

given in this presentation with results obtained with an ultrastable double aberration-corrected and monochromated electron microscope. First of all, we will demonstrate the detection of low-loss features in plasmonic nanostructures down to the infrared part of the electron energy loss spectrum by directly imaging resonances down to 0.5eV, the lowest features currently detected with EELS [1]. Using momentum resolved near-edge structures we will discuss the detection of the strong anisotropy in bonding in carbon nanotubes. After an overview of the imaging conditions used to detect ordering changes in alloy nanoparticles using a combination of X-ray diffraction techniques and high-angle annular dark-field STEM imaging and simulations, we will discuss the study the application of atomic-resolved EELS mapping in the study of interfaces [2], [3]. We will demonstrate how this powerful technique can be used in the study of the structure and substitutional effects on the atomic structure of interfaces and electronic states changes within one or two unit cells from the interface. We will demonstrate how such spectroscopic technique can be used to detect changes in valence and electronic structure as well as the termination of substrate surfaces in contact with epitaxial films. Examples will show how the stability of microscopes, coupled with atomic resolution, can be used to not only obtain spectroscopic information but also to determine, directly from high angle annular dark-field images, the local strain at interfaces and at dislocations [4]. Additional examples will highlight the application of microscopy technique to the analysis of clusters, multiferroic materials based on the perovskite structures, and interfaces in complex oxides. These examples demonstrate that compositional and chemical state (valence and coordination) information can be obtained down to the Ångström level.

[1] D. Rossouw, M. Couillard, J. Vickery, E. Kumacheva, G.A. Botton, *Nano Letters* **2011**, *11*, 1499-1504. [2] G.A. Botton, S. Lazar, C. Dwyer, *Ultramicroscopy* **2010**, *110*, 926-934. [3] S. Lazar, Y. Shao, L. Gunawan, R. Nechache, A. Pignolet, G.A. Botton, *Microscopy and Microanalysis* **2010**, *16*, 416-424. [4] S. Hosseini Vajargah, M. Couillard, K. Cui, S. Ghanad Tavakoli, B. Robinson, R.N. Kleiman, J.S. Preston, G.A. Botton, *Applied Physics Letters* **2011**, *98*, 082113.

Keywords: electron energy loss spectroscopy, transmission electron microscopy, imaging

MS.65.5

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Photo-conductivity and electronic structures of Au-nanoparticle embedded silica-nanowires

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Silica nanowires (SiO_x-NWs) embedded with Au peapods have been studied by energy-filtered scanning transmission electron microscopy (EFTEM), Au L₃- and O K-edge x-ray absorption near-edge structure (XANES) and x-ray emission spectroscopy (XES). XANES and XES data show that band gaps of Au-peapod embedded and pure SiO_x-NWs were 6.8 eV. XANES results indicate illumination induced electron transfer from Au peapod to SiO_x-NWs. Photo-response and EFTEM measurements show that green light has more significant enhancement

of photo conductivity than red and blue light due to surface plasmon resonance.

Keywords: xanes, xes, efem

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Molecular design of multifunctional magnetic materials

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The field of functional molecular materials has seen a very rapid progress since the discovery of a variety of solid-state properties such as conductivity and superconductivity, non-linear optics, and ferromagnetism. One of the most appealing aims in this field is that of creating complex materials exhibiting multifunctional properties. Thus, by a suitable assembly of the starting molecular bricks one can combine in the same material two or more properties that are difficult or impossible to achieve in a conventional inorganic solid. In this lecture I will present some recent examples reported by my group. I will focus in particular in the design of materials with coexistence of magnetism with a second property (superconductivity, molecular switching, chirality, solubility, porosity,...).

[1] E. Coronado, C. Marti-Gastaldo, E. Navarro-Moratalla, A. Ribera, S.J. Blundell, P.J. Baker *Nature Chem.* **2010**, *2*, 1031. [2] M. Clemente-León, E. Coronado, C. Marti-Gastaldo, F.M. Romero *Chem. Soc. Rev.* **2011**, *40*, 473.

Keywords: multifunctional materials, molecular magnetism, molecular conductors

MS.66.2

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Development of molecular materials with electric and/or magnetic functions

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We have tried to develop various types of crystalline molecular systems exhibiting novel electronic functions.

