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 $Nd_{1.5}Sr_{0.5}NiO_4$ (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||a, whereas there is no RXD signal for E||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||c becomes greater than that for E||a. The behavior is consist 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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Keywords: resonant diffraction, orbital order, charge order

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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 an 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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Keywords: polarized neutron diffraction, spin density, magnetic field density,

MS41.P18

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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 0.55Å 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.Å^3 interval, dashed for negative values).

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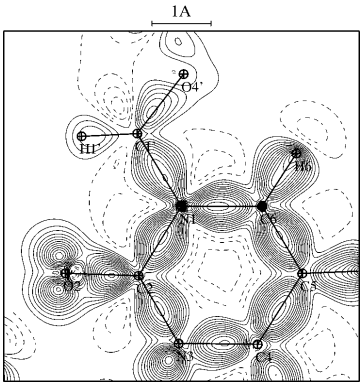

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Keywords: Z-DNA, sub-atomic resolution, deformation density

MS41.P19

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Charge density studies on N-n-butyltetrachlorophthalimide

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The charge density distribution in N-n-butyltetrachloro-phthalimide has been determined by means of high-resolution X-ray diffraction at 100K. The supramolecular structure of the title compound is stabilized by intermolecular halogen bonds C-Cl···O and intermolecular Cl···Cl interactions [1]. In the current presentation the deformation density distribution of electron density and topological analysis of electron density for the title compound crystal are shown. The deformation density clearly indicates a significantly anisotropic distribution of electrons in the halogen atom with less of them in the direction of C-Cl bond and more in the other two directions (see Figure 1 below). The topological analysis confirms conclusions derived from the deformation density distribution.

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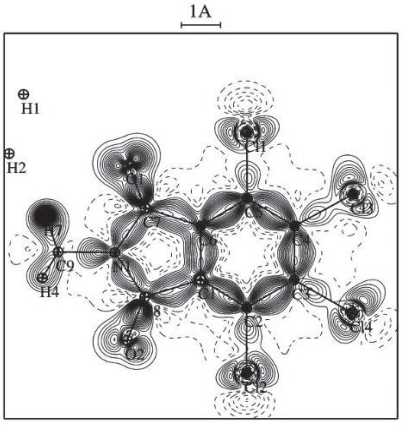

Fig. 1. Deformation density distribution for N-n-butyltetrachlorophthalimide

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Keywords: halogen bonding, electron density, electron density topology

MS41.P20

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Electrostatics of fluoroquinolone antibiotics derived from crystal structures

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A comparison of nine fluoroquinolone antibiotics [1] with respect to their solid-state electrostatic properties is reported. Molecular electrostatic potentials and dipole moments were derived from the electron density distribution after crystal structure refinement with *Invarioms*. The comparison of molecular electrostatic potentials has important implications on their function as anti-infective agents. Molecular electrostatic potentials for the same protonation states show a striking degree of similarity for the whole class of compounds. The relevance of this similarity for rational drug design and optimization of lead structures is discussed. The rapid calculation of electrostatic potentials directly from the invariom database makes the procedure suitable for high-throughput screening.

Deposited, newly determined and re-measured single-crystal diffraction data of varying quality were evaluated in this manner. The structure of lomefloxacin hydrochloride tetrahydrate is reported for the first time and the structural model of enoxacin methanol solvate as reported by Yoon *et al.* [2] needed revision: it turns out to be a water solvate. An *in silico* validation procedure for invariom database entries [3] is presented.

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MS41.P21

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Dipole moment determination in push-pull chromophores from charge density data

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Push-pull chromophores find use in organic optical materials and for many applications their ground state dipole moment and polarizability are important properties. [1] In the condensed phase intermolecular interactions influence these properties and may lead to an enhancement of the dipole moment. The crystalline state provides a rigid surrounding for the intermolecular interactions, thus maximizing the effects.

Experimental charge density studies facilitate the determination of molecular "in-crystal" dipole moments. However, the dipole moment values determined in this way have to be examined critically and are prone to systematic errors. [2] In this study dipole moments obtained from multipole refinements of structure factor amplitudes determined experimentally by diffraction and theoretically by *ab-initio* calculations are compared. The applicability of the invariom model [3]