

exponential of the Hamiltonian was made with the Lanczos method [5].

The optical response of smaller clusters is found to be critically dependent on the atomic structure, even for clusters of the same or very similar size. Very few consistent trends or patterns with size or structure can be identified. The addition of a ligand coating [(PH₃)₁₂Cl₆] to a 55 atom cluster was found to smooth the optical absorption profile, giving better agreement with experimental data. It also reduced the differences between the optical response of structures with a cuboctahedral or icosahedral core.

For the largest structures studied here a convergence in the optical absorption spectra is seen and there is less variation as a consequence of small changes in the atomic arrangements, as we might expect.

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Keywords: nanocrystal, optical, density_functional_theory

MS.65.2

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Chemical mapping at atomic-column resolution by STEM-EDX

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Chemical mapping at atomic-column resolution by energy-dispersive X-ray spectroscopy (EDX) in spherical aberration-corrected scanning transmission electron microscope (STEM) was demonstrated in InGaAs, achieving an element-specific resolving power for the dumbbell atomic columns, InGa and As, separated by 1.47 Å. The structural imaging and the chemical information in the two-dimensional map are directly correlated. Comparisons with the other existing mapping technique of STEM in conjunction with electron energy-loss spectroscopy were discussed from aspects of ionization interactions.

Keywords: scanning transmission electron microscopy, energy dispersive X-ray spectroscopy, chemical mapping

MS.65.3

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Three-dimensional atomic imaging of crystalline nanoparticles

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Nanomaterials in general and nanoparticles in particular play a key role in modern technology and devices because of their unique physical and chemical properties. These properties are controlled by the exact three-dimensional morphology, structure and composition. Therefore, development of new techniques to determine the structure atom by atom in 3D would allow the properties of the resulting materials to be better understood, increasing the number of applications. The strong interaction of electrons with matter makes electron microscopy

a promising technique to achieve atomic resolution in 3D. Electron tomography enables the recovery of the shape of nanoparticles in 3D from a series of projection images. The resolution that can be obtained in 3D using conventional tomography ranges on the nanometer scale although in 2D atomic resolution has been feasible for nearly four decades. In order to help close the gap between the sub-ångstrom resolution that can be reached in 2D and the coarser resolution in 3D, a new method has been devised combining high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM), model-based statistical parameter estimation theory and discrete tomography [1].

Discrete tomography [2] has been proposed as a promising technique for atomic resolution tomography in which prior knowledge about the discrete nature of atoms and their lattice structure is exploited. However, an important requirement is that one should be able to determine the number of atoms in each atomic column with great precision from a set of images taken under zone-axis orientations. We therefore employed a quantitative method to analyze HAADF STEM images [3]. It is generally known that such images show Z-contrast allowing one to visually distinguish between chemically different atomic column types. However, if the difference in atomic number of distinct atomic column types is small or if the signal-to-noise ratio is poor, direct interpretation of HAADF STEM images is inadequate. A performance measure which is sensitive to the chemical composition is the total intensity of scattered electrons. These intensities can now be quantified atomic column - by - atomic column using a parametric model describing the contrast of HAADF STEM images. Next, the unknown parameters of the model including the scattered intensities can be estimated by optimizing a criterion of goodness of fit. As such differences in (averaged) atomic number of only 3 can be identified [3]. The high chemical sensitivity is an advantage that could be further exploited to count the number of atoms in a column with an error of only 1 atom. In [1] this method has been proven to work on a metal nanocluster embedded into a stabilizing matrix with the same crystal structure. By counting the number of atoms from two different viewing directions, it has been shown that the three-dimensional structure can be reconstructed at atomic resolution. Recent results show that the method also works for more challenging structures including free-standing nanoclusters.

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Keywords: 3D, electron microscopy, nanocrystal

MS.65.4

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Bonding and electronic structure of nanomaterials and interfaces with electron energy loss spectroscopy

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Electron microscopy is an invaluable tool to study the detailed structure of materials. Many of the analytical methods available in the transmission electron microscope, electron energy loss spectroscopy (EELS) in particular, provide detailed compositional and spectroscopic information with unprecedented spatial resolution. In today's modern instruments, energy resolution down to 0.1eV with an electron beams approaching 0.1nm size is possible.

Various examples of applications of electron microscopy will be

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.

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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

MS.66.1

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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,...).

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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