis Wizard offers three methods for initial structure determination: a) Direct method, b) Direct space method and c) Charge flipping method.

[1] *The Rigaku Journal* (English version), **2010** *26(1),* 23-27. [2] *The Rigaku Journal* (English version) **2010**, *26(2),* 10-14.

Keywords: Ab-initio crystal structure analysis, charge flipping method, rietveld method

MS96.P01

Acta Cryst. (2011) A**67,** C800

Recent Progress in joint charge and spin densities refinement

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Electron density, in all its representations, plays a key role in the understanding of the nature of interatomic interactions and chemical bonds. In case of molecular magnetic materials, as the experimental electron densities rely on high resolution X-ray diffraction experiments, it is necessary to go further and enrich the electronic model by the use of complementary techniques such as unpolarized and polarized neutron (PND) diffraction or Compton scattering. This implies to be able to include all these different experimental contributions into a unique electronic model, and to carry out a joint refinement. In this respect we are developing a new program to model the charge, spin and momentum densities (ANR CEDA project [*]).

We will report on the first charge and spin densities joint refinement applied to the molecular magnetic compound MnCuPba, (Fig.1 [1],[2]). The results are consistent with the previous separated studies of spin and charge densities. This method can bring new insights in the nature of interactions in the solid.

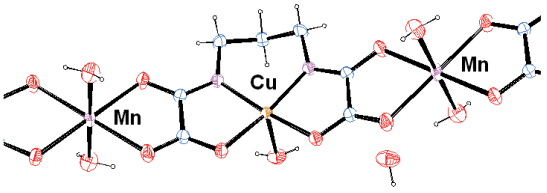

Fig.1. ORTEP view of the MnCuPba complex chain structure at 100K

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Keywords: charge, spin, densities

MS96.P02

Acta Cryst. (2011) A**67,** C800

Structure and magnetic order in CrOCl at low temperatures

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The metal(III) oxyhalide *MOX* structures with *M* = Ti, V, Cr and *X* = Cl, Br are isostructural with FeOCl at room temperature [1-7] (they are built by slabs consisting of M_2O_2 bilayers enclosed by layers of *X* atoms; the interaction between the slabs is of the van der Waals type; the symmetry is orthorhombic, space group *Pmmn*), but they show different magnetic order at low temperatures [8-15]. In CrOCl one phase transition was observed towards antiferromagnetic ordering [13].

We have performed low-temperature single-crystal X-ray diffraction experiments at the synchrotron Hasylab/DESY (Hamburg, Germany) to explore the nuclear structure and the development of nuclear superstructure peaks (*h* , *k*+½ , *l)* below T_N = 13.5 K. We found the phase transition at T_N to be associated upon cooling with a loss of symmetry from orthorhombic towards monoclinic [16]. We also have observed by magnetic susceptibility measurements a second phase transition at T_{c2} = 27.8 K.

Our low temperature powder neutron diffraction experiments at the neutron reactor FRM-II (Garching, Germany) indicate the low temperature phase below T_N as a monoclinic fourfold magnetic superstructure (**a** × 4**b** × **c**) with respect to the room temperature phase and the intermediate phase ($T_N \leq T \leq T_{c2}$) as an incommensurately modulated magnetic superstructure. Both magnetic phases are analyzed with Rietveld refinements against the powder neutron diffraction data. For the structure of the low temperature phase the extended magnetic superspace group symmetry $P\,2_1/m\,1'\,(0\sigma_2\sigma_3)\,0ss$ (monoclinic, **a**-unique) is applied, the extended magnetic superspace group symmetry of the intermediate phase is $P\,mmn\,1'\,(0\sigma_2 0)\,s0ss$ (orthorhombic). The additional symmetry operator (1', *s*) in the extended symbol stands for the time inversion operator combined with an additional shift of ½ of the modulation function to describe antiferromagnetic order [17].

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Keywords: phase transition, magnetic order, superstructure

MS96.P03

Acta Cryst. (2011) A**67,** C800-C801

Probing the local sense of the Dzyaloshinskii-Moriya vector: neutrons vs x-rays

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It is demonstrated how diffraction methods can be used for experimental determination of the sign of the Dzyaloshinskii-Moriya interaction (DMI) in antiferromagnetic crystals with weak ferromagnetism. Previous attempts to measure this sign are carefully analyzed. It is shown that in this case the vector of DMI correlates with the sign of the *local chirality* of centrosymmetric crystal structure. In fact, the canting of atomic moments can be considered as a result of alternating right-hand and left-hand rotations of moments in accordance with alternating local chirality inside the crystal unit cell.

Three different experimental techniques sensitive to the DMI sign are discussed: neutron diffraction, Mössbauer γ-ray diffraction, and magnetic (resonant or non-resonant) x-ray scattering.

