The Abdus Salam
International Centre for Theoretical Physics

POSTER SESSION II

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In alphabetical order of presenting author (underlined)

Optical Properties of α−Se Revealed by ab initio Calculations
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Electronic structure, magnetic ordering and structural instabilities of cubic perovskites based on nitrides and fluorides: A comparative first-principles study
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Magnetostructural dynamics of a Rieske-type [2Fe-2S] protein
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Adsorption of rare-gas atoms and water on graphite and graphene by van der Waals-corrected Density Functional Theory
A. Ambrosetti, F. Ancilotto, F. Toigo and P. L. Silvestrelli
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First-principles study of the Sr3Ru2O7 electronic structure and its effective tight binding description
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Optoelectronic properties of Al:ZnO: critical dosage for an optimal transparent conductive oxide.
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Thermal transport in nanomaterials from first-principles
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Charge Localization Dynamics Induced by Oxygen Vacancies on the TiO2(110) Surface

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Oxidation at the Si(100) surface studied by theoretical high-resolution EELS

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A comparative study of Sin and Snn (n = 1-6) clusters On MgO Surface: An ab-initio method based study

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Modelling yttrium aluminosilicate glass for radiotherapy

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Insights into point defects in silicon from large-scale DFT calculations and maximally-localized Wannier functions

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Structural, thermodynamic and electronic analysis of Zn-Al-Cl LDH exchanged by F−, Br−, OH−, NO−3 , PO−3 and CO2−: A ab initio study. 3

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First-principles investigation of new phases of BiFeO3 and of the BiFeO3-BiCoO3 solid solution

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Mechanochemistry, Metadynamics, QM/MM

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Enhancement of catalytic activity on bimetallic Ni/Cu(110):
a first principles study
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Molecular Dynamic Simulation Studies of the Collision of a Non-rotranslating Diatomic H2 / D2 (v=0,j=0) Molecule with Copper Atomic Cluster (cu13)
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Novel Structures, Superconductivity and Anharmonicity of Calcium Under Pressure from ab initio Calculations
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Direct comparison between two γ-Al2O3 models by DFT calculations
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Crystallization on heating of α-cyclodextrin solutions
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Growth and electronic properties of low-dimensional Fe/Au(111) structures
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Early stages of Pd adsorption on Au(111)
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Ab initio investigation of ZrO2-CeO2 interface properties
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Ab-initio study of the structural and electronic properties of InAs/GaAs radial heterostructures
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First principle study of hydroxyl functional groups on pristine defected graphene and graphene epoxide
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Catalytic activity of gold nanoclusters supported by cerium oxide: interplay between cluster morphology, size and adsorbate stability revealed by DFT+U calculations
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First-principles study of Bi1−xLaxFeO3 multiferroic solid solutions
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Incorporation of iron on the clean and gallium-bilayer GaN(0001) surface
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First-principle approach to the temperature dependence of electronic energies.
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First Principles Study of Cr Doping on Structural Properties of LiMn2O4
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Melting of Hydrogen at High Pressures from Ab-initio Molecular Dynamics Coexistence Simulations
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Pressure-induced transitions from sp2 to sp3 structures in BN
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Ab-initio Models of Disordered Phases of Ice
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Angular dependence of interaction energy components in ammonia – hydrogen halide complexes. Application of Symmetry-Adapted Perturbation Theory
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First-principle calculations of vacancy-hydrogen interactions in iron: V_nH_m systems (n = 1, 3; m = 1, 6)
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BRAGG-WILLIAMS MODEL OF ORDERED B2, L12 and L10 TYPE BINARY INTERMETALLIC COMPOUNDS CONTAINING POINT DEFECTS

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Theoretical investigation of elastic properties of hexagonal boron nitride membranes (h-BN)

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Superlattices based on graphene and graphane. Theoretical investigation of electronic properties

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First-principle calculations of magneto-optical properties of rare earth RAl2 (R = Ce and Pr) compounds

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The energetics induced by interstitial C in Ti-Al-Nb alloys

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Ab initio study of the crystallization kinetics of phase-change materials

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Catalytic Water Splitting for Hydrogen Production: A First-Principles Study of a Ru Complex in Solution

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Comment to “Imaging the atomic orbitals of carbon atomic chains with field-emission electron microscopy”

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Long-range ordered surface alloy of bulk-immiscible components stabilized by magnetism: Fe-Au/Ru(0001)

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Stacking and Registry Effects in Layered Materials: The Case Of Hexagonal Boron Nitride

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Stability of Methane with respect to dissociation and other C-H stoichiometries under pressure

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XPS of amorphous CdTeOx: validation of a structural model

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First principles study of the $LiNH_2/Li_2NH$ transformation

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First principles studies of molecular confinement and degradation in cement

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Promotion of Ethylene Epoxidation Selectivity by Subsurface Oxygen in Ag-Cu Alloy Catalysts
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Structure and Chemical Reactivity of Small Pt Clusters on a Carbon Nanotube: A First-principles Study
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A quantum chemical study on Polythiophenes derivatives as donor materials in bulk-heterojunction polymer solar cells
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Symmetry-Adapted Perturbation Theory study of intermolecular interaction energy between organic molecules with three- and four- membered rings.
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A first principles study of hydrogen and ethanol adsorption on Pd based metallic nanofilms
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Lithium storage and diffusion on inorganic nanotubes from first principles
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Ab-initio modelling of Ru-based homogeneous catalysts for water oxidation
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Ab-initio parameterisation of inter-atomic force fields for the description of solid-solid and liquid-solid interfaces
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Azobenzenes Self Assembled Monolayers
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Ab initio modelling of interfaces: TiO2 grown on A12O3 as a prototype
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Theoretical investigations on the TMG (trimetylogallium) adsorption and the TMG diffusion on the GaN (gallium nitride) surface.
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Structural and electronic properties of GaN surfaces (0001) and (000-1) due to the presence of molecules nearby of the slab face obtained from DFT
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The calculation of experimental spectra using linear-scaling densityfunctional theory
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Imaging and characterization of activated CO2 species on Ni(110)
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Accurate ab initio parametrised atomistic force fields for ionic materials: application to alumina
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Computational studies of the h-BN nanomesh on Rh(111) surface
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Ab-initio investigations of platinum oxides
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Titania-silica interfaces: a combined classical and DFT study.
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Electronic properties of intermetallic Ti3Al
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Raman spectra of amorphous phase change materials from first principles
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H2CO3 forms via HCO−3 in water
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Nanoscale engineering of surface stress
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A Theoretical Investigation of Structural, Mechanical and Electronic Properties of some late Transition-Metal Nitrides
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Vibrational Spectroscopy and Density Functional Theory of Intermolecular Hydrogen Bonding in 2-Thiohydantoins.
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Surface Precursors and Reaction Mechanisms for the Thermal Reduction of Graphene Basal Surfaces Oxidized by Atomic Oxygen

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Atomistic Simulation of Co-doped α-Alumina Interfaces

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First principles non-equilibrium Green's function study of Ta2O5 atomic switch

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Mechanical properties of icosahedral boron carbide explained from first principles

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DFT+U study of oxygen migration processes in nickle doped ceria

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p-type doping and codoping of ZnO based on nitrogen is ineffective: an ab initio clue

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D2 A5 74

Main Topic: A10 Materials Design

Optical Properties of $\alpha-Se$ Revealed by ab initio Calculations

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Abstract

Detailed optical functions and optical properties of a $\alpha-monoclinic$ phase of Selenium ($\alpha-Se$) are presented over a wide range of angular frequencies ω by first-principles calculations. An optical band gap of $2.05eV$ and a mobility gap of $2.17eV \ \pm 0.05$ are observed in the present calculations. The imaginary part of the dielectric function has been obtained from the frequency dependent dielectric matrix and the use of the Kramers-Kronig (KK) relation allows us to determine the real part of the dielectric function. Optical functions and optical properties revealed the occurrence of a long range order in Se. For the first time, infrared and absorption spectra of monoclinic$-Se$ were studied using the Kramers-Kronig (KK) relation by ab initio method. And lastly, detailed studies of other dielectric related optical constants such as reflectivity, transmission, reflection and absorption coefficients were also presented.

keywords: Density Functional Theory, Electronic Structure, Infrared Spectra, Amorphous Semiconductors, First Principles Theory, ab initio simulation, Elemental Semiconductors.

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MainTopic: A11 Other applications

Electronic structure, magnetic ordering and structural instabilities of cubic perovskites based on nitrides and fluorides: A comparative first-principles study

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Perovskite materials constitute a very important niche within materials science, being used in such applications as ferroelectrics, piezoelectrics, frequency converters and other solid state devices. It has the general formula, ABX_3 (where A usually refers to rare-earth, alkaline or alkaline-earth metal, B refers to alkaline metal, alkaline-earth metal or transition metal depending on the perovskite composition and X refers to anions). However, among the perovskite materials, oxides are the most studied and used for technological applications ranging from superconductivity to multiferroic behavior. Fluoroperovskites with the general formula, ABF_3 , constitute a subcategory distinguished by being more ionic than the perovskite oxides. The greater electronegativity of fluorine compared to oxygen results in a larger band gap for fluoroperovskites in their stable structure than for perovskite oxides and a corresponding absorption edge further into the ultraviolet region. Fluoroperovskites also finds many applications in technology. In the semiconductor industry for example, fluoroperovskites that have wide band gaps are potential candidates for vacuum-ultraviolet-transparent lens materials in optical lithography steppers. Perovskite nitrides on the other hand are relatively uncommon, largely due to the high formal charges required of the cations. For a composition ABN_3 , the possible oxidation states for A and B cations are (1, 8), (2, 7), (3, 6) and (4, 5). However, only (3, 6) combination has been explored.

With a motivation to explore ferroelectricity and multiferroicity in perovskites other than oxides, we present first-principles study of structural, electronic and vibrational properties of ABX_3 (where X=N, F) materials in the cubic perovskite structure based on density functional theory with a local density approximation (LDA). We consider alkali, alkaline earth, La and Bi at the A site, and alkaline earth and transition metals at the B site with different magnetic ordering. From the phonon dispersion obtained using density functional perturbation theory (DF.P.T.), we (a) determine the local stability of the cubic structure of ABX_3 materials, (b) predict possibilities of structural distortions (FE or AFE) that would yield low energy structures, and (c) demonstrate spin-phonon coupling in these ABX_3 materials.

Magnetostructural Dynamics of a Rieske-type [2Fe-2S] Protein

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Spin-projected two-determinant Car-Parrinello simulations [1,2,3] are applied to investigate the magnetostructural dynamics of the iron-sulfur cofactor, [2Fe-2S], of a Rieske protein in its oxidized state. The [2Fe-2S] core is bound to the protein via two cysteine and two histidine residues that introduce a highly asymmetric environment for both Fe atoms. The increasing number of reported X-ray crystallographic data suggests that the asymmetric terminal ligands environment do not have any impact on the symmetrical structure of iron-sulfur core [4]. This is markedly different from the structures as obtained by various improved theoretical methods. In a recent study this discrepancy has been attributed to the fact that the protein matrix imposes some stress on the [2Fe-2S] core structure [5]. In this work we have accounted in detail the gap between theoretical and X-ray crystallographic iron-sulful core structure. In the oxidized state both the Fe(III) atoms are antiferromagnetically coupled via the two bridging sulfur atoms. The magnetic exchange interaction (J) is investigated using extended broken symmetry (EBS) technique [2] recently generalized [3] to correct for artificial spin density delocalization using a Hubbard-U correction, EBS+U. The temperature dependence of J and the correlation of its time evolution $J(t)$ with molecular vibrations are analyzed both in the gas phase at room temperature as well as in a fully solvated Rieske protein upon combining the EBS+U technique with a dynamical QM/MM framework [1].

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Main Topic: A6 Surfaces

Adsorption of rare-gas atoms and water on graphite and graphene by van der Waals-corrected Density Functional Theory

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The recently developed, efficient method for the inclusion of the Van der Waals interactions in Density Functional Theory (DFT), based on the use of the maximally localized Wannier functions, is applied to the study of the adsorption of rare-gas atoms (He, Ar and Xe) and a water molecule on graphite and graphene surfaces, at three high-symmetry sites, by evaluating the equilibrium binding energies and distances.

The results, compared to previous theoretical calculations and experimental estimates, are promising, particularly considering that the method is free from system-dependent fitted parameters.

The crucial role of the chosen reference DFT functional is discussed, making explicit comparison between results obtained from PBE and revPBE functionals.

Main Topic: T10 Simulations in Realistic Environments

First-principles study of the Sr3Ru2O7 electronic structure and its effective tight binding description

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We have performed a detailed analysis of the bilayer Sr3Ru2O7 electronic structure for the case of fully distorted orthorhombic configuration [1] by means of density functional theory based on plane wave and pseudopotential [2]. Taking into account the exchange-correlation energy, as proposed by Wu and Cohen in Ref. [3], the equilibrium value of the unit cell volume is obtained in good agreement with respect to the experimental observation. The analysis of the band structure close to the Fermi level reveals a complex Fermi surface with multiple sheets having electron- and hole-like character. The topology and the volume of the Fermi surfaces have been compared to the recent high resolution experimental measurements obtained by means of angle-resolved photoemission [4]. Finally, to extract the character of the electronic bands at the Fermi level, we have used the Slater-Koster interpolation scheme based on the maximally-localised Wannier functions method[5]. This approach allows to calculate the effective tight binding Hamiltonian for the Ru bands. In particular, by means of Wannier functions construction, we are able to show that the two small electron-like pockets around the Gamma point have mainly t2g character.
We consider the effective Ru-Ru hopping parameters of the monolayer Sr2RuO4 and the bilayer Sr3Ru2O7 by comparing their amplitudes as a function of the distance and the symmetry directions. A discussion of the origin of the metamagnetism with respect to the derived electronic structure is also presented.

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Main Topic: A10 Materials Design

Optoelectronic properties of Al:ZnO: critical dosage for an optimal transparent conductive oxide.

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ABSTRACT:

We study the effects of aluminum doping on the electronic and optical properties of ZnO, in the formation of Al:ZnO (AZO) compound, via ab initio simulations. We discuss the band-structure and adsorption properties of AZO as a function of dopant concentration and we compare our results with novel experimental data. Our findings demonstrate that the inclusion of Al imparts novel characteristics to the ZnO host crystal: in particular our results support the formation of a transparent-conducting oxide (TCO) compound up to an incorporation of Al of about 3% in substitutional Zn sites. Furthermore, we elucidate the role of interstitials proposed to occurr at high doping concentrations, beyond the Al solubility limit: these defects have detrimental effects on the optoelectronic properties of this promising TCO.