About two decads ago, we have prepared the magnetic organic conductors based on π donor molecules (BETS) and typical tetrahedral magnetic monoanions (FeX₄⁻, X=Cl, Br) [1]. Since then, various unprecedented organic superconductors, such as the mixed anion system, λ -BETS₂Ga_{1-x}Fe_xCl₄ exhibiting successive metal-to-superconducting and superconducting-to-insulating transitions with lowering temperature, antiferromagnetic organic superconductors, κ -BETS₂FeX₄ and field-induced organic superconductors, λ -BETS₂FeCl₄ and κ -BETS₂FeBr₄ were discovered [2]. Although many works have been made on these BETS conductors, there remain many unsolved questions on their electro-magnetic properties. We will present our recent studies on "mysterious ground state" of λ -BETS₂FeCl₄, where antiferromagnetically ordered π electrons in BETS layers and paramagnetic 5/2 spins of FeCl₄⁻ anions coexist below metal-insulator transition temperature (T_{MI} = 8 K) [3]. We have previously reported the physical properties of BETS conductors with modified λ -type structure, λ' -BETS₂GaBr₄ [4]. Similar to λ -type structure, the crystal belongs to triclinic system and contain two-dimensionally arrays of tetradic columns of BETS molecules. However, in contrast to λ -BETS₂GaCl₄ with

superconducting ground state, λ' -BETS₂GaBr₄ exhibited an insulating transition at about 50 K below which the susceptibility decreased with lowering temperature (after the subtraction of the contribution from Curie impurities), indicating the non-magnetic insulating ground state. The low-temperature resistivity behavior exhibited a fairly large sample-dependence probably due to the relatively low stability of λ' -BETS₂MBr₄ (M=Ga, Fe). Recently it was confirmed that the MI transition (of good quality crystal) was suppressed at around 3 kbar but no indication of superconducting transition was observed at least down to 4.2 K. We are now examining analogous system λ' -BETS₂FeBr₄, which exhibited an electrical behavior quite similar to that of λ' -BETS₂GaBr₄.

For the last decade, we have developed various single-component molecular metals based on the transition metal complexes with extended-TTF ligands [5]. To our best knowledge, [Au(tmdt)₂] is the first molecular metal where magnetic order and metallic electrons coexists above 100 K. We are now trying to develop single-component molecular conductors with diluted paramagnetic molecules (Cu(tmdt)₂), [Ni_{1-x}Cu_x(tmdt)₂] (molecular Kondo alloy).

Besides the magnetic molecular conductors, we are examining the dielectric properties of molecular crystals such as coordination polymer complexes and classical charge transfer complexes, which will be also briefly mentioned.

[1] A. Kobayashi, T. Udagawa, H. Tomita, T. Naito, H. Kobayashi, *Chem. Lett.* **1993**, 2179-2182. [2] H. Kobayashi, H. Cui, A. Kobayashi, *Chem. Rev.* **2004** *104*, 5265-5288. [3] H. Akiba, S. Nakano, Y. Nishio, K. Kajita, B. Zhou, A. Kobayashi, H. Kobayashi, *J. Phys. Soc. Jpn.* **2009**, *78*, 033601. [4] H. Tanaka, A. Kobayashi, H. Kobayashi, *Chem. Lett.* **1999**, 133-134. [5] A. Kobayashi, E. Fujiwara, H. Kobayashi, *Chem. Rev.* **2004**, *104*, 5243-5264.

Keywords: magnetic molecular conductor, single-component molecular metal, dielectric property

MS.66.3

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Jahn-teller effect and ferroelectric phase transition in a metal-organic complex

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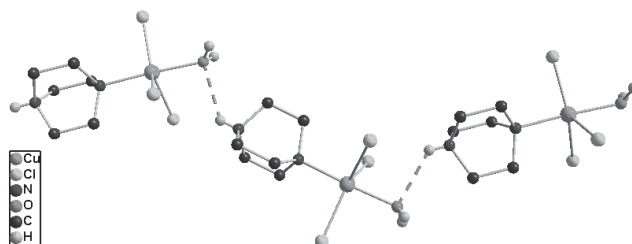
A Jahn-Teller-distorted version of the ABO₃-type structures like A = organic cation, B = Cu²⁺, Ni²⁺ and Mn²⁺, and O = halogen has been widely investigated due in part this effect resulting in the formation of structural phase transition. Most of cases exhibiting ABO₃-type structures with phase transition are octahedron situation. For example, in the copper(II) salts, the octahedra assumes a tetragonally elongated [4 + 2] coordination geometry such that each Cu²⁺ ion has four short (~2.3 Å) and two long (2.8–3.2 Å) Cu–Cl bonds.

