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, 7.65$Å^2$, 1.948$Å$, and 2.054$Å$, respectively. Combined analysis using ^{1}H 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$_2$Py, 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