## MS.48.4

Metal-insulator transitions: a real space picture

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Traditionally the metals and insulators are distinguished by different filling of their electronic bands implying thus an analysis in k-space. Electron localization indices (LI) showing the degree of electron pair exchange inside/between various regions of space represents an attractive alternative to analyze the electronic motion in real space [1]. Recently these indices have been made available also for solids which open new opportunities for the analysis of their electronic structure [2]. We have applied the LI to two different metal-to-insulator transitions in the current study.

First one is the observed experimentally pressure-induced transition of sodium metal having the double-hcp structure (Pearson symbol hP4) into transparent insulating solid [3]. It is found that the LI for QTAIM [4] and ELI-D [5] basins show different picture of electronic motion than for the metallic phase.

Another transition is a representative of large and very important class of Mott transitions which are driven by strong electronic correlation effects. A model system of 1D hydrogen chain calculated with spin-polarized DFT was selected for the study which provided qualitatively acceptable description of Mott transition for this case. A metal to insulator transition is reproduced as an abrupt increase of LI value for the QTAIM basin of hydrogen atom (see Fig.)
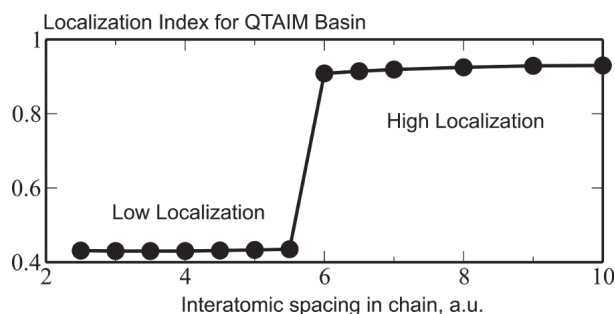
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MS.48.5

Spin-wise decomposed compton profiles

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$$\frac{d^2\sigma}{d\Omega d\omega} = C \cdot J(p_z) + C_{mag} \cdot P_C \cdot \mathbf{S} \cdot (\mathbf{k}\cos\theta + \mathbf{k'})J_{mag}(p_z), \quad (1)$$

A spin-polarized electronic state dominates the magnetic properties

of materials and is decomposed into the up- and down-spin electronic states in a non-relativistic treatment. The spin-polarized state such as magnetization density is a central subject of magnetism and has been studied on various magnetic materials by neuton and X-ray scattering techniques. In this study we propose a method to decompose the spin-polarized state into the corresponding up- and down-spin states by a Compton scattering technique. This method provides unique information on the transport and magnetic properties of half-metallic materials.

When the incident x-rays are circularly polarized, the cross section for Compton scattering is given by,

where P_C is the degree of circular polarization of incident x-rays, **S** the spin direction, **k** (**k'**) the wavevector of incident (scattered) x-rays, θ the scattering angle. C and C_{mag} are constants. The first term contains the charge Compton profile $J(p_z)$ and the second term the magnetic Compton profile $J(p_z)$. They are given by,

$$J(p_z) = \iint \left[n_{up}(\mathbf{p}) + n_{down}(\mathbf{p}) \right] dp_x dp_y = J_{up}(p_z) + J_{down}(p_z), \quad (2)$$

$$J_{mag}(p_z) = \iint \left[n_{up}(\mathbf{p}) - n_{down}(\mathbf{p}) \right] dp_x dp_y = J_{up}(p_z) - J_{down}(p_z), \quad (3)$$

where $n_{up}(\mathbf{p})$ and $n_{down}(\mathbf{p})$ are the electron momentum densities, and $J_{up}(p_z)$ and $J_{down}(p_z)$ are the Compton profiles for up- and down-spin states. $\mathbf{p}=(p_x, p_y, p_z)$ is the electron momentum. Both $J(p_z)$ and $J_{mag}(p_z)$ are accessible to Compton scattering techniques, and once the both profiles are normalized the spin-wise decomposed Compton profiles, $J_{up}(p_z)$ and $J_{down}(p_z)$, are obtained through eqs. (2) and (3) [1].

In this presentation we demonstrate the feasibility of this method by showing its application to ferromagnetic manganites $La_{1-x}Sr_xMnO_3$[2].

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MS.49.1

Molecular-scale 3D visualization of solid-liquid interfaces by FM-AFM

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Solid-liquid interfaces play essential roles in a wide variety of physical and chemical processes, such as crystal growth, electrochemical reactions and various biological functions. Investigations of atomic-scale structures and interactions at solid-liquid interfaces are, therefore, essentially important for understanding theses microscopic processes. Force mapping method based on frequency modulation atomic force microscopy (FM-AFM) is a remarkable technique for atomic-scale investigations of interaction forces on a specific site of crystal surfaces. The technique has been used mainly in vacuum environments, where highly sensitive force detection can be performed due to the high Q-factor in the cantilever oscillation. However, since significant progress has been made in FM-AFM in liquids over the past few years [1, 2], the force mapping method can be used for atomic or molecular scale investigations of interaction forces at solid-liquid interfaces, such as solvation forces.