Note: Please choose one of the following as “Main Topic” above:

Theory and Methods:

T1 Density-Functional Theory beyond LDA

Applications:

A1 Nanoscience

A10 Materials Design

Main Topic: A10 Materials Design

Thermal transport in nanomaterials from first-principles

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Understanding and modelling transport properties and energy dissipation phenomena in nanostructured materials is a key issue for the design of high-performance nanoscale devices. In this poster I will present a first-principles study of the thermal transport processes in graphene and silicon-germanium alloys. Modelling these phenomena requires an accurate description of the vibrational properties of these systems. We use density functional theory to compute both harmonic and cubic anharmonic terms in the crystalline potential, and phonon scattering rates are then computed using perturbation theory. The thermal conductivity is calculated via approximate solutions of the Boltzmann transport equation. Our results provide a detailed characterization of the inelastic relaxation mechanisms and of the relative importance of the individual phonon decay channels. I will discuss the relevance of these findings to obtain design rules for the engineering of nanostructured silicon-germanium thermoelectrics and to understand the thermal transport properties of graphene.

Main Topic: A8 Catalysis and Electrochemistry

Charge Localization Dynamics Induced by Oxygen Vacancies on the TiO2(110) Surface

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Charge Localization Dynamics Induced By Oxygen Vacancies On The TiO_2(110) Surface

The dynamics of an F—center created by an oxygen vacancy on the TiO_2(110) rutile surface has been investigated using ab initio molecular dynamics (1). These simulations uncover a truly complex, time-dependent behavior of fluctuating electron localization topologies in the vicinity of the oxygen vacancy. Although the two excess electrons are found to populate preferentially the second subsurface layer, they occasionally visit surface sites and also the third subsurface layer. This dynamical behavior of the excess charge explains hitherto conflicting interpretations of both theoretical findings and experimental data.

(1) Phys. Rev. Lett. 105, 146405 (2010)

Main Topic: A6 Surfaces

Oxidation at the Si(100) surface studied by theoretical high-resolution EELS

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Electron energy loss spectra of the Si(100) and Si(100):O surfaces are investigated using ab initio methods based on density functional theory. Computed spectra for the clean surface are found to be in good agreement with published experimental data, providing further confirmation that reconstructions of higher order than (2×1) are present on Si(100). The origins of the main spectral structures are analyzed and their relation to the surface bandstructure is illustrated. Oxygen adsorption on the surface dimers is found to cause strong modifications to the calculated spectra, thereby partially explaining the results of surface differential reflectivity experiments.

Main Topic: A6 Surfaces

A comparative study of Si_n and Sn_n (n = 1-6) clusters On MgO Surface: An ab-initio method based study

Abstract:-One of the essential aspects of the architecture of a surface-based electronic device is that the substrate should preferably be an insulator (wide band gap), which enables more than one electrical contact to the adsorbed species. In this respect, the MgO surface (001) could serve as an excellent model system for exploring nanoscale electronic architectures as it is well characterized, is fairly inert and has wide band gap. This surface is also used as catalytic surface. Here we report the atomic and electronic structures of Silicon(Si_n)and Tin(Sn_n) clusters(n =1-6)on the Magnesium Oxide(MgO) surface. The primary focus of this study is to understand the nature of interaction between Si/Sn and MgO substrate,which in turn will affect the geometries and electronic properties of Si/Sn clusters which are of technological relevance. All calculations were carried out under the framework of DFT method. The results reveal that for both the cases the single Si/Sn atom prefers to be adsorbed on the top of oxygen on the surface and hollow sites. The adsorption mechanism is completely driven by the adsorbed atom interaction with the MgO surface. The shapes of gas phase clusters get distorted on adsorption on the surface.

Main Topic: A11 Other applications

Modelling yttrium aluminosilicate glass for radiotherapy

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We have conducted *ab initio* [1] and classical [2] molecular dynamics simulations of yttrium aluminosilicate (YAS) glass, which has an application in radiotherapy. In this application, activated YAS glass microspheres are implanted in or close to the tumour, and the yttrium irradiates the tumour in situ. The glass must be highly durable to prevent the release of radioactive yttrium into the bloodstream, and so it is vital to understand the structure and bonding environment of yttrium in the glass. We find that yttrium acts as a glass modifier, with a wide range of local environments, and an average Y-O coordination number of 6.2. As a modifier atom, yttrium critically affects the connectivity of the glass network, and there is also evidence of yttrium clustering at larger length scales. We discuss the effect of these features on the durability and the use of the glass for radiotherapy.

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Main Topic: A10 Materials Design

Insights into point defects in silicon from large-scale DFT calculations and maximally-localized Wannier functions

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We present a fully *ab initio* study of vacancies and gold impurities in bulk silicon using density-functional theory (DFT). We follow a systematic methodology for converging quantities of interest using the plane-wave supercell approach [1]; our calculations highlight the importance of using large supercells to accurately describe the long-ranged disturbance effects caused by point defects in crystal lattices. The large-scale capabilities of the ONETEP linear-scaling DFT code [2,3] enable us to validate the convergence of our results by performing calculations on systems of 1000 atoms or more without a prohibitive increase in computational cost. We show that the calculated donor and acceptor levels in the band gap are in good agreement with experimental results for both systems. Using the Kohn-Sham orbitals obtained from our simulations we find the maximally-localized Wannier functions (MLWFs) associated with the defect centres; this method gives an optimal partitioning of the density into chemically intuitive localized orbitals from which to analyze the nature of the electronic structure around the defect. We also demonstrate that MLWFs can be used to perform an accurate potential alignment correction between the perfect crystal and defect supercells.

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Structural, thermodynamic and electronic analysis of Zn-Al-Cl LDH exchanged by F^-, Br^-, OH^-, NO_3^-, PO_3^- and CO_3^{2-}: A *ab initio* study.

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We investigated the influence of different anions intercalated in the layered double hydroxides (LDHs). The objectives of this work were understand the layer-anion and intermolecular interactions in hydrotalcite-like compounds with simple univalent anions, such as F^-, Br^-, OH^- and inorganic anions having D_3h symmetry, like NO_3^-, PO_3^-, CO_3^{2-}. This *ab initio* study verified the thermodynamics and structural modifications derived from anion exchange on $Zn_{2/3}Al_{1/3}(OH)_2Cl_{1/3}$. $2/3H_2O$ LDH. When the Cl^- anion was exchanged by F^-, Br^- or OH^- it was not observed any significant structural variation on the material. The NO_3^-, PO_3^-, CO_3^{2-} anions in the free state are identical symmetry, but the behavior as interlayer anions in LDH are very different. After optimization, the carbonate anion kept the parallel orientation to the hydroxide layers. Unlike the carbonate, the nitrate ion has its molecular plane tilted to c parameter. The PO_3^- anion reacts with the intercalated water molecule to form $H_2PO_4^-$ anion into LDH. The calculations showed that the interaction of hydroxyl layers and intercalated anion depends not only on the charge and size of the intercalated guest, but are strongly affected by the rate of hydration of mineral. On the basis of interaction of guest anion and hydroxyl layers, the anion-exchange selectivities in the LDH follow the sequence: $NO_3^- < Br^- < Cl^- < F^- < OH^- < CO_3^{2-} < H_2PO_4^-$.

First-principles investigation of new phases of $BiFeO_3$ and of the $BiFeO_3$-$BiCoO_3$ solid solution

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We used first-principles methods to perform a systematic search for stable phases of multiferroics $BiFeO_3$ and $BiFe_{1-x}Co_xO_3$. For pure $BiFeO_3$ we will analyze the new structures found to be local minima of the energy within 100 meV/f.u. of the ferroelectric ground state (preprint available at http://arxiv.org/abs/1011.0563). We will also present results for the solid solution $BiFe_{1-x}Co_xO_3$, where a morphotropic-phase-boundary region has been experimentally reported. In particular, we will discuss our findings for the chemically induced transitions and the mechanisms by which this chemical substitution enhances the electromechanical responses.

Mechanochemistry, Metadynamics, QM/MM

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Mechanochemistry is field with a long history going back to year 1892. In recent years the term mechanochemistry has also been used to describe mechanically induced chemistry as observed in single-molecule atomic force microscopy (AFM), force-clamp and sonochemical experiments. Latest theoretical freamwork was proposed by Ribas-Arino [1, 2] and Martinez [3]. It allows to investigate most directly how Potential Energy Surface (PES) changes as a function of applied mechanical force F_0 in an exact, fully nonlinear, and self-consisten approach. Now we are going one step further devising the framework based on Car-Parrinello Molecular Dynamics (CPMD) and force-transformed Free Energy Surface (FES), which is able to explore possible reaction pathways as a function of applied external constant force F_0 at desire temparature.

Intriguing force-clamp spectroscopy experimnet have been done last year by Fernandez et al. [4]. Authors have studied effect of mechanical force on the rate of a S_N2 reaction at which a protein disulfide bond is reduced by nucleofiles. Experiment have been performed on 27th immunoglobulin-like domain of cardic titin. The results demostrated that the rate of the reduction reaction exhibits an abrubt change at a force of 500 pN.

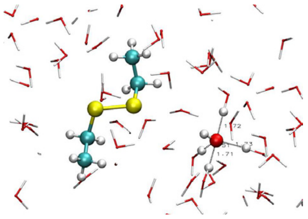

Fig. 1: Simple model system with disulfide bridge in water solution: CH_3-CH_2-S-S-CH_2-CH_3 + OH^-

There are few possible explanations proposed by the authors, nevertheless there is no theoretical evidence what kind of mechanism is involved. Based on our new apprach we are trying to explain the experimentally observed phenomenon. Presented in Fig. 1 model system have been chosen, as well as full 27th immunoglobulin-like domain of cardic titin - Fig. 2.

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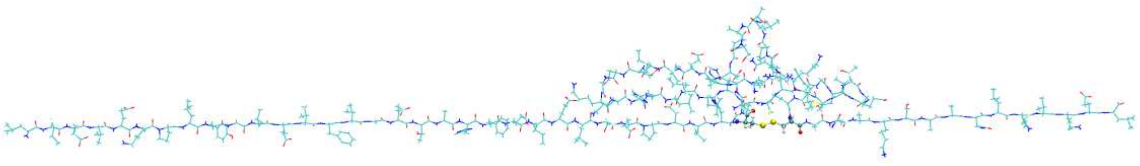

Fig. 2: Stretched 27th immunoglobulin-like domain of cardic titin up to the point of S-S bond - QM/MM with 29000 of water molecules, by courtesy of Padmesh Anjukandi

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Enhancement of catalytic activity on bimetallic Ni/Cu(110): a first principles study

Bimetallic surfaces play a crucial role in heterogeneous catalyst. H, CO and CO2 are essential ingredients in methanol synthesis reaction which is industrially performed on Cu-based catalyst. Recent experiments on a model catalyst have shown that Ni/Cu can be 60 times more active than pure Cu for the reaction of methanol synthesis [1]. Despite the importance of this bimetallic system, little work has been done up to now to understand the promoting role of Ni and the relative role of the different ingredients [2].

We investigate, using Density Functional Theory (DFT) within generalized gradient approximation, the adsorption of H, CO and CO2 on bimetallic Ni/Cu(110) surfaces. We consider alloys with a Ni-rich profile concentration in surface or subsurface layers (surface or near-surface alloys), considering some possible configurations with different nanoscale patterns, selected on the basis of relative energies and on dissolution and diffusion barriers.

Preliminary results for adsorbed CO and CO2 indicate a stronger molecule-metal bond at selected Ni/Cu alloy surface configurations, not only with respect to the pure Cu termination, where it is known that CO2 chemisorption does not occur, but also with respect to pure Ni termination. These results indicate the importance of nanoscale structural modification in order to enhance the interaction with adsorbates and consequently the catalytic activity, confirming the trend already observed in other bimetallic alloys, i.e., that the deposition of a more reactive metal (e.g., Ni) onto a less reactive metal substrate (e.g., Cu) makes the overlayer even more reactive with respect to adsorption. These findings suggest the origin of the peculiar reactivity of the alloy reported in [1].

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Molecular Dynamic Simulation Studies of the Collision of a Non-rotranslating Diatomic H_2 / D_2 (v=0,j=0) Molecule with Copper Atomic Cluster (cu_{13})

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- A quasiclassical molecular dynamics simulation study of the interaction of H2/(D2) with Cu_{13} atoms in both rigid /(non rigid) clusters was reported.
- The geometry of the cluster was obtained by an embedded-atom (EA) mode potential, and the interaction between the molecule and cluster was described by a LEPS (London-Eyring-Polanyi-Sato) potential energy function.
- The dissociative chemisorption probability, cross section and rate constant were studied as functions of the collision energy, impact parameter and the temperature of the clusters.

1.Methodology

In this work the molecule-cluster potential energy surface defining the forces acting on each atom in the entire collision system was represented as

$$V = V_{EAM} + V_{LEPS} \qquad (1)$$

Where V_{EAM} is the Embedded Atom potential developed by Daw and Baskes [2] to describe the interactions between the atoms in the Cu cluster :

$$V_{EAM} = \sum_{i}^{n} F_i(\bar{\rho}_{h,i}) + \frac{1}{2}\sum_{i}\sum_{j(\neq i)}^{n} \phi_{ij}(r_{ij}) \qquad (2)$$

here, $F_i(\bar{\rho}_{h,i})$represents the energy of the embedding i molecule in the back ground host electron density ρ, and $\phi_{ij}(r_{ij})$ is the core-core pair repulsion between atoms i and j separated by the distance (r_{ij}) the derivation and detailed discussions of EAM appeared in the literature [1,4,5,7,8]. The potential energy surfaces represents the diatomic (AB)-cluster interaction system were chosen to be the modified four-body V_{LEPS} (London-Eyring-Polanyi-Sato)

$$V_{LEPS}\left(X_A, X_B, (X_C)\right) = Q_{A,B} + Q_{A,C} + Q_{B,C} \pm \left[J_{A,B}\left(J_{A,B} - J_{A,C} - J_{B,C}\right) + \left(J_{A,C} + J_{B,C}\right)^2\right]^{\frac{1}{2}} \quad (3)$$

Where Q and J are coulomb and exchange integrals respectively, the subscripts AB labeling the molecule atoms and C represents the cluster, and X_A,X_B,$\{X_C\}$are their coordinates. With the use of classical trajectory technique, calculations were done for a fixed relative translation energy E_{tr} from 0 to 1eV with $\Delta E = 0.01$ eV, and impact parameter b was sampled on the range from 0 to b_{max} with $\Delta b = 0.25$ Å for each translation energy. The criterion for the dissociation was that the molecule bond length becomes greater than 2.223 Å (three times the equilibrium H-H bond length) or when the Hydrogen molecule approximately reaches the same region after departing from the cluster. The molecule was send toward the cluster from a distance chosen to be 8.5 Å, and the initial vibration and rotation of the molecule were specified via a standard quasiclassical method developed by R.N.Porter [9].

