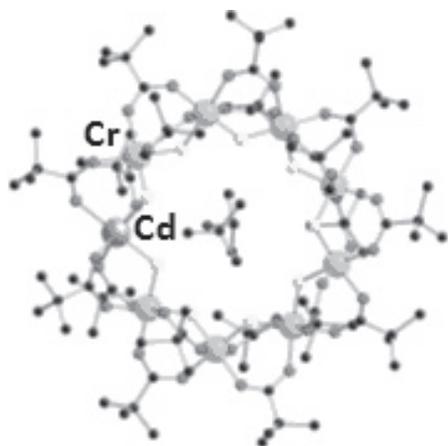the ring which is interrupted by a diamagnetic Cd^{2+} ion[1] (see figure below).

Antiferromagnetic coupling between first nearest neighbors Cr^{3+} ions, via the bridging organic ligands, leads to a singlet spin ground state $S_{tot} = 0$ and to excited states with integer spin values $S_{tot} = 1,...$ Application of a high magnetic field at low temperature induces a lifting of degeneracy of the excited states and the existence of $S_{tot} \neq 0$ spin states with lower energy than the $S_{tot} = 0$ zero-field ground state.

The experimental induced spin density in two different states ($S_{tot} = 1$) and ($S_{tot} = 2$), reached by applying a field of 4.6 and 9 Tesla respectively, was determined from polarised neutron diffraction measurements on a single crystal at 2K (D3, ILL and 5C1, LLB). A non-uniform distribution of the induced magnetic moments on the Cr^{3+} finite chain is observed, with accumulation of positive spin density at the extremities of the chain.

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Keywords: spin, density, neutron

MS.66.5

Interplay between structure and functional properties in spin crossover frameworks

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The recent integration of spin-crossover capabilities (electronic spin-state switching) into nanoporous metal-organic framework materials (MOFs) gives rise to a unique molecular scenario where factors that govern the switching responses to external perturbations (e.g. magnetic field, temperature, pressure, light, and guest/chemical environment) are newly intertwined with factors governing structure-function relationships and host-host/host-guest chemistry [1]. Consequently, these nanoporous spin-crossover MOFs display rare and unprecedented synergistic structure-function properties that offer a new opportunity to develop advanced 'smart' materials capable of a dynamic response to their environment. For example, molecular sensing capabilities become realised when chromic, electronic and magnetic switching properties characteristic of spin-crossover materials can be reversibly and selectively controlled on the molecular level by specific host-guest interactions.

Here we present a porous bimetallic spin-crossover framework material with an unprecedented 3D Kagome-type topology, [Fe(dps)Ag(CN)$_2$]·(ClO$_4$)·*guest* (where dps = 4,4′- dipyridylsulfide) which exhibits a unique structural response to spin-crossover in addition to spin-crossover behaviour that is responsive to guest- and light-induced perturbations. The framework lattice, comprising hexagonal and triangular helicies with the Fe(II) centres at the vertices, contains a network where no simple alternating arrangement of high-spin (HS) and low-spin (LS) Fe(II) sites can occur, creating a molecular scenario loosely analogous to magnetically frustrated materials. Consequently, an interplay between electronic spin-state switching with both internal host-guest pressure and geometric frustration effects manifests as a volume-quadrupling structural modulation. Furthermore, the extended family of isostructural analogues [Fe(dpX)M^I(CN)$_2$]·(ClO$_4$)·*guest* (where X = S or Se, and M^I = Ag$^+$ or Au$^+$) unexpectedly display identical magnetic properties despite elemental substitutions at the chalcogen and/or M^I positions. This unorthodox behaviour can be interpreted as another facet of the structure function-relationship.

To the best of our knowledge, the physical realization of a true 3D Kagome-type topology, the structure-function relationship of a modulation arising from a complex 3D ordering of HS-LS Fe(II) sites *and* the apparent insensitivity of the spin-crossover behavior of a material to elemental substitutions have not been reported to date. Thermo-chromic, optical and photomagnetic phenomena as well as the large porous architecture with host-guest specific properties also add to the multifunctionality displayed by this series of framework materials.

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Keywords: spin-crossover, metal-organic framework, modulation

MS.67.1

News from the world of eni carbon silicate (ECS) materials

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ECS (Eni Carbon Silicate) materials form a new class of crystalline organic-inorganic hybrid aluminosilicates recently discovered in eni's laboratories [1]. Synthesis of ECSs resembles that of zeolites, involving the hydrothermal treatment at 100°C of a reaction mixture being composed by NaAlO$_2$ as source of alumina, NaOH and/or KOH, demineralized water and a bis-trialkoxysylilated organic precursors of general formula (R'O)$_3$Si–R–Si(OR')$_3$ (R = alkyl, aromatic or alkyl-aromatic moiety; R' = Me or Et) as source of silica.

A set of ECS materials has been synthesized so far, by appropriately varying the nature of the bis-silylated precursor and the synthesis conditions. The extensive physico-chemical characterization of these materials demonstrated that most part of the silica precursors do not undergo Si-C hydrolysis and are kept unchanged in the crystalline phase. Only trace amounts of conventional, low-silica zeolite phases (e.g. Sodalite, Na-P1) were occasionally found as by-products.

The determination of the crystal structure of some ECS materials was fundamental for clarifying their properties. The structural characterization of these materials proved to be a challenging problem because of the complexity of the X-ray powder diffraction patterns and even for the impossibility to grow samples suitable for single crystal data collection. In spite of that, for some ECS phases the structure

determination was successful, providing important information on the characteristics of these materials.

