

host scaffolds assembled via O-H...O, N-H...O hydrogen bonds and halogen...halogen, pi-pi stacking interactions based on T-shaped, H-shaped and trigonal tectons have appeared in recent publications from our group [2-4].

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**Keywords:** crystal engineering, guest-host structures, thermal analysis

#### MS87.30.4

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##### Photochemical Reactions in Inclusion Compounds

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In inclusion compounds the guest molecules occupy space formed by the host molecules. Carrying out photochemical reactions in inclusion compounds proved to be a unique method for the synthesis of a large variety of compounds. The research deals with unimolecular and bimolecular photochemical reactions in inclusion compounds. In a recent publication the effect of the reaction core on the homogeneity/heterogeneity of the reaction was studied. A question arises from this recent study: what happens if the volume of the product is smaller than that of the reactant? Free volumes are not anticipated to exist. Therefore it is expected that the following possibilities will occur: either destruction of the crystal as a result of the collapse of the cavity's walls (heterogeneous reaction) or that some other molecules will occupy the free space. We have encountered for the first time few examples where a photochemical dimerization reaction is taking place in a single crystal of inclusion compound and at the end of the reaction water molecules penetrate into the free space without destruction the crystal lattice. Moreover, at the end of the dimerization, the orientation of the dimer with respect to the host molecules is different than that prior to the reaction. Evidently the dimer is rotating during or after the photoreaction.

The aim of the unimolecular study is to examine to what extent the conformation adopted by N,N disubstituted- $\alpha$ -oxoamides determines its photochemical reaction. We have used different host molecules in order to control the conformation of the guest. It was found that indeed the N,N disubstituted- $\alpha$ -oxoamides show different photochemical behavior which depends on their conformation.

**Keywords:** host-guest complexes, homogeneous reactions, photochemistry

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##### Confinement of Gases and Polymers in Van Der Waals Crystals

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The exploitation of weak interactions for the fabrication of binary adducts by self-assembly is receiving a great interest. We could obtain high-melting crystalline materials with macromolecules by simple mechanical mixing and grinding of D<sub>3</sub> and D<sub>3h</sub> molecules with linear polyethylene or several polyconjugated oligomers [1]. A number of weak CH... $\pi$  and  $\pi$ ... $\pi$  interactions cooperatively promote the stabilization of the architecture as recognized by solid state 2D MAS NMR. In particular, tris-(*o*-phenylenedioxy)cyclotriphosphazene (TPP) organizes the aromatic paddles parallel to the nanochannels encasing the elongated molecules. The guest hydrogens are subjected to the strong magnetic susceptibility of the surrounding aromatic groups that demonstrate the topology of the guest hydrogen above the  $\pi$ -system. The favorable intermolecular interactions compensate the loss of entropy necessary for constraining the macromolecules to the stretched geometry. However, <sup>2</sup>H NMR and <sup>13</sup>C(T<sub>1</sub>) show diffusional fast spinning motion ( $\tau_c \approx 10^{-10}$ s) about the polymer axis. The exceptional mobility of the polymer chains in the fully aromatic environment creates unique examples of molecular rotors and

gyroscopes stabilized up to 350°C by soft interactions. The anisotropic alignment of polyconjugated molecules is suitable for growing crystal for electronic applications. The same kind of driving forces determine effective enclathration of light molecules and gases and promote absorption properties from the gas phase [2].

[1] Sozzani P., Comotti A., Bracco S., Simonutti R., *Angew. Chem. Int. Ed.*, 2004, 43, 2811. [2] Sozzani P. et al., *Angew. Chem. Int. Ed.*, 2005, 44, 2.

**Keywords:** self-assembly, weak interactions, gas storage

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##### Homo- and Heterochirality in Crystal

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In the present communication the methods for the recognition of homo (Ho)- and heterochiral (He) crystals are considered [1], as well as the conditions for the transformations Ho→He or He→Ho crystallization [2], the directed construction of Ho-crystals [3], solid-phase reactions Ho $\leftrightarrow$ He, synthesis of Ho-crystals [4], isomerizations during the formation of the solid phase [5] and the spontaneous resolution of Ho-crystals [6].

