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Keywords: multiferroics, electomagnons, neutron scattering

MS.74.4

Crystal and magnetic structures of frustrated antiferromagnet CuCrO$_2$

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The crystal and magnetic structures of the frustrated antiferromagnet delafossite CuCrO$_2$ have been investigated by means of neutron powder diffraction between 1.5K and 300K. CuCrO$_2$ exhibits at 300K a highly anisotropic rhombohedral R-3m structure ($a = b = 2.976(1)$ Å and $c = 17.109(1)$ Å), in which compact CrO$_6$ layers are separated by linearly coordinated Cu+ ions. Within the instrumental resolution, no crystal structure transition is observed down to 1.5K. Below $T_N = 27$K, 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 $\Sigma_i S_i = 0$, as expected for a frustrated antiferromagnet. Second order magnetic exchange between CrO$_6$ 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

Frustration of magnetic and ferroelectric long-range order in Bi$_2$Mn$_{4/3}$Ni$_{2/3}$O$_6$

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Attempts to design a multifunctional material that can be made under ambient conditions, yielded Bi$_2$Mn$_{4/3}$Ni$_{2/3}$O$_6$. 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 $2^{1/2}a_p$, $2x2^{1/2}a_p$ and $4a_p$ ($a_p \sim 3.88$Å) and the polar Pn2$_1$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, $\alpha = 0.4930(3)$, $\beta = 0.4210(7)$). 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 240ºC. Which temperature dependent neutron powder diffraction data confirmed is associated with a structural transition to a GdFeO$_3$ 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 at the spin glass transition temperature.

Keywords: incommensurate structures, magnetic oxides, ferroelectric oxides

MS.75.1

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$_3$[TM(C$_2$)$_2$] (TM = Mn, Fe, Co, Ni) has been explored by combined experimental and theoretical charge density studies. [1] The structures of these organometallic carbides contain one-dimensional infinite TC$_4$ 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$_4$ 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^9) carbide 1 relative its isotypic Fe(d^8) 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$_4$ 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 greatfully acknowledged.
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Keywords: charge density studies, topological properties of charge distribution, quantum chemistry

MS.75.2

Study of electronic structure of tetrakis(μ₂-Acetato)-diaqua-di-copper(II) complex

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The nature of Cu-Cu interaction in tetrakis(μ_2-Acetato)-diaqua-di-copper(ii) complex has been studied by both experimental and theoretical treatments. A large experimental data set (CCD GEMINI R diffractometer, 387268 diffractions at 100 K, resolution of 0.39 Å, an average redundancy of 30.6) was measured. The data reduction (*CrysAlis* [1]) gives a unique 12674 diffractions ($R_{Int} = 0.026$, $R(\sigma) = 0.006$). Refinement with the XD package [2] gives $R\{ F \} = 0.0187$. In order to identify the systematic errors in the experimental data sets of structure factors, the new procedure for obtaining the theoretical structure factors at 100 K from the theoretical grid electron density has been developed. The electron density at grid points is evaluated by CRYSTAL06 software for periodic quantum-chemical calculations at B3LYP level of theory [3]. The distance between the discrete grid point and the closest particular atom is used as a criterion for assigning the temperature factor to each grid point. The procedure developed might enable us to obtain spin density distribution, too.
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Keywords: charge density, spin density, magnetic properties

MS.75.3

Estimation of optical properties from wavefunction fitting of X-ray diffraction data

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In general, the crystallography of important nonlinear optical (NLO) materials is not well described and much remains to be done to characterize their relevant properties (electric and optical) in the solid state. This encouraged us to perform the detailed charge density studies on a series of organic molecular crystals with known NLO properties. The materials of interest are 2-(N-prolinol)-5-nitropyridine (PNP), N-(4-nitrophenyl)-L-prolinol (NPP) and 3-methyl 4-nitropyridine N-oxide (POM), which have very high second order NLO coefficients. Charge density analyses have already been reported for NPP [1] and POM [2], but we are revisiting these materials, along with PNP, to critically test a number of novel approaches to the estimation of linear and nonlinear optical properties using constrained wavefunctions fitted to the X-ray diffraction data [3]. Charge density analyses are based on X-ray diffraction data collected on an Oxford Diffraction Xcalibur S instrument at 100 K. Hydrogen atom ADPs are estimated using a recently described SHADE2 procedure [4]. Results presented will include conventional multipole refinements, details of wavefunction fitting, estimates of the zero-frequency dipole polarisability tensors for the molecules and crystal refractive indices, and molecular first hyperpolarisability tensors. Critical comparison of the estimated results with independent experimental data will be made where possible.

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Keywords: charge density, optical properties of crystals, wavefunction fitting

MS.75.4

Magnetic interactions in thiazyl-based magnets: The role of the charge and spin densities

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The crystal structure of the organic radical p-$O_2NC_6F_4CNSSN$ was determined at 20 K through a single-crystal neutron-diffraction experiment. It crystallises in the tetragonal space group $P4_12_12$, unchanged from a previous single-crystal X-ray diffraction experiment at 220 K although there are some changes in molecular geometry and intermolecular contacts arising from the contraction of the unit cell. Polarized neutron diffraction at 1.5 K revealed that the spin distribution is predominantly localised on the N and S atoms of the heterocyclic ring with a small negative spin density on the heterocyclic C atom. Spin populations determined using a multipolar analysis were -0.06, +0.25 and +0.28 on the C, N and S sites, respectively. These spin populations are in excellent agreement with both ab-initio DFT calculations (spin populations on the C, N and S sites of -0.07, 0.22 and 0.31, respectively) and cw-EPR studies which estimated the spin population on the N site as 0.24. The DFT calculated spin density revealed less than 1% spin delocalisation onto the perfluoroaryl ring, several orders of magnitude lower than the density on the heterocyclic ring. cw-ENDOR studies at both X-band (9 GHz) and Q-band (34 GHz) frequencies probed the spin populations at the two chemically distinct F atoms. These spin populations on the F atoms ortho and meta to the dithiadiazolyl ring are of magnitude 10-3 and 10-4 respectively. Additional high-