Microsymposia

of [Ni(tmdt)2] and [Au(tmdt)2]. It was quite surprising that in spite of the compressed crystalline powder sample, the room temperature conductivity of [Pt(tmdt)2] was as high as 350 S cm⁻¹ and temperature dependence of the resistivity was metallic down to 4 K. Here, our recent studies on crystal structures and their physical properties of single-component molecular conductors with different central metal atoms (Cu, Zn, Co) will also be presented.

Keywords: single-component molecular metal, molecular metals and superconductors, phase transition

MS.31.3

Photoswitchable high spin molecules

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This presentation intends to point out some recent achievements in the field of photoswitchable high spin molecules. These compounds might be viewed as Photo-Magnetic Molecular Devices (PMMDs) devoted to molecular spintronics. Results have been firstly obtained on a polynuclear complex, Mo(IV)Cu(II). Before light irradiation, this complex behaves as a paramagnetic species, as expected for six isolated paramagnetic Cu(II) ions surrounding a Mo(IV) diamagnetic core. After light irradiation, the magnetic properties are found to be consistent with those of a high spin molecule, Mo(V)Cu(I)Cu(II) (S = 3). The long-lived photo-produced metastable state is persistent up to an unusually high temperature (300K). Furthermore, the photo-magnetic effect is thermally reversible. The EPR studies, as well as the X-ray absorption spectroscopy and XMCD performed under synchrotron radiation, allowed us to demonstrate the photo-induced electron transfer. A large family of new MoCu, (x = 1, 2, 4, 6) and hetero-tri-metallic complexes, MoCuM (M=Ni, Mn, ...), have been recently obtained and fully characterized by X-ray crystallography opening the way of photo-switchable single molecule and single chain magnets. Promising results have been done on photocative molecules grafted on surface that would be of great interest for the information storage at the molecular scale.


MS.31.4

Structural aspects of magnetic transitions and high conductivity in ionic complexes of fullerenes

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Structural details governing magnetic and conductivity properties of multicomponent ionic complexes of fullerenes, (D⁺)(D⁻)(C₆₀⁻), are discussed. In these complexes (D⁻) is a cation or strong donor capable to ionize C₆₀ molecules, and D⁺ is a neutral structure-forming molecule. The following examples are highlighted:

1. Complexes (D⁺)CoOEP(C₆₀⁻) (OEP = octaethyl-porphyrine) with coordinating cation of N-methylidiazabicyclooctane (MDABCO) shows reversible dissociation of the Co-C(C₆₀⁻) a-bond in the 50-250K region with the transition of the complex from diamagnetic to paramagnetic state[1].
2. In the complex {(MDABCO⁺)CoOEP(C₆₀⁻) (OEP = octaethyl-porphyrine) there are S(C₆₀⁻): dimers bound by two C-C bonds. The dimers contain about two unpaired spins, whose behaviour is described well by a model presuming a single ground state (S=0) and a close lying excited triplet (S=1) state with the energy gap of 70 cm⁻¹. Additionally, strong AF exchange interaction of spins in the CoOEP(C₆₀⁻)-CoOEP chains with large negative Weiss constant of -34K is observed[2].
3. Complex (MDABCO⁺)(TPC)(C₆₀⁻) (TPC = triptycene) contains closely packed hexagonal layers of monomeric (C₆₀⁻) radical anions and manifests metal-like behaviour. Magnetic and conductivity behaviours are affected much by the interplay of electronic states in two crystallographically independent fullerene layers with ordered and orientationally disordered fullerene molecules, resulting from transformations of interfullerene interactions.


Keywords: complex compound crystal structure, fullerenes, magnetic and transport behaviours

MS.31.5

The spin-crossover triangle in the iron(III) porphyrinoids

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Some iron(III) complexes exhibit a spin-crossover phenomenon. The three possible pathways of spin-crossover processes are; the
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, nanomaterials, 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.


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

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 nanostructured material, in this case TiO₂-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. TiO₂-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 TiO₂-B crystal structure that accompanies formation of the nanotubes results in a...