On the example of glycoluriles the methodology for the development of chiral drugs via the spontaneous resolution is presented [7].

The differences in physical properties of enantiomers and racemates are demonstrated by distinct differences in ESR spectra of polycrystalline samples of the enantiomers and racemates of nitroxide radicals [8]. Recently it has been found that the enantiomers of a series of compounds are effective organogelators, whereas their racemates do not show that property [9].

For the first time the supramolecular H-bonded catenanes and polycatenated structures in crystals have been synthesized [10].

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[1] *Mendeleev Commun.*, 2003, 97, 106. [2] *Tetrahedron: Asymmetry*, 2003, 14, 2059. [3] *Mendeleev Commun.*, 2002, 4. [4] *Tetrahedron: Asymmetry*, 2004, 15, 1445. [5] a) *Tetrahedron*, 1982, 38, 549; b) *Tetrahedron*, 1984, 40, 2151. [6] a) *Mendeleev Commun.*, 2000, 16, 83; b) *Mendeleev Commun.*, 2001, 1; c) *Mendeleev Commun.*, 2003, 111; d) *Tetrahedron: Asymmetry*, 2001, 12, 2721. [7] a) *Mendeleev Commun.*, 1998, 231; b) *Mendeleev Commun.*, 2001, 134; c) *Mendeleev Commun.*, 2002, 6. [8] *Mendeleev Commun.*, 2004, 318. [9] *Mendeleev Commun.*, 2005, in press. [10] a) *Tetrahedron: Asymmetry*, 2002, 13, 2697; b) *Mendeleev Commun.*, 2005, in press.

**Keywords:** chirality, solid phase reactions, recognition of chirality

#### MS88 ELECTRONIC EXCITATIONS

*Chairpersons:* John J. Rehr, Keijo Hamalainen

#### MS88.30.1

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##### Electronic Excitations: What Inelastic X-ray Scattering can Reveal

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A review of inelastic x-ray scattering (IXS) as a method to investigate electronic excitations in solids is presented, where also some aspects of synchrotron radiation based instrumentation are touched. The direct access to the polarizability of electrons in solids by measuring the dynamic structure factor using non-resonant inelastic scattering is stressed. The weight of different terms in the diagrammatic expansion of the proper polarizability can be tested. Special lattice effects on electron correlation as zone boundary collective states, plasmon Fano resonances and the plasmon band structure will be represented, where the role of coherent inelastic x-ray scattering is stressed. The increasing importance of resonant inelastic x-ray scattering (RIXS) is emphasized. It is the sensitivity of this

spectroscopy with respect to the site of excitation, to the spin of the intermediate state and its Bloch-k- and symmetry-selectivity, which opens RIXS a broad field of applications for studies of electronic excitations. Especially shake-up processes in the intermediate state connected with excitations across the Hubbard gap of highly correlated systems have attracted much attention.

**Keywords:** inelastic X-ray scattering, electronic structure, resonant scattering

#### MS88.30.2

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#### Theory and Calculations of Inelastic X-ray Scattering

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Non-resonant inelastic x-ray scattering (IXS) can be used to study the dynamics of the electronic excitations of the sample. Although in many cases the ground state of the sample is well described with the standard computational methods the excited states still pose a challenge. We will present computational results for IXS from core and valence electrons in solids. The behavior of the core excited states is dominated by the localization of the core-hole. In practice this means that the problem can be written as an effective single-particle problem for the final state electron. Since valence excited states are a combination of two delocalized states the problem cannot be reduced to an effective single-particle approach. One is forced to consider the whole complexity of the two-particle problem.

We will analyze recent experimental IXS results for core and valence excited states using band structure based approaches [1,2] and a real space multiple-scattering approach [3]. The role of the electron-hole interaction and quasiparticle effects in IXS will be reviewed. For the core-excited states an analysis of the momentum transfer dependence of the IXS cross-section respect to the final state local density of states will be presented. Calculated dispersions of valence-excitations will be compared to experimental results for selected cases.