In our case [(Hdbco)CuCl₃(H₂O)] (**1**, dbco = 1,4-diazabicyclo[2.2.2]octane), the coordination geometry of the Cu(II) is a distorted trigonal bipyramidal with one oxygen atom and N atom of monoprotonated Hdbco occupying the axial positions while three Cl anion is composed of a equatorial plane. Interestingly, strong H-bonds through a proton H⁺ on N of dbco can be formed between H⁺ and one of coordinated H₂O to result in the formation of 1D zigzag chain (Figure). The crystal structure of **1** at room temperature belongs to a centrosymmetric space group *Pnma* (D_{2h}) and a distorted Hdbco is found in this situation.

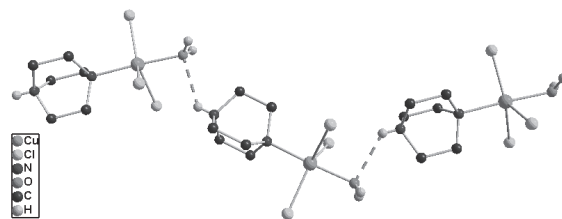
After the temperature decreases down to 80 °C, the crystal structure determination of **1** still belongs to an orthorhombic crystal system but with a noncentrosymmetric space group of *Pna2₁* (C_{2v}) which belongs to a ferroelectric phase. In the solid state structure of **1** below *T_c* the distorted [Hdbco] cation clearly becomes more regular while the

central Cu atom in **1** becomes a relatively-regular trigonal bipyramidal coordinated environment. Typical bond length changes of Cu–Cl both in paraelectric and ferroelectric phases suggest that a similar Jahn-Teller effect-like distortion may exist in the case of **1**.

Thus, in the cooling process symmetry breaking takes place with an Aizu notation of *mmmFmm2*, that is, the eight symmetric elements (e, 3C₂, i, 3σ) at the paraelectric phase (above 236 K) are halved into four (e, C₂, 2σ) owing to the loss of the symmetric elements 2C₂, i and σ, which is attributed to a typical second-order feature according to Landau phase transition theory.^[1-7]



A round-like peak in specific heat curve appears at ca. 231 K, manifesting the presence of a typical second-order phase transition like that of triglycine sulfate. The large value of dielectric constant around *T_c* (Figure) and a good dielectric hysteresis loop just below *T_c* all suggest that the phase transition should be a ferroelectric one.



[1] R.-G. Xiong, et al, *J. Am. Chem. Soc.* **2009**, *131*, 12544. [2] R.-G. Xiong, et al, *J. Am. Chem. Soc.* **2010**, *132*, 7300. [3] R.-G. Xiong, et al, *Chem. Soc. Rev.* **2011**, DOI: 10.1039/c0cs00226g. [4] Z.-M. Wang, S. Gao, et al, *J. Am. Chem. Soc.* **2010**, *132*, 9588. [5] R.-G. Xiong, et al, *Inorg. Chem. Commun.* **2010**, *13*, 1590. [6] R.-G. Xiong, et al, *Coord. Chem. Rev.* **2009**, *253*, 2980. [7] W. Zhang, R.-G. Xiong, et al, *Angew. Chem. Int. Ed.* **2010**, *49*, 6608.

Keywords: copper, Jahn-Teller, ferroelectric

MS.66.4

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Finite size effects in a quantum chain of antiferromagnetically coupled spins 3/2

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Molecular nanomagnets are isolated magnetic systems formed by a finite number of magnetic atoms which present therefore quantum effects in contrast to classical systems with infinite size. The molecular wheel [Cr₈Cd] of nanometric size provides a model of a finite antiferromagnetic chain of spins 3/2 carried by the eight Cr³⁺ ions in