spin-crossover between (i) S=5/2 and S=1/2(type-1), (ii)S=3/2 and S=1/2(type-2), and (iii)S=5/2 and S=3/2(type-3). The type-1 was discovered by Beetlestone back in 1964, while the type-2 was only recently found by ourselves and the structural consequences during the spin-crossover process was observed in a single crystal. As for the type-3, no example has ever been reported. Actually, the mixed S=5/2, 3/2 spin state is considered to be a quantum mechanical spin admixture. Quite recently, we found that highly saddled mono-aqua complexes show the unprecedented type-3 spin-crossover at extremely low temperatures. Shortly after our first finding, several examples of type-3 spin-crossover were found in some azide complexes. So, we have finally completed the "SPIN-CROSSOVER TRIANGLE " in iron(III) heme. In the case of the type-2 and type-3 spin-crossover, the essential requirements for this process are the presence of a small cavity around the metal together with suitable field strength of the axial ligands. Thus, the iron(III) complex of diazaporphyrin is a possible candidate to show such an unusual magnetic behavior because of the presence of a small cavity due to two nitrogen atoms in the macrocycle. Actually, $[Fe(DAzP)(Py)_2]ClO_4$ showed extremely small cavity area, Fe-Np, and Fe-N_p, $7.65Å^2$, 1.948Å, and 2.054Å, respectively. Combined analysis using ^1H NMR, EPR, Mössbauer spectroscopy has revealed that $[Fe(DAzP)L_2]ClO_4$ exhibit the spin-crossover between S=3/2 and S=1/2 if the axial ligands(L) are 3,5-Cl_2Py, 3-CNPy, 4-CNPy, and 3ClPy. The reason for the spin crossover will be discussed in detail.

Keywords: iron(III), spin-crossover, porphyrin

MS.32.1

Nanostructure investigations using atomic pair distribution function and other direct-space methods

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For understanding and development of complex novel materials it is essential to know their structure on the nanometer length-scale. Traditional crystallographic methods are often at their limits when studying nanoscale structures due to the diffraction patterns containing broad diffuse features instead of sharp Bragg peaks. Real-space atomic Pair Distribution Function (PDF) makes no assumption on the periodicity of the material and evaluates both the Bragg and diffuse components of the scattering pattern. I will present examples of technique application for discrete nanoparticles, crystals with local structure distortions and nanoporous materials with molecules and nanoparticles intercalated inside the pores. Recently the scope of the PDF technique was shown to include ab-initio structure determination [1], and there were significant improvements in the user software available for PDF structure analysis [2]; these developments will also be discussed.

[1] P. Juhas, D. M. Cherba, P. M. Duxbury, W. F. Punch, S. J. L. Billinge, Ab initio determination of solid-state nanostructure, Nature 440, 655-658 (2006).
[2] C. L. Farrow, P. Juhas, J. W. Liu, D. Bryndin, E. S. Bozin, J. Bloch, Th. Proffen and S. J. L. Billinge, PDFfit2 and PDFgui: computer programs for studying nanostructure in crystals, J. Phys.: Condens. Matter 19, 335219 (2007)

Keywords: pair distribution function, nanostructures, structure analysis

MS.32.2

Analysis of partially ordered (nano)materials through the Debye function method

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The Debye Function (DF) method is a bottom-up direct-space method for evaluating powder diffraction patterns. After building suitable atomic clusters and evaluating the interatomic distance set, DF directly yields the powder diffraction response[1,2]. Opposite to Bragg formalism, DF does not rely on the system periodicity, although even partial periodicity can be cast into computational advantage. The method is fully complementary to the Bragg approach. The latter works well for periodic order with small deviations and large coherence length. DF can deal with any kind of (dis)order[3]. This is important as the degree of periodic order in nanomaterials is often poor, although disorder actually determines the most useful properties (relaxor ferroelectrics, nanotubes, semi/superconductors, nanometals, etc.). One important issue is that disorder analysis of partially periodic systems needs a statistical description of the defectiveness, while the Debye method is intrinsically deterministic. Building grand-canonical ensembles of atomic clusters is not the way out, except in limited cases. Therefore, an enhancement of the DF approach to make it applicable to stochastically variable atomic structures is extremely important. We recently succeeded in implementing the most important disorder types in a statistically parametrized fashion. These include radial strain fields, dislocations, stacking faults, size/shape biaxial distributions. This talk is devoted to highlighting some of the underlying concepts with examples.
[1] J. Appl. Cryst. 36 (2003) 1148
[2] J. Comp. Chem 27 (2006) 995
[3] Nano Lett. 6 (2006) 1966

Keywords: diffraction applied to materials science problems, computer simulation of non-crystalline solid, nanocrystalline structure defects