For each temperature T defined as

$$T(k) = \frac{2\langle E_k \rangle}{(3n-6)k} \tag{4}$$

where E_k is the total kinetic energy of the cluster, k is the Boltzmann constant and by the use of Molecular Dynamic (MD) and Thermal Quenching Simulation

Techniques [3], the geometrical structures (coordinates and momenta)of the most stable non rotating and nontranslating Cu clusters were identified. After calculating the dissociation probability P(b ,E_{tr}) via standard histogram techniques the reaction cross section was obtained from

$$\sigma_{v'',j',T.......}\left(E_{tr}\right) = 2\pi \int_{0}^{b_{\max}} bP_{v'',j',T.......}\left(b,E_{tr}\right)db \tag{5}$$

and the thermal rate constant was calculated by

$$K_{v'',j',T.......}\left(T_{tr}\right)\sigma_{v'',j',T.......}\left(E_{tr}\right)=\left(\frac{2}{\pi\mu kT_{tr}}\right)^{\frac{3}{2}}\int_{0}^{\infty}\sigma_{v'',j',T.......}\left(E_{tr}\right)E_{tr}\left(-\frac{E_{tr}}{kT_{tr}}\right)dE_{tr} \tag{6}$$

where μ is the collision reduced math.

2. Results and discussion

To study the difference in the reactivity of H molecule to that of D molecule with Copper cluster we calculate the reaction cross section for each of them in Cu_{13} at different temperature scales, the results are plotted in Fig.1. The reaction cross sections demonstrate a strong isotope effects and that the hydrogen molecule was always have a greater cross section than the heavier deuterium molecule. Also, as seen from Table .1, the reaction rate constant sensitivity to the isotopic effect was detected and as expected that the rate constant for the Hydrogen molecule was greater than that of Deuterium molecule, which was founded to be in a good accord to that reported for Cu_7 by J.Harris etal [8].

The Cu_{13} cluster was prepared at different temperatures T=0K,295K,834K,1014K, 1554K. The change in the temperature shows a slight change in the reaction cross section, same as reached for Ni cluster [5]. However, this change cannot said to be very clear for the temperature below 1554K, only at that temperature there was a considerable increase in the reaction cross section Fig.[2.a]. This conclusion was similar for both cases of H_2 and D_2 isotopes Fig.[2.b]. The effect of temperature on the reaction rate constant was also investigated (see Table 1). At temperature below 900K the rate constant shows weak increase with the temperature increments, unexpected increase was detected for D molecule at 1014K.

To see which one was more dominant for the reactivity, the graphs in Figure 1a and Figure 1b shows that the isotopic effect was so clear and more dominant than that of temperature effect, even at that high temperature the hydrogen cross section at 0K is larger than the deuterium cross section at 1554K (Fig. 1.b.).

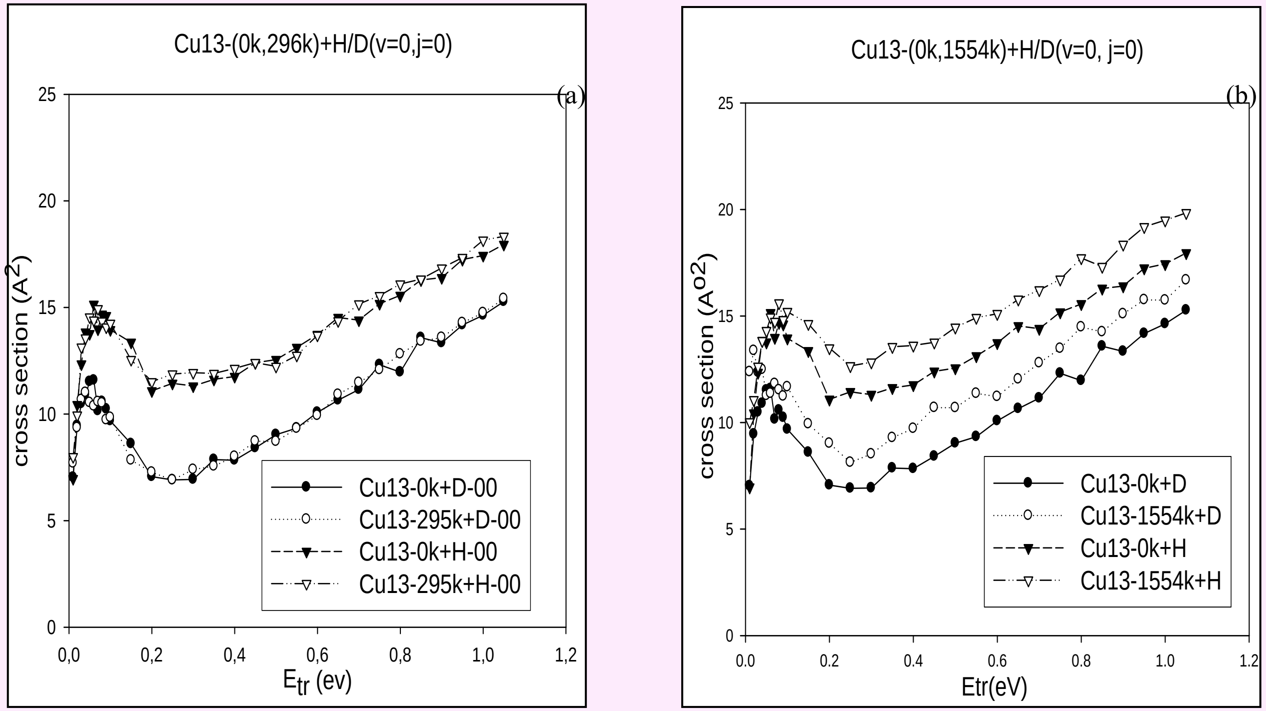

Fig. 1. Dissociation cross section of the reaction H_2/D_2(v=0,j=0)+Cu_n(T~300K) as a funtion of translation energy for (a) H_2/D_2+Cu_{13}(T=0/ 295K) ; (b) H_2/D_2+Cu_{13} (T=0/ 1554K)

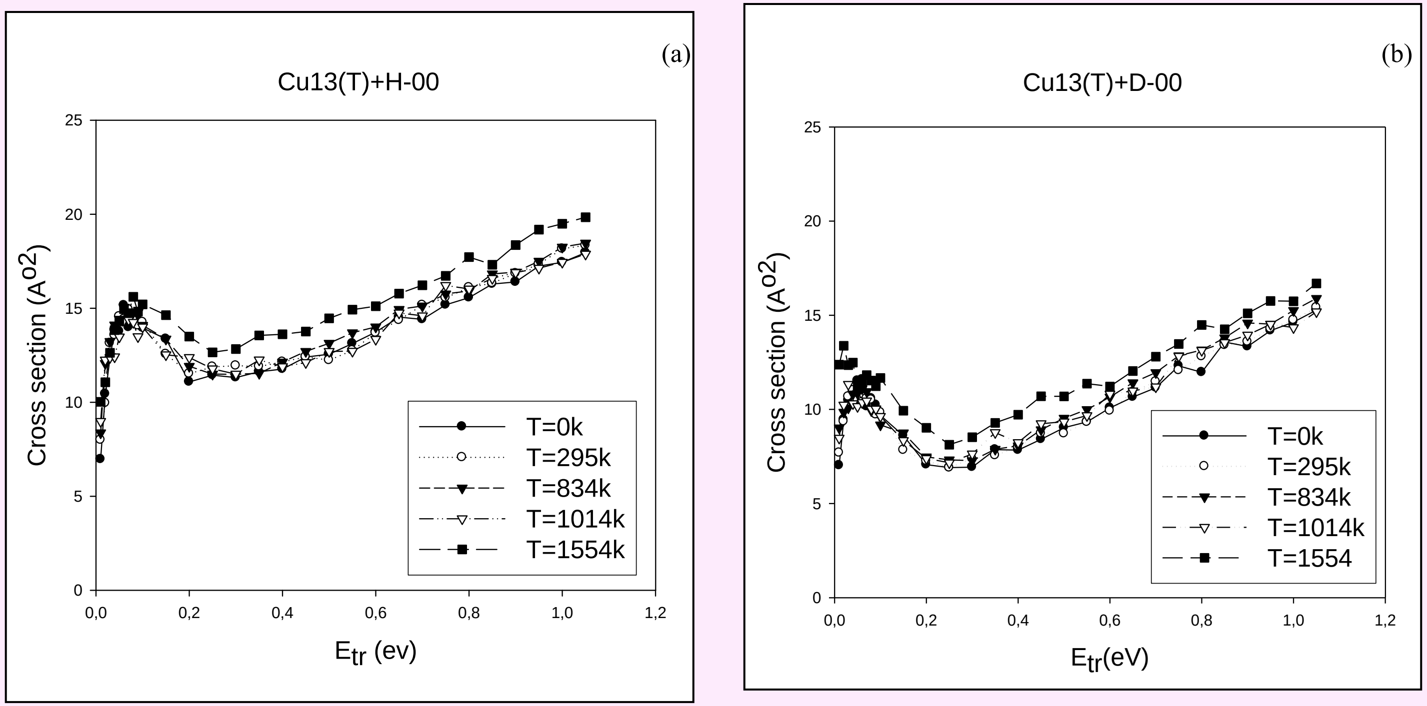

Fig. 2. The cluster Cu_{13}(T=0K ,295K,834K,1014K, 1554K) temperature effects on the dissociation reaction of(a) H and (b) D molecules (v=0, j=0).

Cu_{13}(T)	$+H_2$Rate Constant (xe^{-10} cm^3/s) (v=0,j=0)	$+D_2$Rate Constant (xe^{-10} cm^3/s) (v=0,j=0)	H_2/D_2 Rate Constant Ratio
T=0K	2,236	1,263	1,800
T=295K	2,266	1,248	1,816
T=834K	2,352	1,269	1,850
T=1014K	2,260	1,787	1,265
T=1554K	2,372	1,510	1,570

Table.1 The rate constant for H_2/D_2 +Cu13 at different temperatures.

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Novel Structures, Superconductivity and Anharmonicity of Calcium Under Pressure from ab initio Calculations

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Experimental studies at room temperature suggest that calcium undergoes a series of phase transitions under pressure: fcc → bcc → sc → CaIV → CaV. Remarkably, Ca is a superconductor above 50 GPa and its Tc rapidly soars with pressure reaching 25 K at 161 Gpa, the largest Tc ever recorded in an element. Nevertheless, using evolutionary ab initio simulations at 0 K, we found a different phase diagram for Ca [3]. The fcc to bcc phase transition is properly predicted by our calculation, but between 33 and 134 GPa we find a series of simple-cubic-related structures ($I4_1/amd$, $C2/c-12$, $P4_32_12-8$, $Pnma-4$). Above 134 GPa an incommensurate phase becomes favorable. Although the predicted phase sequence and the one measured at room temperature differ, the experimental values obtained for the superconducting critical temperature, Tc, agree well with our theoretical ab initio results. This result strongly suggest that at 0 K the phase sequence may be different than at room temperature. Possible transitions between the simple cubic phase at room temperature and lower coordinated phases at 0 temperature may be related to strong anharmonic effects. Moreover, the possibility of anharmonic stabilization of the simple cubic phase of calcium cannot be ruled out.

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Main Topic: A11 Other applications

Direct comparison between two γ-Al_2O_3 models by DFT calculations

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We selected two important γ-alumina models proposed in literature, a *spinel-like* one and a *nonspinel* one, to perform a theoretical comparison. With *ab initio* calculations, the models were compared considering their thermodynamic stability in the temperature range from 0 to 1000 K, the lattice vibrational modes, the bulk electronic properties and the practicality of modeling surfaces to be used in theoretical simulation of adsorption processes. The *spinel-like* model is thermodynamically more stable by 4.55 kcal/mol per formula unit. Whereas the density of states, the vibrational analysis and charge transfer between atoms reveal the equivalence between the two models, despite some minor differences. The morphological comparison of the unitary cells can be conclusive when choosing which one would be more appropriate, providing slab models with larger surface areas, suitable thickness and lower computational cost.

CRYSTALLIZATION ON HEATING OF α-CYCLODEXTRIN SOLUTIONS

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We have reported a reversible liquid to solid transition upon heating of a simple solution composed of *α*-cyclodextrin (*α*CD), 4-methylpyridine (4MP) and water [1]. Initially, in order to characterize the structure and molecular motions across the phase transition, neutron scattering experiments were performed at the Institute Laue-Langevin (ILL). Quasielastic neutron scattering with instruments of different energy resolution IN5, IN10, IN16 probed the dynamics at different time scales. Structural changes accompanying the phase transitions were characterized by neutron diffraction at the instruments D16 and D11, using fully deuterated 4MP to minimize the contribution of incoherent scattering. On the following, high-resolution powder diffraction measurements were measured at the European Synchrotron Radiation Facility (ESRF), beamlines BM1 and BM8. The crystalline solid phases undergo further phase transformations at higher temperatures, five crystalline phases being identified [2]. Subsequently, solutions with different isotopic compositions: *α*CD-water/ 4MP = H/H, H/D, D/H and D/D were analyzed by quasielastic neutron scattering. If the deuteration of the 4MP doesn’t influence the transition temperature, the deuteration of *α*CD (and water) increases it, indicating the critical role of inter-molecular hydrogen bonding [3]. This unusual behavior has been also characterized by differential scanning calorimetry and solubility measurements, proving that it is caused by an extraordinarily strong negative temperature coefficient of the solubility of αCD in the mixture of 4MP and a small quantity of water, water playing a crucial role in the solidification process. By means of time-resolved transient grating spectroscopy a glass transition at low temperature was also identified [4]. The pure binary mixtures of αCD in water free 4MP were also recently characterized [5].

This contribution is a review of the results obtained until now on the investigation of this peculiar effect and we also present our recent results obtained using proton NMR relaxation technique, the ab initio calculations and molecular dynamics simulations.

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Growth and electronic properties of low-dimensional Fe/Au(111) structures

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We present an experimental and theoretical investigation of the first stages of growth and of the electronic properties of the Fe/Au(111) system, by combining Scanning Tunneling Microscopy (STM) and Spectroscopy (STS) experiments and Density Functional Theory (DFT) simulations. The growth of Fe on the Au(111) surface is characterized by an initial ordered island nucleation at the elbows of the surface herringbone reconstruction; the system shows a switch of magnetization from in-plane to out-of-plane when larger coverage results in island coalescence, interpreted as related to the structural and electronic properties of the growing nanostructures.

We identified experimentally the onset of out-of-elbow growth, coalescence and second layer growth at about 35% coverage. dI/dV differential conductivity maps permit to ascertain the presence of Fe stripes adjacent to the Au steps (step-flow growth), of Fe substitutions in the Au surface and of an electronic contrast between island core and edge. Theoretical evaluation of the LDOS highlights the role of the Au(111) Shockley state upon hybridization with the overlayer Fe states, in forming the features appearing in the STS signal. States originating especially from Fe ones having d_{z^2} symmetry around the nucleus, contribute significantly in the region outside the surface to a dominating peak close to Fermi energy. Its position, as determined by spatially resolved STS measurements, shifts to higher energy when moving from the center towards the island edge. This is ascribed to the change in the Fe-Fe first neighbour distance as the island extends out of the nucleation site.

