

compound semiconductors such as Cu(In,Ga)Se₂ as absorbers. Since the availability of indium is an object of concern regarding solar cell large scale production, its replacement with Zn and Sn is beneficial in this sense. The alternative compound kesterite (Cu₂ZnSnS₄) has promising characteristic optical properties. The structure of kesterite consists of a *ccp* array of sulfur atoms, with metal atoms occupying one half of the tetrahedral voids. In literature an ordered distribution of Cu⁺, Zn²⁺ and Sn⁴⁺ is described. A disordered distribution may cause site defects and hence influences the electronic properties of the material. Thus the degree of cation order plays a crucial role and was therefore the focus of the presented investigations. Combined neutron and X-ray diffraction experiments revealed that the degree of cation order depends on the thermal history of the kesterite. In quenched samples Cu⁺ and Zn²⁺ are disordered, whereas in samples where a controlled cooling was applied, a certain degree of cation order is achieved. To shed more light into the formation process of kesterite, *in-situ* high temperature synchrotron X-ray diffraction experiments on stoichiometric mixtures of binary and ternary sulfides were performed. Structural phase transitions and formation of new phases, resulting in kesterite formation, can be observed in detail by mapping the diffractograms and Rietveld analysis. The variation of the kesterite lattice parameter with temperature, especially during the kesterite nascency, indicates changes in the cation distribution. Completing the presentation, first promising results of kesterite thin film solar cells will be shown.

Keywords: solar cells, cation distribution, *in-situ* high temperature diffraction

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Phase composition of mineral trioxide aggregate and its role on properties as biomaterial cement

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Quantitative phase analysis of ProRoot Mineral Trioxide Aggregate (MTA) was performed applying the Rietveld method to its X-ray powder diffraction data (XRD). Six crystalline phases were identified as constituents: bismuth oxide, tricalcium silicate, dicalcium silicate, calcium dialuminate, calcium sulphate dehydrated, and tricalcium aluminate. In order to limit the entries for phase identification, chemical analysis by Energy Dispersive Spectrometry (EDS), Rutherford Backscattering Spectrometry (RBS) and Particle induced X-ray emission (PIXE) were used and was found in agreement with the phases identified by XRD. As cement for use in dentistry, MTA has been investigated as root-end filling and as sealing material in periapical dental surgeries, showing good response in the forming tissue. In cases of open apices, MTA seems to act in cell reactions stimulating the regeneration of biological tissue. The action of MTA can be explained on the basis that when tricalcium and dicalcium silicates are hydrated, they produce calcium silicate hydrate gel (CSH) and calcium hydroxide. The last acts as alkaline reservoir, keeping the pH at higher values creating an unfavourable environment for bacteria to survive. On the other hand, the release of calcium atoms from the cement in adjacent tissues stimulate hard tissue deposition.

Keywords: biomaterial, mineral trioxide aggregate, biocement

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Switching magnetic molecular materials

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The field of functional molecular materials has seen a very rapid progress since the discovery of a variety of cooperative solid-state properties such as conductivity and superconductivity, non-linear optics, and ferromagnetism. Currently, one of the most appealing aims in this field is that of creating complex materials in which these cooperative properties can be tuned by external stimuli (light, temperature, pressure). One can imagine two possible approaches to reach this goal: a) The two-network approach, which is based on materials formed by two molecular networks. In this case the magnetic or conducting properties of one of the two networks are influenced by the structural changes induced in the crystal lattice by the second network, which is formed by a switchable molecule; b) The one-network approach, which is based on materials formed by a single magnetic or conducting molecule-based network. In this case the material contains in this network an electroactive or photoactive molecular component that can switch when the external perturbation is applied. Here we will show two examples that illustrate this concept in molecular magnetism. The first one is provided by two-network materials formed by bimetallic oxalato-based magnets and spin-crossover Fe(II) and Fe(III) complexes, while the second one is provided by one-network Prussian-Blue materials that undergo magnetic switching when an external pressure is applied.

