

Poster Sessions

Hence we present MoProViewer: a molecular viewer designed as an interface to VMoPro, and thus especially dedicated to the field of charge density analysis. MoProViewer offers a wide range of features, among which:

- Compatibility with the MoPro molecular file format (including exportation), and with all the other formats allowed by the MoPro conversion program (CIF, shelxl RES, XD ...).
- Several molecule representation modes (lines, balls & sticks).
- All standard molecular viewer capabilities (configurable atoms labeling and atoms coloring scheme, images exportation).
- All "classical" crystal structure analysis tools (stereochemistry measurements, symmetry handling, thermal ellipsoids drawing).
- Representation and modification of multipolar model atomic axis systems and chemical equivalencies constraints.
- Setup and control of most of the VMoPro possible computations (electron densities, electrostatic potentials, $\rho(r)$ topology ...).
- Representation of the properties computed by VMoPro, or readable in XPLOR or Gaussian CUBE format, as 3D isosurfaces, 2D isocontours plots, 3D gradient lines or 2D slices of scalar fields.
- Possibility to color any isosurface on the basis of values of any other loaded scalar field.
- Drawing of critical points and bond paths obtained from an electron density topology analysis.
- A powerful atom selection tool, which allows for instance to easily perform computation focusing on any fragments or regions of a molecule.
- Computation of the electrostatic interaction energy between two molecules in the crystal, or between any selected fragments of the loaded crystal structure.
- Handling of transferable electron density parameters database.
- Specific tools for protein structures: hydrogen atoms and water molecules handling, sequence explorer.
- Specific tool for a fast and efficient model examination in the context of a MoPro structural or charge density refinement.

MoProViewer is written in C++ and is based on the Qt SDK and on the Armadillo [2] and OpenGL libraries. It will be released as free of charge and open-source software under the GNU-GPL license.

[1] C. Jelsch, B. Guillot, A. Lagoutte, C. Lecomte *J. Applied Cryst.* **2005**, *38*, 38-54. [2] C. Sanderson, "Armadillo: An Open Source C++ Linear Algebra Library for Fast Prototyping and Computationally Intensive Experiments" *NICTA Technical Report*, **2010**.

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Electron microscopy and x-ray diffraction study of the 1-D (NbSe₄)_{10/3}I system

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The linear chain compound (NbSe₄)_{10/3}I [1] shows nonlinear transport properties with a CDW transition at 285K [2]. Single crystals were examined with a four-circle x-ray diffractometer, with HREM and by measuring the temperature dependent electrical resistivity. Diffuse streaking perpendicular to the c^* direction was clearly detected

in electron and x-ray diffraction patterns, both above and below the CDW transition temperature. A reversible structural transformation was observed on cooling through the CDW transition at 285K.

The RT (NbSe₄)_{10/3}I structure (P4/mcc, $a = 0.9464$ nm, $c = 3.1906$ nm) is formed of NbSe₄ antiprisms, stacked along the c direction in a screw-like arrangement with 10 Nb-Se antiprisms per unit cell. Nb atoms are grouped into Nb₂ and Nb₃ segments and the Se-Se distances are correlated with the Nb chains. In accord with previous studies [3], the I atoms occupy two types of channels; those running along the [00z] direction contain four iodine atoms connected to four Se atoms, while the channels along the [11z] direction host two I atoms bonded to eight Se atoms in a square antiprismatic arrangement. Although the symmetry of the LT phase is reduced (at 100K: P2/c, $a = 0.9442$ nm, $b = 0.9424$ nm, $c = 3.1883$ nm and $\beta = 92.35^\circ$) its structure is obtained from the RT one by a minor deformation.

The electron diffraction patterns show strong diffuse streaks perpendicular to the c^* directions, confined to the ($l = \pm 10n$) layers. Additional, short and very weak diffuse streaks appear on ($l = \pm 2n$) layers. Due to the needle-like crystal morphology, the planes perpendicular to c^* direction were examined by x-ray diffraction. Reconstruction of the reciprocal space (CrysAlis software) show that the diffuse scattering observed in electron diffraction patterns at ($h,k,\pm 10n$) represent projections of concentric diffuse rings. A model for the disorder in the crystal structure, based on a mismatch between the infinite NbSe₄ chains with random shifts along the c direction is proposed. A computer simulation of the disordered structure was performed for the x-ray patterns with the DISCUS package [4,5], where in addition to the shifts of the infinite NbSe₄ chains correlated displacements within the thermal factors were applied to the I atoms. It is shown that the disorder of the NbSe₄ chains is responsible for the diffuse scattering on the ($h,k,\pm 10n$) planes, whereas the disorder in I positions is responsible for the weak streaking at ($l = \pm 2n$). The proposed model is used to simulate the HREM images showing defects, attributed to a precursor effect to the phase transition.

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Resonant X-ray diffraction from CB-type charge-orbital order in Nd_{1.5}Sr_{0.5}NiO₄

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Layered nickelate Nd_{2-x}Sr_xNiO₄ (NSNO) with K₂NiF₄-type structure is a rare example of a two-dimensional antiferromagnetic insulator-metal transition system, providing a contrastive counterpart to superconducting La_{2-x}Sr_xCuO₄ (LSCO) with the same crystal structure.