Early stages of Pd adsorption on Au(111)

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PdAu surfaces are among the most important mixed-metal catalysts, exhibiting interesting features: the energetically favorable formation of second neighbor Pd configurations provides the appropriate ensemble effect for, e.g., vinyl acetate synthesis; regular arrays of Pd islands grow from Pd atoms evaporated on Au(111) following nucleation at the elbows of the Au(111)-$(22 \times \sqrt{3})$ surface reconstruction, where lattice site substitution is believed to release superficial stress. While numerical simulations for atomic ensembles of Pd at Au(111) have already addressed some of the aforementioned aspects [1], recent Scanning Tunneling Spectroscopy and Microscopy (STM/STS) investigations at the atomic resolution [2,3] call for additional theoretical analysis.

This contribution presents the results of Density Functional Theory (DFT) simulations of the adsorption of Pd on the Au(111) surface at low-coverage [4]. The potential energy surface for Pd adatoms is determined and found to be shallower than that related to atomic-size features observed by STM [2]. The commonly found Pd-Pd repulsion within Au applies also in case of adatoms on a perfect Au(111) surface interacting with surface/subsurface ones, despite the role of the latter entities in the island nucleation on the real, reconstructed surface. Alteration of the surface lattice parameter or of the relative matching of Au layers, featured by the Au(111)-$(22\times\sqrt{3})$ surface, is also modeled and found not to modify the energetics of Pd islands. The appearence of Pd monomers in simulated scanning tunneling topographies is discussed and shows an important contribution by the Au surface state in determining the relative height of surface and subsurface Pd atoms, in agreement with recent experimental findings [3].

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Ab initio investigation of ZrO_2-CeO_2 interface properties

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The study of ionic transport properties of materials has a critical role in the development of a new class of electrolyte materials with high ion conductivity at low temperature, used for solid oxide fuel cells.[1,2]

Cerium oxide as well as zirconium oxide, has been the object of wide interest since they show a high oxygen mobility when they crystallize in a fluorite structure.[3,4] Nevertheless the role of the doping has shown to be crucial since it strongly enhances ion mobility at the bulk level[5-7]. However, recent observation have shown how the interface yttrium stabilized zirconia and samarium doped ceria (YSZ-SDC) under specific experimental conditions, exhibits an oxygen conduction up to two order of magnitude higher that the bulk materials.[8] The mechanism of ion transport in those heterojunctions is not completely clear yet.

It is crucial, therefore, to shed light on the mechanism of conduction at the interface level and the conditions to obtain a maximum enhancement.

In the present work we use a computational Density Functional Theory approach to investigate the structural and electronic properties of the (100) and (111) ZrO_2-CeO_2 interface. Optimization of the lattice geometry for the separate ZrO_2 and CeO_2 bulks as well as the interface is carried out and the structural morphology is analyzed. The energy formation of the oxygen vacancies are analyzed at different values of lattice parameter, in order to verify its dependency on the strain. This eventually allow us to identify vacancy concentration difference in bulks and interfaces.

Activation energy of the oxygen migration are also calculated in the bulk as well as at the interfaces level to identify eventual preferential migration channel.

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Ab-initio study of the structural and electronic properties of InAs/GaAs radial heterostructures

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Semiconductor nanowires (NWs) offer interesting properties which make them appropriate candidates for future semiconductor industry including nanoelectronics, nanooptoelectronics and biosensors. Nowadays, high quality NWs are grown on different substrates and exhibit WZ or ZB structures depending on the growth mechanism. Recently, also (GaAs,InAs) radial NWs have been fabricated, with GaAs radially deposited on InAs NWs. Radial NWs offer a further opportunity for potential applications due to the possibility of engineering their electronic properties by varying the core/shell composition, thickness and structure. Among others, an important parameter determining the stability is the lattice mismatch of the constituents, which is about 7% in case of (GaAs,InAs) heterostructures. We study here the structural stability and electronic properties of (GaAs,InAs) radial NWs, with WZ or ZB structures, starting from the GaAs/InAs interfaces (GaAs epitaxially grown on InAs substrate and viceversa)

First principle study of hydroxyl functional groups on pristine defected graphene and graphene epoxide

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Oxygen-containing functional groups can be present in considerable amount intentionally or unintentionally on graphene, and a complete reduction of graphene oxide is difficult to achieve. In order to address the origin of this behavior, we have performed pseudopotential density functional theory calculations to investigate in particular the adsorption of hydroxyl (OH) on perfect and defected graphene, individually and in presence of other coadsorbed functional groups. We found that hydroxyl groups weakly adsorbs on perfect graphene, easily aggregate, also with coadsorbed epoxy groups, and can react with each other with a barrier of about 0.5 eV forming water. Defect sites are more reactive for OH adsorption but play different roles. At variance with single vacancy defects where the OH adsorption is highly dissociative, Stone-Wales defects could stabilize the hydroxyl groups on the graphene basal plane, with a much stronger binding and higher barriers for recombination and water formation than pristine.

Catalytic activity of gold nanoclusters supported by cerium oxide: interplay between cluster morphology, size, and adsorbate stability revealed by DFT+U calculations.

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The low-temperature oxidation of molecular CO can be efficiently catalyzed by highly dispersed Au nanoparticles supported by transition- metal oxides. The activity of these catalysts is controlled by several factors, most notably the size of the metal cluster, the ability of the support to supply oxygen during the reaction, and the excess electrons at the metal/oxide interface determining the oxidation state of the gold atoms. Reducible oxides represent very active catalytic supports, and among them, ceria (CeO_2) is one of the most efficient due to its oxygen storage capacity. Gold nanoclusters supported by ceria surfaces have been shown to catalyze important reactions such as low-temperature CO oxidation, hydrogenation or water gas shift.

In this work, the mechanisms for the oxidation of CO catalyzed by isolated Au atoms as well as small clusters (Au_3) in Au/CeO_2 catalysts are studied by means of Density functional theory calculations that account for the on-site Coulomb interaction via a Hubbard term (DFT+U). $CeO_2(111)$ surfaces containing positively charged Au ions, either as supported Au^+ or as substitutional Au^{3+} ions, are shown to activate molecular CO and to catalyze its oxidation to CO_2 via participation of lattice O. For the Au^+ adatoms, the limiting rate is determined by the adsorbate spillover. The reaction then proceeds with CO oxidation via O vacancy formation. Crucially, these vacancies readily attract the Au adatoms, turn them into negatively charged $Au^{\delta-}$ ad-species that prevent further CO adsorption, thus deactivating the catalyst. The reactivity of gold nanoparticles nucleated at O vacancies is predicted to be recovered for cluster sizes as small as Au_2. The analysis is extended to larger clusters up to Au_4. These display a rich structural flexibility that is shown to play an important role in preserving their reactivity upon formation of O vacancies on the ceria surface during CO oxidation via ceria lattice oxygen, These results are discussed in the context of the cluster cohesive energy, binding energies of the clusters with both the stoichiometric and reduced ceria surfaces and the binding of molecular adsorbates on the Au clusters.

First-principles study of $Bi_{1-x}La_xFeO_3$ multiferroic solid solutions

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Perovskite oxide $BiFeO_3$ (BFO) is one of the few materials that present coupled ferroelectric and magnetic orders at room temperature [1]. However, because its ferroelectric and anti-ferromagnetic transition temperatures are relatively high (about 1100 K and 640 K, respectively), BFO's electromechanical and magnetoelectric responses are small at ambient conditions [1,2]. Interestingly, recent works show that it is possible to improve such responses via strain engineering of BFO films [3] or chemical substitution to form solid solutions like $Bi_{1-x}La_xFeO_3$ [1,4] or $BiFe_{1-x}Co_xO_3$ [5]. We have performed a first-principles study of one such alternative system, namely, the $Bi_{1-x}La_xFeO_3$ solid solution (BLFO) in order to better understand the physical and chemical underpinnings of this strategy to optimize the properties of BFO.

We will present our results for the phase diagram of BLFO as a function of La conntent, showing that the material undergoes a strongly first-order transition between the ferroelectric and paraelectric phases corresponding, respectively, to the parent compounds BFO and $LaFeO_3$ (LFO). We will also show that the electromechanical responses of the parent compound BFO (resp. LFO) are strongly enhanced as soon as the Bi (resp. La) cation is partly substituted. We find such enhancements can be the result of two different mechanisms: (i) the induction of a ferroelectric instability, as in LFO with small Bi content, and (ii) the softening of the lattice around the minority species, as in the ferroelectric phase of BFO with small La content. These insights allow us to propose new strategies to further optimize the response properties of these materials.

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Main Topic: A6 Surfaces

Incorporation of iron on the clean and gallium-bilayer GaN(0001) surface

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In this work, we have investigated by first-principles spin-polarized calculations, the electronic and magnetic properties of iron (Fe) incorporation on the clean and gallium bilayer GaN(0001) surface using density functional theory within a plane-wave pseudopotential scheme [1]. On the clean Ga-rich surface, the Fe atom prefers a surface substitutional Ga site to a near-surface interstitial site by about 2.0 eV, thus suggesting that interstitial concentrations could be suppressed near the surface during growth. The calculated values of the surface energy show that the substitution of Ga by Fe atoms in the first layer is the most stable structure, in good agreement with the experimental findings. In addition, when Fe replaces Ga atoms in deeper layers of the GaN(0001) surface, the magnetic moment of the doped surface increases from 2.81 μ_B to 4.19 μ_B. Calculations for Ga-bilayer terminated surfaces suggest that it is possible to enhance incorporation of Fe on the Ga site by performing the growth under extreme Ga-rich conditions. We found that the Fe incorporation on the clean GaN(0001) surface have a half-metallic property with a spin band gap and stable ferromagnetism, which is a desirable property for high-efficiency magnetoelectronic devices. Partial densities of states (projected by layer and by orbital angular momentum), surface states, and charge (and spin) densities are presented and their differences employed to discuss the origin of surface magnetism.

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Main Topic: T10 Simulations in Realistic Environments

First-principle approach to the temperature dependence of electronic energies.

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The energy bands of semiconductors exhibit significant shifts with temperature at constant volume. This is an effect of the renormalization of band energies by electron-phonon interactions. In search of an efficient first-principle approach to this effect, beyond semi-empirical approximations or frozen-phonon DFT, we have found that formulas derived by Allen, Heine and Cardona [1-3] cannot be transposed to DFT or to Many-Body Perturbation Theory [4] without critical reexamination. Indeed these are valid in the rigid-ion approximation, and the correct formulation includes a extra term, the non-site-diagonal Debye-Waller term, which is dependent on second-order derivatives of the self-consistent electron-lattice potential with respects to atomic displacements. We have studied the importance of this extra term for diatomic molecules and found that it partially cancels the standard Debye-Waller and Fan terms leading a decrease by 52% for H2, 10% for N2 and 37% for LiF. For CO it adds about 15% to the temperature dependence. The lack of this term might explain the discrepancy found between previous theory and experiment for solids. Furthermore, the slow convergence of the sum-over-states approach of Allen-Heine-Cardona can be avoided in a new formalism proposed here, based on Density-Functional Perturbation Theory, leading to a dramatic decrease of calculation times.

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Main Topic: A10 Materials Design

First Principles Study of Cr Doping on Structural Properties of $LiMn_2O_4$

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A comparative study of the effect of Cr doping on the structural properties of spinel $LiMn_2O_4$ has been done using the first-principles spin density functional theory within the GGA (generalized gradient approximation) and GGA+U using VASP. GGA gives the body centered tetragonal ground state whereas GGA+U gives face centered orthorhombic ground state for $LiMn_2O_4$, while for doped compositions, both approaches predict the same ground states. The ground state is base centered monoclinic for $LiCr_{0.5}Mn_{1.5}O_4$ and body centered orthorhombic for $LiCrMnO_4$. The Jahn-Teller active mode is found to be smaller for the chromium doped compounds compared to pristine $LiMn_2O_4$, which means the Jahn-Teller distortion has been suppressed on Cr doping. Average oxidation state of transition metal ions have been calculated from the calculated bond lengths of metal-oxygen bonds. We report close agreement between GGA+U results and the experimental observations.

Main Topic: T5 Ab-initio Molecular Dynamics

Melting of Hydrogen at High Pressures from Ab-initio Molecular Dynamics Coexistence Simulations

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Ab-initio simulations of hydrogen melting at high pressures are reported. We conduct large-scale coexistence simulations, in which solid and liquid phases are simultaneously considered within the same simulation cell. Molecular Dynamics simulations are performed within the constant enthalpy (NPH) ensemble [1], imposing the external pressure via a barostat. In total the simulation cell typically contains ~2000 hydrogen atoms, modelled using the Projector Augmented Wave method [2] and a plane-wave basis set. We use the Perdew-Burke-Ernzerhof functional [3] to account for exchange and correlation energy, and simulations were performed with VASP [4]. We consider pressures ranging between 30 and 300 GPa. As well as the low-pressure $P6_3/mmc$ phase we have considered a number of other phases, such as $P6_3/m$, $P2_1/c$, $C2/c$, $Cmca$ and $Pca2_1$, all of them candidate high-pressure phases recently proposed in the work of Pickard and Needs [5]. Our predicted melting temperatures are in agreement with existing experimental values. Although our resulting melting temperature values in the range 100-200 GPa are somewhat higher than the earlier ones obtained by Bonev *et al.* [6], we nevertheless reproduce the re-entring behaviour of the melting line found in their work.

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Main Topic: A10 Materials Design

Pressure-induced transitions from sp^2 to sp^3 structures in BN

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We report here results of ab initio metadynamics simulations of structural transitions in boron nitride starting from sp^2 bonded (graphite-like) structures in temperature range from 300 to 3000 K. Rhombohedral boron nitride (r-BN) was found to directly transform at all temperatures into cubic boron nitride (c-BN), at a minimal pressure of 15 GPa. Hexagonal boron nitride (h-BN) transforms at room temperature and pressure of 30 GPa into wurtzite boron nitride (w-BN). At higher temperatures (3000 K) and pressure of 20 GPa we found a new possible transformation pathway resulting in the metastable tetragonal structure ($P4_2/mnm$). This structure is also fully tetrahedrally (sp^3) bonded and is an analogue of the 'bct C4' ($I4/mmm$) structure discussed for carbon. This structure was predicted theoretically but so far not reported experimentally. We calculate structural, elastic and electronic properties of the $P4_2/mnm$ structure and analyze the transition mechanism.

Main Topic: T5 Ab-initio Molecular Dynamics

Ab-initio Models of Disordered Phases of Ice.

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The water ice exists not only in multiple crystalline phases but also forms disordered phases with varying densities. The empirical potentials have been used quite successfully to model the structure of the amorphous ices, but to get deeper insight into the electronic properties of the disordered phases, the need for the modeling at the ab-initio level is eminent. Here we present a novel approach to model the disordered phases of ice using first principle methods. we show that the structural similarities between the amorphous phases of ice and the a-Si can be exploited to construct reliable ab initio models of the low and high density phases of amorphous ice. Starting with the Wooten Winer Weaire (WWW) model of amorphous silicon, we replace the Si sites by H2O molecules and minimize the total energy of the system at constant pressure. In this way we obtain the low density amorphous (LDA) ice structure. The high density phase of ice (HDA) is obtained in a similar way starting from the high density phase of amorphous silicon. The atomic configurations resulting from this procedure show very good comparison with the diffraction measurements. Further we present the electronic density of states of low and high density phases and the band tail properties.