MS.32.3

Atomic arrangement in a nanotube from powder X-ray diffraction

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The bulk crystal structures of materials distort as they fold to form a particular nanoshape. Here we show that by using the Debye equation it is possible to establish the exact structure of a nanostrutured material, in this case TiO_2-B nanotubes (inner diameter 4.6, outer diameter 10 nm). The ordered regions within the nanotubes are confined to segments of dimension 3.2 nm along the circumference of the outer wall and 14.2 nm along the axis of the nanotube. Each segment exhibits non-uniform deformation along the annulus of the tube. TiO_2-B acts as a host for Li intercalation but the nanotubes can store significantly more Li and the rate of Li insertion/removal is higher for the nanotubes. Distortion of the ideal TiO_2-B crystal structure that accompanies formation of the nanotubes results in a

continuous increase in the interatomic distances extending radially outwards across the tube wall. The distances in the outer half of the tube are greater than those in the ideal structure, resulting in wider bottlenecks for Li^+ ion transport, consistent with a higher rate of Li^+ intercalation, and with the greater accessibility of Li^+ sites, consistent with a higher maximum Li composition
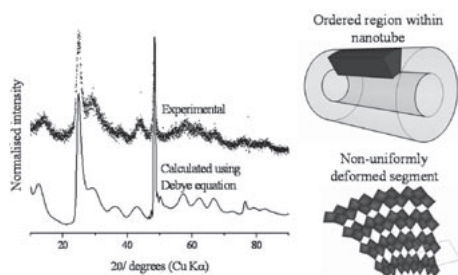
Keywords: powder diffraction techniques, nanotubes, structure-properties relationships

MS.32.4

The application of a molecular replacement approach to the refinment of a copper nanoball complex

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The reaction of equimolar amounts of $Cu(NO_3)$ and bdc-5-OH (benzene-1,3-dicarboxylate-5-hydroxy) is an example of a one-step synthetic method which may be used to generate nanoscale molecules via self-assembly. In this case, the discrete structures, termed 'nanoballs' are molecular versions of faceted polyhedra, namely small rhombihexahedra. The structural characterization of specific nanoball complexes, $[Cu_2(bdc-5-OH)_2L_2]_{12}$ (where L is a dimethyl sulfoxide, methanol or water ligand), via single crystal x-ray diffraction is very difficult. In many respects, the diffraction patterns obtained from these large metal-organic molecules resemble those obtained from protein crystals. largely due to disordered solvent molecules inside the nanoballs and between the nanoballs. We have utilized an approach similar to isomorphous replacement to refine the structure of $[Cu_2(bdc-5-OH)_2(H_2O)_2]_{12}$ (1) from 1.4 Å data. An idealized small rhombihexahedron structure based upon the previously-determined $[Cu_2(bdc-5-OH)_2(DMSO)(MeOH)]_{12}$ (2) structure, was used to generate a 432-atom rigid body unit (with axially coordinated solvent ligands removed). The orthogonal Angstrom coordinates for this idealized unit were then imported into SHELXTL, using the FRAG instruction. This fragment was fit to the 48 Cu atoms for two independent molecules in structure 1, resulting in the generation of fractional coordinates for all of the nanoball atoms. Complex 1 crystallizes in the space group $P2/n$ with $a = 47.993(2)$ Å, $b = 27.763(1)$ Å, $c = 48.131(2)$ Å, $\beta = 110.341(2)$ °, volume $= 25095(1)$ Å^3, with $Z = 2$. The Cu atoms were refined anisotropically and all other non-hydrogen atoms were refined isotropically to yield $R1 = 13.77\%$ for 13551 observed reflections and 1577 parameters.

Keywords: refinement problematic structures, SHELX, isomorphous replacement

MS.32.5

Coherent diffractive imaging of nanostructures at synchrotron and FEL sources

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Coherent X-ray Diffractive Imaging (CXDI) is a new microscopy technique that has potentiality to produce images up to diffraction limited resolution at x-ray wavelengths. The basic principles of the technique will be presented in this talk. A number of applications for imaging the shape and strain fields of the nanometer size crystals will be presented as well. It will be demonstrated how a few nanometer resolution can be achieved if a large number of identical samples are illuminated coherently. In the end recent results of CXDI at FLASH Facility at Hamburg will be given.

Keywords: coherent diffractive imaging, phase retrieval, nanosamples

MS.33.1

New liquid structures of alkali metals under pressure predicted from first principles theory

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We present results from ab initio calculations that predict a series of electronic and structural transitions in alkali liquids under pressure. The transitions are initially driven Peierls distortions in the local order of the liquids, followed at higher pressure by electron core overlap effects. In the case of Li, weakly bound tetrahedral clusters are found at pressures above 150 GPa. Similarities and differences between the phase diagrams of Li, Na and K are studied. We establish correlations between the solid and liquid phases of these elements, on the basis of which we predict their melting properties and provide evidence for the low-temperature crystalline phases likely to be found at extreme pressures.

Keywords: high-pressure physics, *ab initio* calculations, liquid structure

MS.33.2

Total scattering studies of pressure induced amorphization

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Solid state amorphization is a widely studied effect, recently highlighted in the interpretation of the structural process underlying rewritable digital versatile discs [1]. Pressure-induced amorphization (PIA) falls within this field and is typified by the behaviour of ZrW_2O_8. Indeed, the mechanism for amorphization in this system