In particular, it is demonstrated that the DMI sign can be directly extracted from interference between magnetic X-ray scattering, sensitive to the phase of antiferromagnetic order, and charge scattering, sensitive to the phase of crystal structure. Classical examples of hematite (α-Fe_2O_3) and $FeBO_3$ crystals are considered in detail (see [1] for preliminary consideration). This interference distorts strongly the azimuthal dependence of forbidden reflections and was recently observed in hematite [2]. However, the results of [2] cannot be directly used for the sign determination because the orientation of the weak ferromagnetic moment was indefinite in that work. The application of external magnetic field, fixing the orientation of the weak ferromagnetic moment and (owing to the DMI) fixing the phase of antiferromagnetic order relative to the crystal structure, will be crucial for this type of experiments.

The expected details of azimuthal dependence are simulated using FDMNES codes [3] for x-ray scattering amplitude the near absorption edges of magnetic atoms. We hope that the DMI sign of $FeBO_3$ will be measured in July at XMAS beamline in Grenoble. Results for more complicated cases of the DMI in crystals of La_2CuO_4 and MnSi types are also presented.

Two other possible techniques, neutron diffraction and Mössbauer γ-ray diffraction, sensitive to the DMI sign, are carefully discussed in comparison with magnetic x-ray scattering. Advantages and disadvantages of different techniques are analyzed. For example, the analysis of neutron data is straightforward whereas for resonant x-ray diffraction one needs rather sophisticated programs [3].

This work was supported by the Russian Foundation for Basic Research (project 10-02-00768) and by the Program of Fundamental Studies of Presidium of Russian Academy of Sciences (project 21).

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Keywords: X-ray magnetic scattering, neutron diffraction, dzyaloshinskii-moriya vector

MS96.P04

Acta Cryst. (2011) A**67,** C801

Magnetic structures of the Co^{+2} doped $Mn_{1-x}Co_xWO_4$ Wolframites

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New materials, in which magnetic and ferroelectric long range order coexist and strongly interact, have become of great interest due to the fact that magnetism can be controlled by electric fields and vice versa. The interest in these magnetoelectric multiferroic materials has been enhanced since a new class of multiferroics have been discovered: materials the complex magnetic structure of which induces ferroelectricity.

It is known that $MnWO_4$ belongs to this new class of multiferroics and exhibits large magnetoelectric effects [1-3]. When decreasing the temperature, it undergoes three successive phase transitions to three different long-range antiferromagnetic states [1,2]. Below T_N=13.5 K moments order in the *ac* plane, the spins are collinear and sinusoidally modulated. This phase is the so called AF3 and is paraelectric. The AF2 phase appears in the interval 7.5 K < T <12.5 K, presents an additional magnetic component along *b* and is ferroelectric. A spontaneous polarization along *b* axis coexists with an elliptical spiral-spin structure. These two structures have the same propagation vector: **k**=(-0.214, ½, 0.457). Below 7.5 K the system is collinear (*ac* plane) and commensurate with **k**=(±1/4,1/2,1/2) (AF1). This succession of magnetic states at low temperature is a consequence of geometrical magnetic frustration effects in the intrachain and interchain magnetic interactions.

By substituting Mn^{+2} ions by isovalent M^{+2} (M: transition metal) the magnetoelectric properties change [3, 5, 6]. Doping the sample with Co^{2+} is specially interesting: this doping is the only known that strongly stabilizes the multiferroic magnetic phase. According to preliminary data on powder samples [5] the incommensurate multiferroic AF2 phase is expected to substitute the commensurate AF1 ordering at low temperature for x>0.03.

We have studied the magnetic structure of the 10% Co doped composition by single crystal neutron diffraction. We confirm the disappearence of the paraelectric AF1 phase which is substituted by the multiferroic AF2* phase, which is different from the AF2 phase of the pure compound. Moreover, it was observed that at this doping the orientation of the magnetic moments in the AF3 magnetic phase changes as well. In addition, an external magnetic field was applied along the *c* axis and modifications of the magnetic structure of the multiferroic phase were studied: the rotation plane of the magnetic moments flips and the spins lay perpendicular to the applied field. This magnetically induced transition transforms a multiferroic phase into another one in which the electric polarization is also flipped compared polarization appearing in the zero-field structure. To summarize, we confirm that substituting Mn^{+2} by Co^{+2} is an efficient mechanism to stabilize the multiferroic phase in the $Mn_{1-x}M_xWO_4$ family, and that the application of magnetic fields modifies the cycloidal and polar orderings.

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Keywords: multiferroics, magnetic structures, single crystals

MS96.P05

Acta Cryst. (2011) A**67,** C801-C802

Structural, magnetic and magnetocaloric properties of $CoMnGe_{1.95}Ga_{0.05}$

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