Main Topic: A9 Chemical Reactions and Kinetics

Angular dependence of interaction energy components in ammonia – hydrogen halide complexes. Application of Symmetry-Adapted Perturbation Theory

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Intermolecular forces govern the behavior of molecules in gas, liquid and solid phases. Their long- and medium-range components are responsible for mutual arrangement of molecules in the initial phases leading to chemical reactions. Packing of molecular crystals is also dependent on the interplay between stronger and more directional forces (e.g. hydrogen bonds, dipole-dipole interactions) and weaker, but omnipresent dispersion forces. Among many methods of study, Symmetry-Adapted Perturbation Theory (SAPT) [1] allows one to divide intermolecular energy into physically well-defined components on the basis of many-body perturbative calculus applied to both inter- and intra-molecular parts of the Hamiltonian.

Here, we present our SAPT study [2] on directional dependence of interaction energy components for hydrogen-bonded complexes of ammonia with hydrogen fluoride, chloride and bromide. Pyridine – HF system was added to investigate the role of extended aromatic system. Trimeric systems of ammonia and HF were also described to shed light onto many-body corrections to the intermolecular interaction energy. The results underline the specific nature of hydrogen bond, which allows this type of bonding to be recognized among other interactions of similar magnitude.

We would like to thank Prof. K. Szalewicz and Dr. R. Bukowski for the preprint of their publication on the three-body SAPT theory. We gratefully acknowledge the grants of computer time at the Wrocław Center for Networking and Supercomputing (WCSS), Wrocław, Poland as well as at the Academic Computer Centre CYFRONET AGH in Kraków, Poland (grants KBN/SGI2800/UWrocł/078/2001 and KBN/S2000/UWrocł/156/1998).

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Main Topic: A11 Other applications

First-principle calculations of vacancy-hydrogen interactions in iron: V_nH_m systems (n = 1, 3; m = 1, 6)

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Interactions of multivacancies with hydrogen atoms in iron have been investigated by means of the Density Functional Theory (DFT) method.

In a first step, formation and migration enthalpies of mono- di- and trivacancies are presented. We show that a significant binding energy between vacancies is observed allowing the formation of di- and trivacancies. Morever we show that the vacancy –vacancy interaction has a short-range character and that the formation of multivacancies allows an easier migration process.

Interaction of mono- and divacancies with several hydrogen atoms is also presented. We show that only up to five H atoms may be trapped by a monovacancy, the more favourable being the trapping of to H, while divacancies and more particularly (100) oriented divacancies are able to trap easily up to 6 hydrogens. The process of the reaction $V_nH_m + V_kH_l \dashrightarrow V_{n+k}H_{m+l}$ is also discussed.

Main Topic: A10 Materials Design

BRAGG-WILLIAMS MODEL OF ORDERED B2, L12 and L10 TYPE BINARY INTERMETALLIC COMPOUNDS CONTAINING POINT DEFECTS

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Ordered intermetallic compounds draw great interest at the present time because of both possible applications and fundamental scientific importance. The scientific interest is derived from the recognition that many intermetallics exhibit considerable ranges of nonstoichiometry which correspond to the presence of constitutional point defects which are temperature independent. Additional to these constitutional point defects thermally activated point defects can occur. The total defect structure (i.e. the types and the concentrations of the point defects) determines important properties of the intermetallic compounds (e.g. all diffusion dependent properties). Hence, for understanding and control of these properties a detailed knowledge of the defect structure in intermetallic compounds as function of composition and temperature within the homogeneity range of the compounds is a prerequisite. This thesis is aimed at formulating a model which can be used to calculating the ordering energy parameters ΔH_{AB} and $\Delta H_{B\square}$, and the concentration of vacancy (z) and the concentration of Anti Structure Defect (ASDs) as a function of the composition parameter χ and the temperature T. The ordering energy is related to but different from the formation energy, because the former is the energy change from the disordered alloy AB to the ordered alloy AB, while the latter is the energy change from the pure metals A and B to the ordered AB. Having obtained the model parameters (note that these are ΔH_{ij} and ΔS_{ij} for the fitting of the vacancy concentration and h_{ij} and s_{ij} for the fitting of the thermodynamic properties, respectively), the temperature dependence of the vacancy concentration can also be determined.

Main Topic: T6 Large-Scale and Multiscale Simulations

Theoretical investigation of elastic properties of hexagonal boron nitride membranes (h-BN)

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Boron Nitride (BN) is a wide band gap III-V compounds with remarkable physical properties and chemical stabilities. Hexagonal BN comprises alternate boron and nitrogen atoms in a honeycomb arrange, consisting of sp^2-bonded two-dimensional (2D) layers. Atomic layers of *h*-BN can be isolated similar to graphene, and have been used as substrate for approaching high quality graphene electronics [1].

The mechanical properties of experimentally obtained [1] few-layered h-BN 2D films were studied in details in presented work. For the explanation of reported experimental data where low value of Young's modulus was obtained the theoretical simulation was carried out by classical molecular mechanics technique. It was suggested that the lower breaking stress in the *h*-BN film compared with monolayer graphene is due to some possible vacancy-defects on studied freestanding as-grown membranes.

Before the study, the Tersoff-like BN classical potential was parameterized. Obtained potential was tested on bulk h-BN, the experimental lattice constants and elastic properties were obtained with good accuracy. In the simulation, the hemisphere of the mutually-static atoms (imitating the AFM tip) strained the BN membrane with fixed edges up to failure, with indentation increments of 0.02 Å. At each step system was relaxed using conjugated gradient minimization. For initially-perfect BN sheet the stiffness constant E^{2D} = 258.6 N/m was obtained closed to early ab initio estimations (271 N/m) [2]. After that the behavior of BN sheets with 1 % to 10 % vacancy concentrations was simulated.

It was found that the E^{2D} values decrease almost linearly with defect concentration, down to 102.1 ±13.1 N/m (at 10 % vacancies), which corresponds to experimental value [1]. Similarly, the maximum stress σ_m^{2D} decreases linearly from 67.5 N/m (perfect BN) to closed to experimental data value 25.0 ±1.6 N/m (10% vacancies). It is important to note that breaking strain $\varepsilon = \frac{\langle \sigma_m^{2D} \rangle}{\langle E^{2D} \rangle} \approx 0.25$ is nearly unaffected by vacancies. This contrasts with well-known stress-concentration by microcracks, but is understandable for atomic-size voids.

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Main Topic: T6 Large-Scale and Multiscale Simulations

Superlattices based on graphene and graphane. Theoretical investigation of electronic properties

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Well known that carbon is a base for different structures with different properties. For example, the diamond is insulator, carbon nanotubes are demonstrated semimetal or semicon-ducting properties. Now, in the last time, the big interest has a material called graphene. Gra-phene is two-dimensional, plane material. The structure of graphene is the basis for fullerenes [1], nanotubes, graphite and graphene nanoribbons [2].

Although graphene is considered as the main candidate for many applications in various fields of technology. The main problem is a lack of band gap, which complicated using graphene in the semiconductor nanoelectronic.

In this work was theoretical study of the evolution of the electron properties of graphene superlattices - nanostructures based on graphene with periodically adsorbed hydrogen atoms forming regions of graphane on a sheet of graphene.

For a qualitative description of the evolution of the electrical properties of recent structures was selected tight binding method based on the program dOXON with periodic boundary conditions.

Was estimated the evolution of the electronic properties of considered structures depends of the relative number of hydrogen atoms. Was shown that the adding of each new hydrogen atoms on the graphene surface leads to a change in the wave functions of electrons in graphene, change the DOS and appearance of the band gap.

Was shown, that at the adding of hydrogen atoms on the surface of graphene sheet we can see the appearance of the areas of electron localization, which correspond the pure lines in the band structure as in a case of quantum dots.

By received data was obtained dependence of the band gap E_{gap} on the stehiometric coefficient X, which assigns the chemical formula of the unit cells of current structures $C_{1-x}H_x$.

Obtaining of current dependence gave a chance to estimated values of the band gap for all of GSL structures, and we can a piori predicted the type of conductivity. Also in that dependence we can conclude that the main role in conductivity of the presented structures played the presence or absence of the crossing between the armchair and zigzag paths, but not the concentration of hydrogen atoms on the graphene surface.

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Main Topic: A10 Materials Design

First-principle calculations of magneto-optical properties of rare earth RAl_2 (R = Ce and Pr) compounds

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We present investigation on the magneto-optical properties of RAl_2 (R = Ce and Pr) compounds including the spin-orbit coupling using full potential Linear Augmented Plane Wave (FPLAPW) method as implemented in WIEN2k which is based on precise first principle density functional theory (DFT). We have adopted the Coulomb corrected local spin density approximation (LSDA+U) as the exchange correlation functional in the calculations to account better for the on-site *f*-electrons correlation. The total magnetic moment in $PrAl_2$ (4.75 μ_B) and $CeAl_2$ (1.62 μ_B) has main contribution only from rare earth (Pr or Ce) element while there is negligible small induced magnetic moment on Al site in both compounds. The Kerr rotation spectrum shows two positive peaks such that both peaks shift towards lower energy as we go from $CeAl_2$ to $PrAl_2$. Moreover, Kerr rotation is larger in $PrAl_2$ than that in $CeAl_2$ which can be attributed to an increase in the valence *f*-electrons of rare earth element from Ce to Pr. The calculated spectra help to identify the features of the experimental spectra with some overestimation in magnitude. It consists of more structures as compared to experimental spectra. The Kerr spectrum is analyzed to ascertain the origin of the various peaks in terms of optical transitions.

Main Topic: A10 Materials Design

The energetics induced by interstitial C in Ti-Al-Nb alloys

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Ti-Al based alloys exhibit attractive properties such as low density, high strength at high temperatures, and very good oxidation resistance, but they are brittle at room temperature. Addition of transition-metal elements or elements like carbon, nitrogen and oxygen can significantly improve the ductility and increase the strength by as much as 30%. Recently, the alloys composed of lamellar structure of alternating single phases of γ ($L1_0$) and α_2 ($D0_{19}$ structure) increase the ductility and creep strength at room temperature. The solubility of the carbon is here enhanced but the combined effects of interstitial elements as well as alloying transition elements on the mechanical properties are not well understood. We perform first-principles calculations based on density-functional theory to investigate the influence of interstitial carbon on the energetics of both, the γ and α_2 structure of this alloy system. We study the heats of formation with respect to the pure TiAl phases, taking into account various possible Nb sites as well as the presence of carbon on one of the two interstitial sites as a function of C concentration. At first, the Al amount is fixed and Ti atoms are replaced by Nb. In the second case, we keep a Ti concentration of 50% varying the Nb and Al contents. Thereby Nb is allowed to populate Ti sites while corresponding Ti-atoms in turn occupy Al positions. Finally, we study the role of interstitial carbon on the mechanical properties by calculating elastic constants of both alloyed TiAl phases and estimated the ductility change with respect to pure phases.

Ab initio study of the crystallization kinetics of phase-change materials

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Phase change materials based on chalcogenide alloys are presently used in rewritable optical discs (CDs, DVDs, Blu-Rays discs) and are promising materials for non-volatile electronic memories. Both applications rely on the reversible and fast transitions between the amorphous and crystalline phases, which have different optical and electronic properties. Despite much experimental and theoretical effort to understand the phase-change mechanism, the detailed atomistic changes involved in the transitions are still unknown. Only a few studies have addressed the crystallization phenomena in these materials by first-principles methods.
The models employed in these works are however small and the goal of the present ab initio study is to consider larger models of GeTe in order to obtain a more realistic description of the crystallization processes in this prototypical system. To achieve this goal, the metadynamics method is used to bridge the time scale for crystallization. Within this method, the relevant processes are described in terms of a small number of descriptors called collective variables. In our simulations, GeTe coordination, the Steinhardt parameter Q6 and the ring statistics have been used as collective variables. Preliminary studies on small models of GeTe (64 atoms) show that it is possible to reproduce the crystallization efficiently using this combined method. Simulations of more realistic models of GeTe containing 216 atoms are under way.

Main Topic: A8 Catalysis and Electrochemistry

Catalytic Water Splitting for Hydrogen Production: A First-Principles Study of a Ru Complex in Solution

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Water splitting is at the basis of artificial photosynthesis for solar energy conversion into chemical fuels [1]. The reaction is typically catalyzed by multi-center complexes, i.e. Photosynthesis II has 4 Mn metal centers. Recent advances provide insight into the molecular processes governing the catalytic activity of these natural and artificial photosynthetic complexes, but many fundamental aspects still need to be clarified [2].

Besides multi-center molecular complexes, simpler single-center catalysts have been recently synthesized, yet capable of splitting efficiently water molecules. These systems represent an appealing opportunity to study the relevant reaction mechanism in structurally simpler systems. They can clarify why multi-center active cores are more reactive than single centers. Here we focus on a model single-center Ru-based organic complex that has been shown to catalyze both the oxidation of water as well as the production of hydrogen, the two reactions at the anode and cathode typically promoted by different catalysts [3]. The use of the metadynamics technique [4, 5] allowed us to find a reaction mechanism that is different significantly from the one previously proposed.

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UNIVERSITÀ DEGLI STUDI DI MILANO

Comment to “Imaging the atomic orbitals of carbon atomic chains with field-emission electron microscopy”

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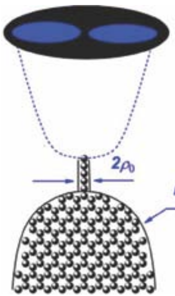
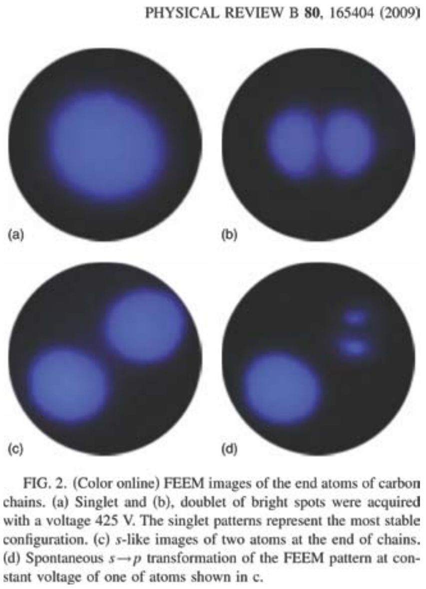
Summary

The observation of a stable doublet pattern in the field-emission electron microscopy (FEEM) of a linear atomic chain requires a stable mechanism breaking the axial symmetry, which is not identified correctly by Mikhailovskij *et al.* [Phys. Rev. B **80**, 165404 (2009)]. Using DFT-LDA calculations, we attribute the observed pattern to the symmetry breaking produced by the ligand where the chain is attached, plus carbon π-bonding alternation.



The observed FEEM patterns

41 different carbon atomic chains were produced by high-field treatment. The atomic chain lengths are distributed with mean value of 5.9 nm and variance of 2.5 nm.