In particular, the structure of ECS-2 (with R = phenylene) was solved by direct methods starting from high resolution synchrotron powder diffraction data [1]. It consists of a regular stacking of alternating inorganic and organic layers and can be classified as a clathrasil-like structure since the arrangement of the phenylene rings in the organic layers produces large cages not open to the exterior but able to clathrate ethanol molecules.

Still more interesting is the structure of ECS-3 (with R = phenylene as ECS-2, but synthesized in the presence of a mixture of Na and K ions), which was determined starting from electron diffraction data collected on sub-micrometer single crystals with the new Automated Diffraction Tomography (ADT) technique [2], [3]. The structure consists again in a regular stacking of inorganic and organic layers but, differently from ECS-2, the relative arrangement of the phenylene rings generates an open porosity, classifying this material as the first microporous aluminosilica-based hybrid organic-inorganic material [4].

For other ECS materials recently synthesized the structure determination is in progress and the results will be illustrated and discussed to provide a first overview of this interesting class of materials.

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Keywords: hybrid materials, layered, porous

MS.67.2

Revision of the crystal chemistry of the astrophyllite group

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Until recently, there have been known seven structurally characterized astrophyllite-group minerals: astrophyllite, magnesiumastrophyllite, nalivkinite, niobophyllite, kupletskite, niobokupletskite, and kupletskite-(Cs), with the general formula $A_2BC_7D_2(T_4O_{12})_2O_2(OH)_4X_{0-1}$, where A = [5,12,13](dominant K, Cs, Li, minor Rb, Pb, Na, Ca and □); B B = [10](dominant Na, minor Ca); C = [6](dominant Fe^{2+}, Mn^{2+}, minor Fe^{3+}, Na, Mg, Ca, Li, Zr and Zn); D = [5,6](dominant Ti and Nb, minor Zr, Sn, Ta and Mg); T = [4](dominant Si, minor Al) and X = dominant F, O, minor OH [1,2]. The characteristic feature of the astrophyllite structure is an (T_4O_{12}) ribbon that extends along [100]. The (Si_4O_{12}) astrophyllite ribbons share common vertices with D octahedra to form a heteropolyhedral (H) sheet. The octahedral (O) sheet is formed by the M(1-4) close-packed octahedra of the C-group. In the crystal structures of the astrophyllite-group minerals, the O sheet and two H sheets form an HOH block of composition $C_7D_2(T_4O_{12})_2O_2(OH)_4X_{0-1}$. Linkage of two H sheets and a central O sheet is identical for all structures, except for magnesiumastrophhyllite. Along [001], these HOH blocks connect *via* common X anions of D octahedra (except for magnesiumastrophyllite where the D atom is [5]-coordinated) and interstitial cations at the A and B sites.

In 2009, two new minerals of the astrophyllite group were structurally characterized: devitoite, $[Ba_6(PO_4)_2(CO_3)]Fe^{2+}_7F$ e$^{3+}_2$ $(Si_4O_{12})_2O_2(OH)_4$, [3], and sveinbergeite, $Ca(Fe^{2+}_6Fe^{3+})Ti_2(Si_4O_{12})_2O_2(OH)_5(H_2O)_4$, [4]. Discovery of these two minerals makes structural hierarchy of the astrophyllite group more complex. Here, I introduce an intermediate (I) block which comprises all atoms which occur between two adjacent HOH blocks. In seven astrophyllite-group structures, the I block comprises cations at the A and B sites. In devitoite and sveinbergeite, the I blocks are of different topologies and compositions, $[Ba_6(PO_4)_2(CO_3)]$ and $Ca(H_2O)_3$, respectively.

In this talk, I revise the crystal chemistry of the astrophyllite group, explain why the topology of the HOH block in magnesiumastrophyllite is different from other eight structures, and predict new structure types based on a stable structural unit, an HOH block, and intermediate blocks of various topologies and chemical compositions.

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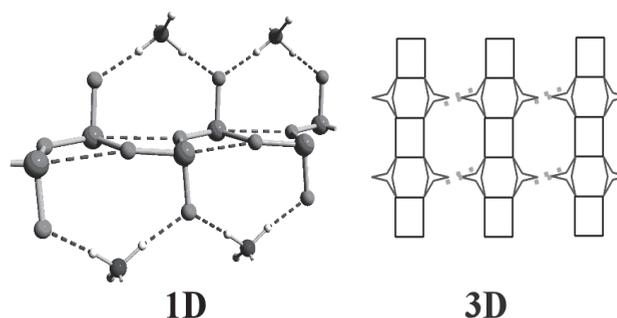
Keywords: layered, structure, prediction

MS.67.3

Ammonium polyoxoarsenates(III) – from columns to 3D structure

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1D   **3D**

Understanding how the forces driving supramolecular organisation in crystals balance one another is the key into rational development in the field of crystal engineering.

Reactions between arsenic(III) oxide with either ammonia or organic amines lead to the formation of hybrid inorganic-organic polyoxoarsenates(III). The following polyoxoarsenates(III) have been synthesized: ammonium (**1**), ethylenediammonium (**2**), benzylammonium (**3**), methylammonium (**4**) and ethanolammonium (**5**). The crystal structures of investigated compounds can be divided into three distinct levels reflecting the supramolecular organisation of entities in the structures.

Primary structure contains polyoxoarsenite chains decorated with ammonium cations. The inorganic polyanion is built of ψ-tetrahedra sharing two of their corners. The arsenic atom possesses distorted ψ-tetrahedral geometry, being surrounded by two bridging oxygen ligands, one terminal oxygen ligand and a stereoactive lone electron pair. Terminal oxygen ligands alternate on both sides of plane defined by arsenic atoms and bridging ligands. Such a chain conformation is stabilised by weak As···O interactions. Terminal ligands are spanned