In NSNO, diagonal-stripe charge ordering is observed at $x=1/3$ [1] in contrast to LSCO with vertical-stripe charge ordering at $x=1/8$ [2]. NSNO also shows checkerboard (CB) charge ordering at $x=1/2$ [3]. This system undergoes an insulator-metal transition with melting of its charge ordered state but shows no superconductivity up to $x = 1.6$ [4]. Hitherto there has been no study of the electronic structure in the insulator-metal critical region. The comparison between these layered nickelate and cuprate Mott transition systems will be of benefit for understanding the uniqueness of high- T_c cuprates.

We have investigated the resonant x-ray diffraction (RXD) at Ni K-edge (~ 8.3 keV) photon energy to clarify the electric structure in CB-type charge order phase in $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_4$ ($x=0.5$). In the present case, we consider a dipole transition between Ni 1s and 4p. The 4p-level are influenced by their interaction with the e_g electrons. In CB-type order phase, we have succeeded in observing the non-zero RXD signal at (100) for an incident x-ray polarization $E\parallel a$, whereas there is no RXD signal for $E\parallel c$. The polarization dependence of (100) diffraction suggests that the (x^2-y^2) -type hole orbital order of e_g -state is realized in $x=0.5$. The charge disproportionation is estimated less than 0.2, thus the CB-type modulation of electronic structure should be originated from the orbital order rather than the charge order.

As decreasing temperature, the material undergoes a tetragonal-orthorhombic structural transition at around 250 K. Upon the transition the polarization dependence of the RXD signal changes, that is, the intensity of RXD for $E\parallel c$ becomes greater than that for $E\parallel a$. The behavior is consistent with the $(3z^2-r^2)$ -type hole orbital order of e_g -state. Therefore the (x^2-y^2) -type hole orbital order transmutes into the $(3z^2-r^2)$ -type order in accordance with the orthorhombic transition. The tilting of NiO_6 -cage should affect the e_g orbital state. We consider that the $(3z^2-r^2)$ -type orbital order plays an important role in the insulator-metal transition.

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Can negative spin densities really be detected in the magnetic field densities of a nitronyl nitroxide radical?

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Unpaired electrons are usually valence electrons and are of great chemical interest. The polarized neutron diffraction (PND) experiment is usually analysed in such a way as to produce the unpaired electron density or spin density [1]. In many cases, the spin density is, or should be, a positive quantity because (i) there is a higher population of up-spin electrons than down-spin electrons (when a magnetic field is applied), and (ii) electrons tend to always be paired so that only the unpaired electrons contribute to the spin density (i.e. the spin density from the paired electrons cancels out).

Unfortunately the PND experiment does not directly determine the unpaired electron density. Instead, polarised neutrons are scattered from the magnetic field density in the crystal (they are also scattered from the nuclei, but this effect can usually be modelled) [1]. Therefore,

one should examine the magnetic field density rather than the spin density itself.

This work examines the magnetic field density at different levels of theory (as seen by the neutrons) within the NitPh radical where it is known that negative spin densities are produced from certain (unrestricted Hartree-Fock) theoretical calculations; the negative spin densities are not so severe when quantum chemical methods which incorporate electron correlation are used [2]. The question is: How different are the magnetic fields produced from these methods? The magnetic field in NitPh is traced back to the underlying spin density [3]. The part of the spin density which does not lead to PND scattering i.e. the part which is not measurable will be identified and compared with the actual spin density. Hence, the question as to whether PND experiments can see negative spin density will be answered.

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Preliminary deformation density studies of Z-DNA hexamer duplex d(CGCGCG)₂

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Crystals of the left-handed Z-DNA duplex have the potential to diffract X-rays to the highest resolution. Recently, using synchrotron radiation, we have measured X-ray diffraction data extending to 0.55 Å resolution for a single crystal of d(CGCGCG)₂ crystal, and described its high-quality structural model obtained through conventional least-squares refinement ($R=7.77\%$; [1]). At the very high resolution of the diffraction data, not only are the positions of the hydrogen atoms clearly revealed, but there are also indications of electron density related to bonding electrons visible well above the map noise level. The high ratio of observations to individual atom parameters makes it possible to carry out a deformation density study of this DNA model.

We have used the program MOPRO [2] for the high-order refinement and consequently for the transfer of the ELMAM library [3] data to build a starting model for a multipolar refinement. The results show the importance of deformation effects, visible both in successful convergence of the refinement (for instance, systematic decrease of residual densities) and in the drop of the R-factor. The transferred and refined multipolar parameters will allow us to analyze electron-density-derived properties of the DNA molecule, including topological analysis, base pairing, hydrogen bonding, etc. The Figure shows the static deformation density for one of the cytosine fragments at the current stage of MOPRO refinement (contours at 0.0x e.Å³ interval, dashed for negative values).

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