PHYSICAL REVIEW B **80**, 165404 (2009)

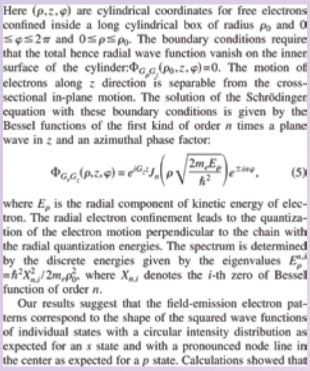
FIG. 2. (Color online) FEEM images of the end atoms of carbon chains. (a) Singlet and (b), doublet of bright spots were acquired with a voltage 425 V. The singlet patterns represent the most stable configuration. (c) s-like images of two atoms at the end of chains. (d) Spontaneous $s \to p$ transformation of the FEEM pattern at constant voltage of one of atoms shown in c.

The first field-emission electron image of the end atom has circular symmetric intensity distribution with maximum intensity at the center as expected for s-like states, while the second one has a pronounced node in the center as expected for p-like states.

Deletion or movement of only a portion of a FEEM pattern was never registered: singlet and doublet patterns always behaved as single units. Some of the singlet and doublet patterns disappeared within about ten second after they appeared. The rest of the localized FEEM patterns remained stable. At the electron current greater then 100 pA singlets occasionally change to doublets and vice versa.

A naive explanation

?



Here (ρ,z,φ) are cylindrical coordinates for free electrons confined inside a long cylindrical box of radius ρ_0 and $0 \le \varphi \le 2\pi$ and $0 \le \rho \le \rho_0$. The boundary conditions require that the total hence radial wave function vanish on the inner surface of the cylinder: $\Phi_{G_\rho G_z}(\rho_0,z,\varphi)=0$. The motion of electrons along z direction is separable from the cross-sectional in-plane motion. The solution of the Schrödinger equation with these boundary conditions is given by the Bessel functions of the first kind of order n times a plane wave in z and an azimuthal phase factor:

$$\Phi_{G_\rho G_z}(\rho,z,\varphi)=e^{iG_z z}J_n\left(\rho\sqrt{\frac{2m_eE_\rho}{\hbar^2}}\right)e^{\pm in\varphi}, \qquad (5)$$

where E_ρ is the radial component of kinetic energy of electron. The radial electron confinement leads to the quantization of the electron motion perpendicular to the chain with the radial quantization energies. The spectrum is determined by the discrete energies given by the eigenvalues $E_\rho^{n,i}=\hbar^2X_{n,i}^2/2m_e\rho_0^2$, where $X_{n,i}$ denotes the i-th zero of Bessel function of order n.

Our results suggest that the field-emission electron patterns correspond to the shape of the squared wave functions of individual states with a circular intensity distribution as expected for an s state and with a pronounced node line in the center as expected for a p state. Calculations showed that

?

In fact, the pattern should turn out cylindrically symmetric regardless of n!

If e.g. $\exp(\pm i\varphi)$ was the angular dependency, FEEM would display an axially symmetric (possibly ring-shaped) pattern.

Of course, a perturbation could localize the electron in the azimuthal angle, by inducing a splitting between the $\cos(\varphi-\varphi_0)$ and $\sin(\varphi-\varphi_0)$ components of the p state, which do in turn display nodes. However, any sort of fluctuating perturbation, such as those associated to the thermal oscillation of the free standing chain, would produce a rapidly fluctuating phase φ_0, with the eventual result of an axially symmetric pattern.

The correct explanation

What can induce a **stable** symmetry-breaking perturbation in a several-atom-long free-standing chain?

the anchored end of the chain!

Whenever this end binds an sp^2 hybridized atom of the carbon tip, (e.g. to the zig-zag or armchair boundary of a graphene sheet), the chain acquires a partial cumulenic character[1]. All bonds are double, and the memory of the orientation of the sp^2 termination propagates along the chain through an alternating orientation of π bonds [2].

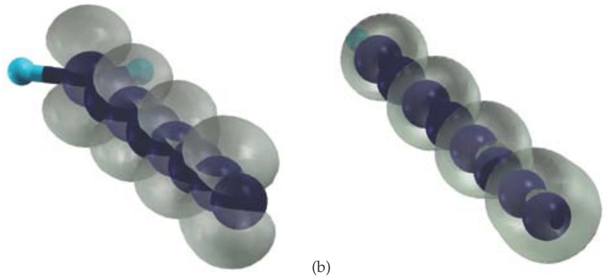


Figure (a) shows the highest-occupied molecular orbital (HOMO), made of the four π bonds oriented normally to the sp^2 plane defined by the attachment point of the cumulenic chain; figure (b) shows the highest-occupied molecular orbital when the chain is connected to a symmetrical (e.g. sp^3) ligand: single-triple alternation: a polyyne.

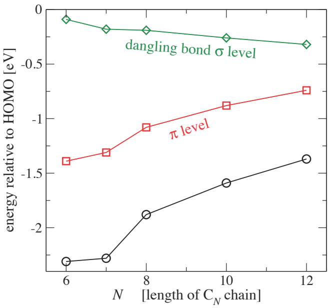
When the bonded atom is sp^2, emission from the terminal atom is dominated by this asymmetric π orbital, and displays a clear nodal plane which is parallel/antiparallel to the sp^2 plane, depending on the chain being composed by an even/odd number of atoms. Alternatively, the anchored end, rather than sp^2, could have sp^3 hybridization, e.g. a generic atom in the “bulk” of a graphene fragment or fullerene or nanotube cap, represented by a simple H atom in figure b. Such a ligand would induce a polyyinic-type electronic structure of the chain. As a result, a highly dimerized configuration, with alternating single/triple bonds and an essentially unbroken axial symmetry is realized. However, even in this case, eventually the HOMO is a π bonding orbital. The main difference is that as the cylindrical symmetry is unbroken, a cylindrically symmetric “doughnut-shaped” orbital is generated, precisely of the type described by Eq. (5) of Ref. [3].

Technical details

We carry out standard calculations within DFT-LDA with the quantum espresso package [4, 5] using default ultrasoft pseudopotentials, and wavefunction/charge cutoffs of 15/120 Hartree. We relax the atomic positions until the largest residual force is less than 10^{-4} Hartree/a_0 (8 pN).

Check: the π bonding HOMO remains above...

... regardless of the carbyne length n.



The HOMO-1 dangling-bond σ level moves deeper as the chain lengthens

deeper bonding levels move upward slowly

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[5] The Quantum ESPRESSO package is available at `http://www.quantum-espresso.org`.

Main Topic: A6 Surfaces

Long-range ordered surface alloy of bulk-immiscible components stabilized by magnetism: Fe-Au/Ru(0001)

Madhura Marathe[1], *S. Mehendale*[2], *Y. Girard*[2], *V. Repain*[2], *C. Chacon*[2], *J. Lagoute*[2], *S. Rousset*[2] *and Shobhana Narasimhan*[1]

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Large differences have been observed in the bulk and the surface properties of materials; even small changes in the surface environment (such as annealing temperature, presence of adsorbates) are known to alter the surface properties drastically. This phenomenon can be utilized to find materials with better functionalities if we get a better understanding of various interactions involved. More importantly if we can control the surface structure, it is better for applications such as catalytic activity, magnetic storage, etc. In this project, we have found a surface alloy of two bulk-immiscible components - Fe and Au - when deposited on the Ru(0001) surface. Using STM and LEED characterization, a long-range ordered alloy with the composition $Fe_{0.33}Au_{0.67}$ was observed for submonolayer coverages. For such systems, it was speculated that the elastic interactions are dominant and govern the mixing. However, our extensive calculations have shown that for this system, it is not the elastic interaction that drives the alloy formation, but magnetic interactions. We have shown that the magnetic interactions not only promote mixing, but also tilt the balance from Fe-rich phases being more stable (as indicated by smaller surface stress for Fe-rich phases) to more stable Au-rich phases as observed in the experiments and calculations. Our work opens a way of finding new ordered alloys on surfaces and ultrathin films; and the dominance of magnetism is of interest for device applications.

Reference: S. Mehendale, Y. Girard, V. Repain, C. Chacon, J. Lagoute, S. Rousset, M. Marathe and S. Narasimhan, Phys. Rev. Lett. **105**, 056101 (2010).

Main Topic: A5 Functional Materials

Stacking and Registry Effects in Layered Materials: The Case Of Hexagonal Boron Nitride

Noa Marom[1,4], *Jonathan Bernstein*[3], *Jonathan Garel*[1], *Alexandre Tkatchenko*[2], *Ernesto Joselevich*[1], *Leeor Kronik*[1], *and Oded Hod*[3]

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2. Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195, Berlin, Germany.
3. School of Chemistry, The Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 69978, Israel.
4. Center for Computational Materials, Institute of Computational Engineering and Sciences, University of Texas, Austin, Texas 78712, USA.

The interlayer sliding energy landscape of hexagonal boron nitride (h-BN) is investigated via a van der Waals corrected density functional theory approach. It is found that the main role of the van der Waals forces is to “anchor” the layers at a fixed distance, whereas the electrostatic forces dictate the optimal stacking mode and the interlayer sliding energy. A nearly free sliding path is identified, along which band gap modulations of ~0.6 eV are obtained. We propose a simple geometrical model that quantifies the registry matching between the layers and captures the essence of the corrugated h-BN interlayer energy landscape. The simplicity of this phenomenological model opens the way to the modeling of complex layered structures, such as carbon and boron nitride nanotubes.

Stability of Methane with respect to dissociation and other C-H stoichiometries under pressure.

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Hydrogen is the most abundant element in the universe, while carbon plays a main role in the nucleosynthesis sequence. As a result, methane is one of the most common compound gasses in universe, while other carbon-hydrides are also bound to be abundant. Thus, studying the behaviour of such a system under pressure has astrophysical implications. Similar implications could be drawn from analysing how the stable hydrocarbon stoichiometries might be affected at conditions far away from standard pressure and temperature.

One of the most interesting developments of first-principles calculations in recent years has been the adoption of reliable methods for structure prediction. Coupled with density functional theory (DFT), random sampling has been successfully used in order to predict stable structures [1].

This work presents an analysis of the stability of several carbon hydride stoichiometries at high pressure. Using DFT coupled with random sampling for structure prediction, different CH compounds have been studied from 100 GPa up to 10 TPa. The obtained results are in agreement with previous calculations [2] and experiments [3], which found methane to be unstable towards decomposition above 100 GPa. We find polyvinyl to be the most stable carbon hydride form between 200 and 400 GPa, while higher pressures see full segregation as the most stable form.

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Main Topic: A10 Materials Design

15th International Workshop on Computational Physics and Materials Science: Total Energy and Force Methods

XPS of amorphous $CdTeO_x$: validation of a structural model

E. Menéndez-Proupin[1], P. Giannozzi[2], G. Gutiérrez[1], J. Peralta[1],
A. Amézaga[1,3], E. Holmstrom[4], R. Lizárraga[4], and P. Bartolo-Pérez[5]
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We present structural models of amorphous $CdTeO_x$ (x=0.2,1,2, and 3) obtained by ab initio molecular dynamics. We report density functional theory calculations of core level shifts (CLS). Using the CLS, we compute the X-ray photoelectron spectra and develop a method to determine the composition by comparison of the theoretical and experimental spectra. We conclude that the correlation between the area ratios of tellurium peaks in the CLS spectrum and the oxygen concentration does not obey simple rules. Hence, computer simulations are needed in order to obtain concentrations correctly in experimental samples.

Motivation

CdTeO*x* amorphous thin films grown by r.f. sputtering.
Tunable band gap.
Possible windows materials of CdTe solar cells.
Indium-doped $CdTeO_3$ is a transparent conductor.

Past work

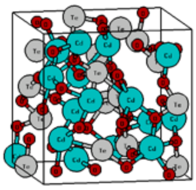
Structural Model studied by Born-Oppenheimer MD [1]
Optimization of growth techniques and XPS spectroscopy [2].

Goals of this work

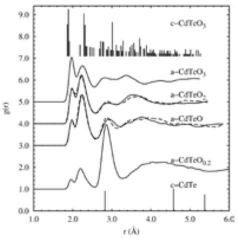
Obtain structural models of a-CdTeO*x*, and validate them with experimental spectra.

Computational Details

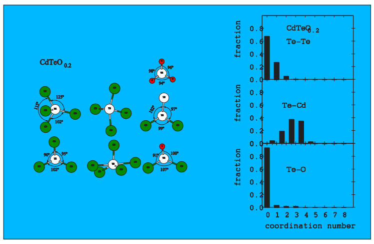
Energies with DFT/PBE.
Codes: VASP and Quantum ESPRESSO. PAW and US pseudopotentials.
Core Level Shifts obtained from the Z+1 approximation [3].

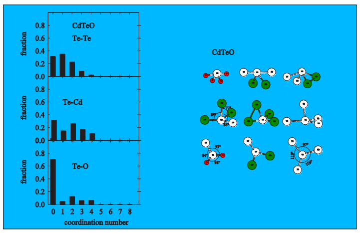


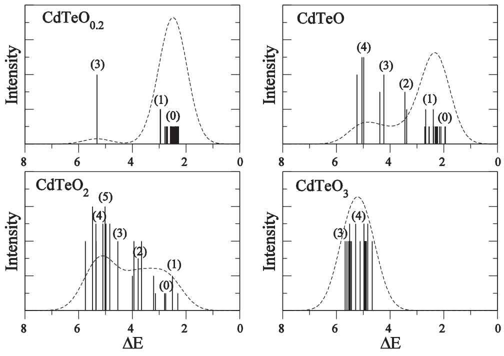
Supercell ← **Structural models from ab initio molecular dynamics [1] (start point)** → Characterization

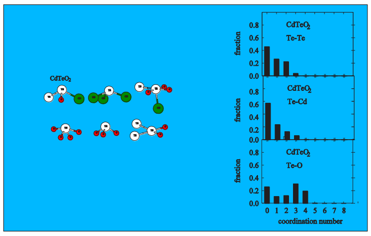


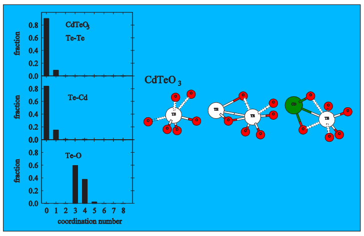
Results



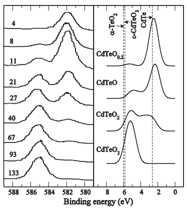








Experimental and theoretical XPS spectra from the Te 3d core level



Conclusions

The structural models of $CdTeO_x$, obtained by ab initio molecular dynamics, have simulated XPS spectra consistent with the experiments.

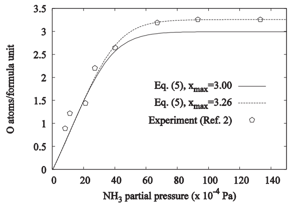
Combining first principle calculations with experimental spectra, one can obtain precise information on the local environment of Te atoms.