Keywords: materials chemistry, magnets, molecular magnets

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Structures and physical properties of single-component molecular metals

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In contrast to typical inorganic metals composed of single elements, such as sodium and copper, all of the molecular metals developed until recently had been consisted of more than two kinds of molecules. In 2001, we developed the first single-component molecular metal with extended-TTF ligands, [Ni(tmdt)₂] (tmdt = tri methylenetetrafulvalenedithiolate) exhibiting metallic behavior down to very low temperature. A direct experimental evidence for the three-dimensional electron and hole Fermi surfaces in [Ni(tmdt)₂] was obtained by detecting the quantum oscillations in magnetization (de Haas-van Alphen (dHvA) effect) at low temperature under very high magnetic field. The neutral bis(dithiolato)gold complex [Au(tmdt)₂] is isostructure to [Ni(tmdt)₂]. The ESR, ¹H NMR, μ SR and magnetic susceptibility measurements revealed that [Au(tmdt)₂] has the antiferromagnetic phase transition around 110 K. The single crystal resistivity measurement of [Au(tmdt)₂] using extremely small crystal of ca. 30 μ m showed the system to be metallic down to 4 K. All these data shows that [Au(tmdt)₂] is the first AF molecular metal with T_N above 100 K and metal electron and magnetic order coexist down to low temperature. Recently we have prepared [Pd(tmdt)₂] and [Pt(tmdt)₂] whose crystal structures were almost the same with those

of $[\text{Ni}(\text{tmdt})_2]$ and $[\text{Au}(\text{tmdt})_2]$. It was quite surprising that in spite of the compressed crystalline powder sample, the room temperature conductivity of $[\text{Pt}(\text{tmdt})_2]$ 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

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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, $\text{Mo}(\text{IV})\text{Cu}(\text{II})_6$. 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, $\text{Mo}(\text{V})\text{Cu}(\text{I})\text{Cu}(\text{II})_5$ ($S = 3$). 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 ($x = 1, 2, 4, 6$) and hetero-tri-metallic complexes, MoCuM ($M = \text{Ni}, \text{Mn}, \dots$), 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 photoactive molecules grafted on surface that would be of great interest for the information storage at the molecular scale.

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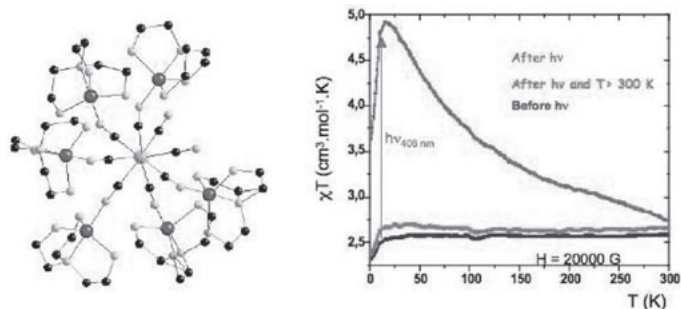


figure 1 : MoCu_6 complex and photoswitchable magnetic properties

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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, $(\text{D}_1^+)(\text{D}_2)(\text{C}_{60}^-)$, are discussed. In these complexes (D_1^+) is a cation or strong donor capable to ionize C_{60} molecules, and D_2 is a neutral structure-forming molecule. The following examples are highlighted:

1. Complexes $(\text{D}^+)\text{Co}^{\text{II}}\text{OEP}(\text{C}_{60}^-)$ (OEP = octaethyl-porphyrine) with coordinating cation of N-methyldiazabicyclooctane (MDABCO⁺) shows reversible dissociation of the Co-C(C_{60}^-) σ -bond in the 50-250K region with the transition of the complex from diamagnetic to paramagnetic state[1].

2. In the complex $\{(\text{MDABCO}^+)\cdot\text{Co}^{\text{II}}\text{TMPP}\}_2\cdot(\text{C}_{60}^-)_2$ (TMPP = tetramethoxyphenyl-porphyrine) there are π - $(\text{C}_{60}^-)_2$ dimers bound by two C-C bonds. The dimers contain about two unpaired spins, whose behaviour is described well by a model presuming a singlet 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 $\text{Co}^{\text{II}}\text{TMPP}-(\text{C}_{60}^-)_2-\text{Co}^{\text{II}}\text{TMPP}$ chains with large negative Weiss constant of -34K is observed[2].

3. Complex $(\text{MDABCO}^+)(\text{TPC})(\text{C}_{60}^-)$ (TPC = triptycene) contains closely packed hexagonal layers of monomeric (C_{60}^-) 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.

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

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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