In this study three-dimensional (3D) force (frequency shift: d*f*) mapping method has been applied to the investigations of molecular-scale hydration structures at solid-liquid interfaces as well as those around biomolecules such as proteins and DNA molecules. The 3D visualization of the hydration structures allows us to make a precise comparison of the experimental data with theoretical calculations of water structures, which can provide a molecular scale understanding of the hydration structure. However, there have been several difficulties in the 3D force mapping in liquids because of a large, linear and nonlinear thermal drift of the tip position relative to the surface in an unstable liquid environment. We have developed a low-thermal-drift FM-AFM working in liquids based on a commercial AFM instrument. A sufficiently low, lateral thermal drift rate of less than 1 nm/min was achieved in liquids by an accurate temperature control of the environment and by a large reduction of the liquid evaporation. We obtained 3D frequency shift (d*f*) data on a muscovite mica surface in a 1M KCl solution [3]. The result was compared with water density distributions calculated using the 3D reference interaction site model (3D-RISM) theory. In addition, we also discuss a latest result of 3D visualization of hydration structures around biomolecules such as DNA molecules.

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MS.49.2

Step flow and interface structure during the growth of semiconductor nanowires

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Silicon, germanium and III-V semiconductor nanowires, formed via the vapour-liquid-solid and vapour-solid-solid mechanisms, can be grown *in situ* in an ultra high vacuum transmission electron microscope [1]. This enables structural and kinetic observations to be made during growth under different conditions and for a range of catalyst materials. Since growth takes place at the catalyst/nanowire interface, measurements at this interface provide insights into the surprisingly complex nanowire growth mechanism.

Observations of Si nanowires growing *in situ* from liquid catalysts, such as AuSi, and solid catalysts, such as Cu_3Si, show that growth is by the flow of steps across the catalyst/nanowire interface [2]. However, the kinetics of step flow are strikingly different for solid versus liquid catalysts, in terms of the speed of step flow and the time interval between step flow events [3]. Furthermore, an unexpected interface morphology is visible *in situ*: rather than having a planar catalyst/nanowire interface, the nanowire is truncated around its edges, and the size of this edge truncation oscillates in synchronization with the flow of steps [4]. A similar edge oscillation is also visible during the growth of Ge nanowires [5] and GaP nanowires from AuGa liquid catalysts [4].

In this presentation, we will describe a kinetic model that can explain both the step flow kinetics and the interface structure and edge oscillation. From the step flow kinetics, this model allows us to identify the key parameters that control growth, and evaluate changes in the catalyst composition and supersaturation during growth. We can also understand the conditions under which we expect to form abrupt heterojunctions in nanowires, as required for fabricating electronic nanowire devices.

The edge oscillations are also related to the catalyst supersaturation, and provide a direct visualization of the supersaturation as it varies during the step flow cycle. Because edge oscillations are present in at least one III-V nanowire system, they force us to re-examine our understanding of polytypism in III-V nanowires, which is thought to be determined by the nucleation process of each new layer of semiconductor at the periphery of the growth interface. Both step flow and the changing interface structure therefore provide a window into the nanowire growth process, helping to relate structure to growth mechanism and suggesting how to optimise nanowires for advanced applications.

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Keywords: nanowire, semiconductor, growth mechanism

MS.49.3

Transient phases and prenucleation clusters in biomimetic calcium phosphate mineralization

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The often astonishing materials properties of crystalline biominerals are generally related to the hierarchical assembly of specifically interacting organic and inorganic components. A yet unfulfilled dream of many scientists is to synthesize new materials with similar advanced properties applying Nature's biomimeralization strategies.[1] An absolute prerequisite for the design of such hybrid materials with predetermined structure and properties is to unravel the mechanisms of biologically and biomimetically controlled mineral formation.

The in situ study of the development of mineral formation can make an important contribution to the understanding of the processes involved in biomineralization.[2] CryoTEM has been demonstrated as a method to investigate the early stages of mineral formation without removing the developing particles from their aqueous environment. [3,4] For calcium phosphate these investigations revealed that the formation of apatite is preceded by an amorphous phase, which itself is formed through the assembly and aggregation of what we have called "prenucleation clusters" [5,6]. Here we will discuss the precise structure of these "clusters" and their role in the formation of the subsequent amorphous and crystalline phases. It will be demonstrated that these recent insights re-unite classical and non-classical theories about mineral formation.

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