The XPS Te 3d doublet contain contributions from Te atoms in different environments. Te atoms with O neighbors contribute to both peaks of the doublet, in contrast to previous assignements.

Our structural models describe the global oxygen content well by comparing the area ratios of the two Te 3d peaks obtained from the calculations and the experiments.

This results shows the importance of first principles calculations when quantifying the details of XPS spectra in amorphous oxides in particular and complex materials in general.

Determination of the Oxygen content by comparing experimental and calculated XPS spectra, and analyzing the areas of the peaks of the Te 3d doublet. The pentagons show the quantification made in Ref. 2.



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Main Topic: T5 Ab-initio Molecular Dynamics

First principles study of the $LiNH_2/Li_2NH$ transformation

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Lithium amide ($LiNH_2$) has been extensively studied in recent years as a promising material for hydrogen storage [1]. Hydrogen release occurs in the mixture $LiNH_2/LiH$ via a reversible solid state decomposition reaction into lithium imide (Li_2NH) and molecular hydrogen ($LiNH_2+LiH \rightarrow Li_2NH+H_2$). Although the thermodynamical decomposition temperature is probably too high for on-board applications, the amide decomposition reaction is under deep scrutiny since this material represents a prototypical, relatively simple system, which could shed light on the mechanisms of reversible H-release in the more complex, and more promising, reactive hydrides made of mixtures of amides, borohydrides and/or alanates. In spite of a substantial amount of experimental work, the detailed mechanism of amide decomposition is still matter of debate.

Aiming at providing theoretical support to the decomposition mechanism and clarifying the role of the surfaces in this process, we performed ab-initio calculations of activation energies of elementary steps that we hypothesize to be crucial for ammonia mediated transformation path[2]. We first analyzed the formation of ammonia via a proton transfer between two NH_2^- groups in the presence or in the absence of a Li Frenkel pair in the bulk and at the surface of $LiNH_2$. Diffusivity of H+ (i.e. NH_3 via a Grohttus mechanism), H+ vacancy (NH^{2-}) and Li+ species in $LiNH_2$ and Li_2NH were then computed to contrast the alternative scenarios presented in Refs. [3,4]. The H+ and Li+ transfer across the $LiNH_2/Li_2NH$ interface was also investigated as well as the ammonia desorption at the Li_2NH and $LiNH_2$ surfaces. Ions diffusivity in the high temperature phase of Li_2NH has been also monitored directly by means of ab-initio molecular dynamics simulations. The scenario for the decomposition mechanism of $LiNH_2$ emerging from the simulations actually suggests that the transformation path depends on the surface-to-volume-ratio. The formation of sub-stoichiometric phases [3] is possibly favored in bulky material with a small surface-to-volume ratio, while the direct formation of imide is favored in the presence of small crystallites (large surface-to-volume ratio) which transform according to the core-shrinking model of Ref. [4].

Furthermore, by a deep analysis of our dynamical simulations we propose a low temperature structure for Li_2NH which solves the contradictions of previous proposals.

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Theory and Methods:
T5 Ab-initio Molecular Dynamics

Applications:
A10 Materials Design

Main Topic: A11 Other applications

First principles studies of molecular confinement and degradation in cement

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In order to improve the mechanical properties, control degradation and obtain more protected and durable concrete, it becomes fundamental to understand the thermodynamics, kinetics and dynamics of the interaction of absorbed molecules (CO_2, chlorine, nitrates) into cement at various conditions (temperature, pressure and salinity). In this work, we have focused on two problems on the Concrete Science using First Principles Methods. Firstly, we have determined the free energy formation of ettringitite ($(CaO)_3(Al_2O_3)(CaSO_4)_3 \cdot 32H_2O$) and its relation with cement degradation. Secondly*, the structural, electronic and dynamic properties of confined molecules (H_2O and CO_2) on layered Tobermorite with varying amounts have been characterized by ab-initio molecular dynamics within density functional theory (DFT) formalism and generalized gradient approximation (GGA). The obtained properties such as thermal decomposition reactions, vibrational spectra, diffusion coefficient and molecular ordering are important to understand the degradation effect, the hydration and CO_2 content influence on cement as a whole and could be used to predict concrete properties at larger scale.

*In collaboration with James Almeida (UFABC) and Adalberto Fazzio (USP – Brazil)

Main Topic: A8 Catalysis and Electrochemistry

Promotion of Ethylene Epoxidation Selectivity by Subsurface Oxygen in Ag-Cu Alloy Catalysts

Ngoc Linh Nguyen, Simone Piccinin and Stefano de Gironcoli

SISSA and CNR-IOM DEMOCRITOS, Trieste

Recent studies have shown the importance of subsurface oxygen in Ethylene Epoxidation reaction on pure Ag catalysts. In this work, we investigate by means of first-principles density functional theory calculations the significantly improved selectivity induced by the presence of subsurface oxygen in the (111) surface of the Ag-Cu catalysts. Our calculations show that subsurface oxygen adsorption on fcc sites under the thin oxide-like CuO layer is energetically favorable. On this substrate the reaction mechanism proceeds via a common Oxametallacycle intermediate state and the calculated activation energy of the pathway leading to the formation of the undesired product, acetaldehyde, is significantly higher than that leading to the formation of the desired product, ethylene oxide, while these barrier heights are in opposite order on a pure Ag catalyst. This finding could provide an insight to understand the selectivity promotion of Ag-Cu alloy with respect to pure Ag catalysts.

Structure and Chemical Reactivity of Small Pt Clusters on a Carbon Nanotube: A First-principles Study

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3. Japan Science and Technology Agency, CREST, 5 Sanbancho, Chiyoda-ku, Tokyo 102-0075, Japan

Recently, highly dispersed Pt nanoclusters on carbon nanotube (CNT) support have showed a superior catalytic activity in fuel cell, a promising renewable energy resource [1]. Properties of metal nanoclusters can be governed by several factors, such as geometry, support, environments. Characterization and precise control of the properties of metal nanoclusters are among the outstanding challenges in the research fields of both physics and chemistry. In this presentation, we report our theoretical studies on the interplay between Pt_3 and Pt_4 clusters and CNT support, based on density functional theory calculations. We find that there is a strong interaction between Pt clusters and CNT via hybridizations between *d*-states of P and *p*-states of C atoms. Small Pt clusters on CNT exhibit several structural isomers with rather low-energy barriers, resulting in a high degree of dynamic structure [2]. The dynamic structure allows the Pt clusters on CNT to interact easily with O_2 gas by adapting their structures, resulting in a high chemical reactivity. We also show the effect of electric field on the structure and chemical reactivity of Pt clusters on CNT. These findings provide insight into understanding behaviors of small Pt clusters on CNT under realistic electrochemical environment.

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2. Nguyen Thanh Cuong *et al.*, Phys. Rev. B, 79 (2009) 235417.

A quantum chemical study on Polythiophenes derivatives as donor materials in bulk-heterojunction polymer solar cells

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(Dated: 30 September 2010)

Summary

A semi-empirical study for investigating the higher occupied molecular orbital (HOMO) and lower unoccupied molecular orbital (LUMO) of polythiophenes derivatives/fullerenes combination (bulk-heterojunction polymer solar cells) was done using Austin Model 1 (AM1) quantum chemical method. The overestimation on the values of the HOMO and LUMO obtained from AM1 model was corrected by using experimental data from literature as criteria of correctness. Using our correction method a reasonable linear relationship between the computed energy band gaps of polythiophenes derivatives and the experimental band gaps was found. The corrected HOMO and LUMO energies of polythiophenes derivatives obtained from our method match well with the experimental one. This method can serve as a road map in order to design and synthesis appropriate combination of polythiophenes derivatives/fullerenes for bulk-heterojunction solar cells.

Main Topic: A9 Chemical Reactions and Kinetics

Symmetry-Adapted Perturbation Theory study of intermolecular interaction energy between organic molecules with three- and four-membered rings.

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Aggregation of chemical molecules in the gas and condensed phases is driven by the intermolecular forces acting between them. Properties of liquid water, stacking of base pairs in DNA, and ability of chemically inert noble gases to form liquid and solid phase, are examples of processes governed by various intermolecular forces. Study of such forces is made difficult by their overlapping nature and strength. For example, strong interaction of molecular dipoles, caused by the presence of polar substituents, is also frequently accompanied by intermolecular hydrogen bonding. The latter phenomenon can be in some instances weak enough to be barely different from dispersion (Van der Waals) forces.

The current study shows various types of intermolecular interactions present in dimeric systems, where the constituent monomers are simple organic molecules with three- and four-membered rings (cyclopropane, aziridine, oxirane, cyclobutane, azetidine, oxetane). Calculations are carried out within Symmetry-Adapted Perturbation Theory [1] formalism.

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A first principles study of hydrogen and ethanol adsorption on Pd based metallic nanofilms

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Hydrogen is believed to be the fuel for future [1]. It is a clean and renewable source of energy and presents a high density of energy by mass, about three times higher than that generated from gasoline and almost seven times higher than the energy obtained from coal in an equal mass. In order to use hydrogen efficiently as a fuel, better technologies for production and storage are needed [2]. Hydrogen production from ethanol is a promising alternative because it is easy to produce, nontoxicity, cheap and easy to handle. Usually it is obtained from stream reforming and catalytic oxidation [3]. Thus, a better understanding of the adsorption/desorption processes of hydrogen and the adsorption and oxidation process of ethanol presents a significant contribution. Recent results have shown that metallic nanofilms formed by different layers of metals are excellent candidates for hydrogen storage [4,5]. Particularly, Pd metallic based nanofilms deposited on Pt substrate presents a good reversibility of adsorption/desorption process [5]. In this context, we study hydrogen and ethanol adsorption on metallic nanofilms of Pd/Pt(111) and Pt/Pd(111), as well as the oxidation process of ethanol on these surfaces. The first principles calculations were carried out using density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP). We have used the generalized gradient approximation (GGA) PW91 to treat the exchange and correlation term. Analyzing the atomic hydrogen preferential sites behavior on nanofilms surfaces, we observed that hydrogen adsorption induces an expansion of the outer atomic layer. This expansion suggests a hydride formation. Such behavior is not observed on inner layers of the film, indicating that the substrate prevents hydride formation. Similar effect was found in an experimental study of hydrogen adsorption on Pd/Pt(111) nanofilms [5]. We also investigate the preferential adsorption sites for ethanol [6] on these nanofilms surfaces with respect to the number of atomic layers. The dissociation pathway for ethanol oxidation, as well as the activation barrier were calculated using the nudged elastic band method (NEB).

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Lithium storage and diffusion on inorganic nanotubes from first principles

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The search for cleaner and more efficient energy storage and conversion technologies for replacement of fossil fuels has received a tremendous amount of interest in the last fewer years [1-3]. Rechargeable lithium-ion batteries can be an important contribution to this area. However, the large scale commercial use of theses batteries depends on the improvement of two important aspects: charging time and the amount of power that the battery can supply. Nanostructures have gained steadily growing interest as a result of their properties superior to their bulk counterparts. Particularly, it has been proposed that inorganic nanotubes can improve the speed of charging and discharging of a particular material and provides better performance for storage and diffusion of lithium [4]. These inorganic nanotubes are mainly metal dichalcogenide ones which are consisted by layered nanotubes in the form MX_2 (M=transition metal, X=S, Se). In this work, we focus our attention to investigate the effect of curvature on Li voltage and activation barrier for diffusion on the surface of MoS_2 and WS_2 nanotubes. Calculations were carried out using density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP). We have used the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) to treat the exchange and correlation term. The nanotube was simulated using the curved surface method [4]. In this method, the full nanotube is modeled by a curved surface with constant curvature. These surfaces are similar to a nanotube surface everywhere except at the inflection points, thus it can accurately estimate local properties as lithium voltage and activation barrier for diffusion using fewer atoms. Activation barriers for lithium were calculated using the nudged elastic band (NEB) method.

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Main Topic: A8 Catalysis and Electrochemistry

Ab-initio modelling of Ru-based homogeneous catalysts for water oxidation

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Splitting water to produce molecular oxygen and hydrogen is a promising way to convert and store solar energy in the form of chemical fuels [1]. Efficient catalysts are needed to promote this electrochemical reaction, which, especially on the oxidation side, is extremely challenging, requiring the loss of four electrons and four protons and the creation of the O-O bond. For this semi-reaction several catalysts have been proposed in the past three decades, both heterogeneous (metal oxide surfaces) and homogeneous (transition metals with organic ligands), while Pt is typically used at the cathode. Here we present the results of our first-principles Density Functional Theory calculations on the reaction mechanism promoted by an all-inorganic tetraruthenium-polyoxometalate homogeneous catalyst, able to efficiently oxidize water at a low overpotential (~ 0.3 V) [2,3]. We show how state-of-the-art theoretical methods help to shed light on the complex mechanism of this reaction. In particular, we combine hybrid functional calculations for the energetics of the intermediates and metadynamics to explore the free energy surface in the space of a few collective variables. We find that the mechanism proposed in the literature needs to be critically re-examined and we propose alternative reaction pathways.

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Ab-initio parameterisation of inter-atomic force fields for the description of solid-solid and liquid-solid interfaces

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We present a discussion on the generation of classical force field for the description of solid-solid and solid-liquid interfaces. We use the Tangney-Scandolo method [1] based on the use of forces, energies and stresses from ab-initio calculations for the generation of a potential able to provide a fully atomistic representation of the interface, by the inclusion of the most relevant two and three body interactions as well as polarisation. Hence, yielding a potential capable to describe correctly the structural properties of the interface within a wide range of pressures and temperatures. We discuss the application of this method to the generation of a force field for the a-SiO_2/water interface and extend our study to the TiO_2/a-SiO_2 interface. Finally, we look into the generation of potentials that include ionic impurities. We compare our classical results to density functional calculations and show how our procedure leads to potentials that are greatly improved in comparison to the ones currently used to describe interfaces. This work is part of the FP7 project ADGLASS.

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Main Topic: A5 Functional Materials

Azobenzenes Self Assembled Monolayers

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The photoisomerization process of azobenzene is widely studied both in solution and on metal surfaces [1,2] , because of its efficiency and controllability. These features makes the azo-SAM a promising tool for controlling the movement of nano-objects with light. A preliminary study on the thio-azobenzene single molecule (thio-AZO) and on structural properties of a thio-AZO self assembled monolayer (SAM) on gold (111) surface is presented in this work. Both quantum mechanical calculations and classical simulations are used: electronic structure and geometry optimizations are performed with DFT methods whereas molecular dynamics (MD) simulations are run with pairwise potentials (OPLS/AA) and fixed charges. Using models based on these approaches, we have studied the mechanical stiffness of the monolayer in the cis- and in the trans- form. Calculated results agree with available experimental data, notwithstanding the use of a literature potential [3] which is not fully optimized for our systems. The testing of new reactive force fields and the optimization of a specific pairwise potential are in progress. For this purpose a wide sampling of the potential energy surface (PES) function has been done by means of QM methods. Preliminary tests show that QM-PES functions are well reproduced by our optimized force field.