[1] Soinenin J.A., Shirley E.L., *Phys. Rev. B*, 2001, **64**, 165112. [2] Soinenin J.A., Shirley E.L., *Phys. Rev. B*, 2000, **61**, 16423. [3] Soinenin J.A., Ankudinova A.L., Rehr J.J., to be submitted.

**Keywords:** inelastic X-ray scattering, electronic structure calculations, spectroscopy

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#### Across the Mott Gap: Electronic Excitations in Transition Metal Oxides

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Studies of the electronic excitations in strongly correlated systems are important because these excitations may play a key role in the materials' behavior and because such measurements provide stringent tests of the various theoretical approaches to the strongly correlated problem. Here, we report inelastic x-ray scattering studies of momentum-resolved excitations in cuprates and manganites.

In the 1D cuprate, SrCuO<sub>2</sub> results suggest that the excitation spectrum consists of a holon-anti-holon continuum together with a broad resonance, consistent with a parameter-free calculation of the dynamical response function [1]. In contrast, in the 2D cuprate system, La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> [2] better-defined excitations were observed. At x=0, two broad peaks are found that are strongly momentum dependent. Higher-resolution measurements suggest that these are in fact comprised of a number of long-lived excitations. As carriers are doped into the system, excitations below 3eV are replaced by a momentum dependent continuum. Finally, the dependence of the excitations on the electronic ground state is revealed in 3D manganites in which the observed temperature dependence is correlated with changes in the magnetism and associated with intersite *d-d* excitations.

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*Phys. Rev. Lett.*, 2002, **89**, 177003. [3] Grenier S. et al., *Phys. Rev. Lett.*, 2005, **94**, 047203.

**Keywords:** inelastic X-ray scattering, electronic excitations, strongly correlated systems

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#### Magnetic Inelastic X-ray Scattering as a Probe of Electronic Excitations in Correlated Electron Materials

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The magnetic x-ray scattering technique in the deeply inelastic (Compton) regime is emerging as a powerful new spectroscopic window for understanding the properties of magnetic electrons in complex materials. Here we consider results on three correlated electron systems of current interest: The double layer manganite La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7</sub>, the perovskite manganite La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> and the magnetite F<sub>3</sub>O<sub>4</sub>. First principles band theory computations using the conventional local density approximation (LDA) as well as computations going beyond the LDA framework for treating correlation effects are used to gain insight into recent magnetic Compton scattering measurements. We show how in the double layer manganite the [110] magnetic Compton profile (MCP) contains a distinct signature of the d-electrons of x<sup>2</sup>-y<sup>2</sup> symmetry, allowing us to monitor significant changes in the occupancy of these orbitals as a function of temperature over the range of 5-200K. An itinerant electron contribution is suggested at all temperatures in magnetite. In magnetite, we find that the magnetic moment associated with unpaired spins is non-integral and we adduce that the charge ordering model of the Verwey transition is not tenable.

**Keywords:** magnetic, compton, electronic

#### MS88.30.5

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#### Correlations in Inelastic Scattering and Plasmon Filtered Imaging

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It is often assumed that inelastic electron scattering from the plasmon is incoherent and confined to small angles. However it can be seen that this is not the case in elements and compounds that share the 'simple' metal form of electron correlation. A continuous electron density distribution results in a characteristic 'bare' plasmon spectrum. In this case it can be shown that through the filtering of electrons that have suffered multiple interactions with the plasmon region of a material, images can be formed from regions at thicknesses that would conventionally provide little to no contrast [1].

However, in order for this to occur, the primary interaction must be with conduction electrons, thereby generating a 'bare' plasmon form of low loss spectrum. When the primary interaction is no longer with the conduction electrons, then this 'bare' or simple form is lost.

Thus we endeavour to show that analysis and imaging from the low loss spectrum of EELS can provide information not only about the physical structure of the material e.g. dislocations, but also about electronic properties beyond the band gap.

[1] Moodie A.F. et al., *ultramic*, 2004, **101**, 247.

**Keywords:** plasmon, correlation, eels