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Main Topic: A10 Materials Design

Ab initio modelling of interfaces: TiO_2 grown on Al_2O_3 as a prototype

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Oxide-based layered structures are increasingly exploited for hard coatings. As a model system we study the interface between a TiO_2 thin film grown on a single crystal Al_2O_3 (0001) substrate by sputter deposition. Xray diffraction analysis reveals that TiO_2 grows in the rutile structure with the (100) plane parallel to the substrate. Within the framework of density functional theory (DFT) we study local atomic rearrangements, charge redistribution, and the nature of bonding at the interface region. In particular, we discuss the influence of elasticity on the interface structure to account for the lattice misfit of the constituents and present a model to predict local strain fields in the vicinity of the interface. The basic idea here is to distort both lattices such that arising stresses compensate each other. To this extent, we first compute the elastic tensors for the two bulk materials and construct the interface supercell taking into account the anisotropic nature of the deformations on either side. Hence, all the information we need is the bulk elastic tensors and the Miller indices of the lattice planes forming the interface. The so obtained structure provides an ideal starting point for the following abintio relaxation procedure. After having successfully applied this model to the TiO_2/Al_2O_3 system, we investigate its applicability to a range of different interfaces.

Main Topic: A6 Surfaces

Theoretical investigations on the TMG (trimetylogallium) adsorption and the TMG diffusion on the GaN (gallium nitride) surface.

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There are many well-known precursors used for preparation of group III-V nitrides. Among them there are TMG and NH3 (ammonia) precursors which are widely used as reactants in the metal organic chemical vapor deposition (MOCVD) to receive GaN crystals. Recently we examined TMG adsorption on GaN(0001) surface to study bands formation between Ga and N. The calculation was conducted using the density functional theory DFT implemented in the VASP package. Due to computation limits four-layer GaN system was employed. Dangling bands on GaN(000-1) surface was saturated with the hydrogen atoms. Due to dangling bands on GaN(0001) surface we observed the slab polarization. The slab polarization and the system energy in the vicinity of TMG was computed for different distances between the surface atoms and TMG. Another important goal of our research is to study TMG diffusion on the GaN surface. As a result we obtained the energy path for diffusion from Top_N to Hollow.

Structural and electronic properties of GaN surfaces (0001) and (000-1) due to the presence of molecules nearby of the slab face obtained from DFT.

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Abstract. A nitrogen terminated GaN($000\bar{1}$) and a gallium terminated GaN(0001) surface was studied using the density functional theory (DFT) implemented in the VASP package. It was shown that some extra bands, located near the valence-band maximum, emerge due to dangling bonds existing at non-saturated N or Ga surfaces, respectively. These dangling bonds were subsequently saturated by the hydrogen atoms. The surface related electron bands, were calculated for different distances between the surface atoms and hydrogen saturation atoms as well as between the surface atoms and simple molecules like NH3. The electric field within the GaN slab was computed, showing that the slab polarization depends on the distance between the slab surfaces and the add atoms. The Fermi level is pinned at both faces of the slab, and this fact determines the electric field within the slab. In addition, the properties of the 2H-GaN(0001) surface, as a function of the Fermi energy of the system, were examined. The obtained results were compared with experimental and earlier theoretical investigations data.

The calculation of experimental spectra using linear-scaling density-functional theory

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The theoretical calculation of spectra is highly useful both in understanding experimental results and making predictions about new materials. This work will combine the power of spectroscopy with the ability of linear-scaling density-functional theory (DFT) to study much larger systems than previously possible. A necessary first step involves finding a method to calculate conduction states and implementing it in the linear-scaling DFT code ONETEP, which is currently limited to the calculation of valence states. These can then be used to calculate spectra via Fermi's golden rule.

A 'toy model' was created to mimic the main elements of ONETEP, and used as a test environment to compare different methods for calculating conduction states. A comparison of these methods will be presented, followed by some results from the implementation of the best method within ONETEP. Finally, preliminary results will be presented for spectra such as optical absorption spectra in ONETEP, demonstrating the importance of accurate conduction states for such calculations.

Imaging and characterization of activated CO_2 species on Ni(110)

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By means of a joint experimental and theoretical approach we provide the first single molecule imaging and characterization of CO_2 on Ni(110), chemisorbed with high charge transfer from the substrate in an activated state that plays a crucial role in the hydrogenation process. Low temperature scanning tunneling microscopy images of single CO_2 molecules are combined with ab-initio density functional theory calculations, where dispersive forces and zero point energy estimates have been explicitly accounted for. We obtain a detailed characterization of the adsorption geometries and an estimate of the energies corresponding to the different adsorbed states. A consistent picture of CO_2 chemisorption on Ni(110) is provided on the basis of the newly available information, yielding a deeper insight into the previously existing spectroscopic and theoretical data.

Accurate *ab initio* parametrised atomistic force fields for ionic materials: application to alumina

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We present an atomistic potential for bulk alumina Al_2O_3), which has been parametrised by fitting the energies, forces, and stresses of a large database of reference configurations to those calculated with density functional theory (DFT) [1]. Our functional form is simpler and less expensive than previous models of alumina parametrised by this technique. We compare our potential to those existing models [2], and to experimental and *ab initio* data on crystal structures and energies, elastic constants, phonon spectra, and thermal expansion. We demonstrate an overall accuracy that is close to that of DFT for these quantities. We also describe the development of a method with which the charge and induced dipole on an ion can simultaneously be varied during an atomistic simulation.

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Computational studies of the *h*-BN nanomesh on Rh(111) surface

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The hexagonal BN layer forms a corrugated Moiré pattern on the Rh(111) substrate, having a periodicity of 3.2 nm [1]. The nanomesh provides a periodic potential energy landscape that can be used for example to trap molecules in a regular pattern.

We have studied the properties of the nanomesh system using density-functional theory. We have thus access to the microscopic properties of the whole structure. The cell involves the whole 13×13-on-12×12 mesh of *h*-BN on the substrate. The first applications of these calculations have been to study the proton disorder in the ice clusters adsorbed in the pores of the nanomesh [2], and the intercalation of hydrogen atoms between the nanomesh and the substrate, thereby lifting the vertical corrugation in the *h*-BN layer [3].

Here we report results from our calculations for the clean nanomesh and with adsorbed molecules. We analyse quantities such as the electronic states and the influence of the lateral variation of the electro-static potential on adsorbates.

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Main Topic: A6 Surfaces

Ab-initio investigations of platinum oxides.

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Platinum oxidizes to form a variety of phases under the oxygen-rich conditions relevant for oxidation catalysis. Using DFT and ab-initio thermodynamics we have investigated these oxide phases, their stability and their role in catalysis. Our calculations predict that, while Pt mainly oxidizes to an inactive PtO_2 phase, the most active phase for CO oxidation is Pt_3O_4. Recent experiments seem to confirm that the most active phases involve platinum in intermediate oxidation states, but an unambiguous identification of the active oxide phase is still lacking.

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Titania-silica interfaces: a combined classical and DFT study.

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In photocatalytic applications of titanium dioxide on glasses, the titania-silica interface not only determines the mechanical stability of the system, but modifies the photocatalytic properties as well. Through a combination of classical and quantum simulations we have investigated realistic interface models in order to elucidate the effect of the interface on the electronic structure of titania. At the interface, the only defects are 5-fold coordinated Ti atoms, whereas all silicon atoms preserve the tetrahedral coordination. Band bending is observed in a neighborhood of the interface, which might be responsible for the modified photocatalytic properties of titania-silica materials. This work is part of the FP7 project ADGLASS.

Electronic properties of intermetallic Ti_3Al

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Abstract

The Ti-Al system mainly has three intermetallic alloys (Ti_3Al, TiAl and $TiAl_3$) based on the Ti and Al compositions. The electronic properties in the intermetallic alloy Ti_3Al are reported in this work. The density of states are computed by using LCAO, SPR-KKR and FP-LAPW methods. In order to examine the charge transfer, the momentum densities are also calculated for the alloy and constituent metals. The present study reveals a charge transfer from Al to Ti atom on alloy formation.

Key Words: Electronic structure, momentum density, DOS, Charge transfer etc.

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Main Topic: T5 Ab-initio Molecular Dynamics

Raman spectra of amorphous phase change materials from first principles

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We investigated the vibrational properties of amorphous phase change materials from first principles. Models of amorphous $Ge_2Sb_2Te_5$, Sb_2Te_3, GeTe and $InGeTe_2$ were generated by quenching from the melt by means of ab-initio molecular dynamics simulations. Sb and Te atoms are in a defective octahedral-like geometry [1,2] in all compounds while coexistence of defective octahedral sites with tetrahedral sites for In and Ge is found in $Ge_2Sb_2Te_5$, $InGeTe_2$ and GeTe. Raman spectra were computed from ab-initio phonons and the empirical Bond Polarizability Model with parameters fitted on ab-initio Raman spectra of reference systems. The calculated Raman spectra are in very good agreement with experimental data [2] and contain signatures of the peculiar local structures of the amorphous phase. In particular, the Raman spectrum of GeTe above 190 cm^{-1} is dominated by tetrahedral structures, while the most prominent peaks around 120 and 165 cm^{-1} are mainly due to vibrations of defective octahedra. The contribution of $GeTe_4$ tetrahedra to the Raman spectra of GST is instead hidden by the much more intense peaks due to vibrations of more polarizable Sb-Te bonds in defective octahedra. The Raman spectra of GST and a-Sb_2Te_3 are actually very similar.

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H_2CO_3 forms via HCO_3^- in water

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The ubiquitous CO_2 and its interaction with water bears enormous significance for the living and non-living systems of Earth. Hydration of CO_2 plays essential roles in various chemical, biochemical and geochemical processes. According to the generally accepted picture of CO_2 dissolution in water, the formation of H_2CO_3 proceeds in a single step, that involves the attack of a water oxygen to the CO_2 carbon in concert with a proton transfer to a CO_2 oxygen. In the present work, a series of ab initio molecular dynamics simulations have been carried out along with the metadynamics technique. Our results indicated that the typical textbook picture of the H_2CO_3 formation in a single concerted step can be challenged. In fact, the simulations revealed a stepwise mechanism: the reaction of a water molecule with CO_2 yields HCO_3^- as an intermediate and a hydronium ion, whereas the protonation of the CO_2 moiety occurs in a separate step representing a well-defined activation barrier towards the H_2CO_3 molecule. This alternative scenario was already taken into consideration decades ago, but subsequent experiments and calculations have given preference to the concerted mechanism. Employing extended periodic models of the CO_2-water system that mimic the bulk aqueous environment, the present simulations yield the complete free energy profile of the stepwise mechanism and provide a detailed microscopic mechanism of the elementary steps. The HCO_3^- formation is found to be the rate determining step of the entire CO2 hydration process. The present findings have important implications. For instance our results may provide new information for the interpretation of kinetic measurements that assumed the one-step formation of H_2CO_3 and the rate laws associated with the decomposition of H_2CO_3. Secondly the kinetic stability of H_2CO_3 demonstrated experimentally in various ways can be readily explained by the consecutive steps forming the overall decomposition process. The present mechanism also supports the recent observation that the main cause of H_2CO_3 instability is acid dissociation.

Nanoscale engineering of surface stress

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Recent experimental studies [1] demonstrated the existence of a stress-induced stripe phase for a submonolayer Pd on W(110). The physical basis of such patterns is a competition between local effects (boundary energy) and long-ranged elastic interactions, as described by the formulation of Alerhand et al. [2] and adsorbate-pattern model theory by Lu and Suo [3]. Here we report our density-functional theory (DFT) results confirming the observed stress anisotropy in Pd/W(110). Furthermore, we discuss the drastic modifications in the mesoscopic pattern when oxygen is added to this adsorbate system. In particular, our calculations reveal an alteration of the stress-anisotropy upon oxygen adsorption on the submonolayer Pd stripes. This change in surface stress with increasing amounts of oxygen is shown to explain the 90° rotation of the stripes observed in a very recent experiment [4]. Lastly, we discuss the issues regarding comparisons between DFT calculations and experiments, such as incommensurability or lack of long-range order [5].

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Main Topic: A11 Other applications

A Theoretical Investigation of Structural, Mechanical and Electronic Properties of some late Transition-Metal Nitrides

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Abstract: The crystal structures, mechanical and electronic properties of some late transition metal-nitrides at different stoichiometries and different structures have been investigated using first-principles density-functional theory. Obtained results were compared with previous calculations and with experiment whenever possible.

1. Introduction

Electronic devices use gold extensively as a conductor due to its chemical stability. However, due to its expensive nature, it is often alloyed with cheaper materials such as nickel, iron and cobalt salt to improve its hardness. Gold nitride was recently synthesized for the first time [1]. The successful production of gold nitride may be advantageous as it is harder than the other alloys. Its improved durability could also mean that thinner gold plating could be used, reducing manufacturing costs.

Very little theoretical work has been done on the structural, electronic and optical properties of gold nitride. In this investigation the structural and electronic properties of some of the group 9, 10 and 11 transition metal nitrides will be investigated within density functional theory. The study of a group of transition-metal nitrides will help to identify the unique properties of gold nitride and/or to highlight other possible transition metal nitrides for use in electronic devices.

2. Calculations Method

In this study, our calculations were based on the density-functional theory (DFT) in conjunction with the projector augmented wave potential (PAW) within the generalized gradient approximation (GGA-PBE), using the Vienna *ab initio* simulation package (Vasp), in which the method is implemented [2]. For a chosen chemical formula, we calculated total (ground-state) energy of each of some possible structures and identify those with the lowest energy; those might be the most likely candidates for the true crystal structure. Equilibrium parameters: lattice constants, cell volume, cell energy, and bulk modulus and its pressure derivative at zero pressure were obtained by fitting energies and cell volumes with the Birch-Murnaghan third-order equation of state (EOS) [3].

3. References

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Main Topic: A7 Spectroscopies

Vibrational Spectroscopy and Density Functional Theory of Intermolecular Hydrogen Bonding in 2-Thiohydantoins.

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The hydrogen bond is probably the most important non-covalent interaction in chemistry and biology, especially as it determines the structure and behavior of biologically important systems and processes. Density functional theory is successfully utilized for the computation of vibrational frequencies and elucidation of structural details of molecules, and is a quite powerful method for studying the effects of hydrogen bonding, because it is almost free to manipulate the hydrogen bonding sites and partners. Vibrational spectroscopic techniques , such as IR and Raman are useful not only in identifying molecules but also in shedding light on molecular structures, at the same time they also reflect changes in surroundings of the molecule and are thus helpful in studying intra and inter molecular interactions.

2-Thiohydantoins (2-thioxo-imidazolizin-4-ones) are the 2-thioxo analogues of hydantoins and the simplest of all its derivatives, which provide useful synthetic intermediates with a wide range of applications such as therapeutics, fungicides and herbicides. This compound carries a thioamide and an amide group in a molecule, providing equal number of proton donor(D) and acceptor(A) in D-A-D-A manner. Because of this structural feature 2-Thiohydantoins (2-TH) are expected to form intricate hydrogen bonding networks in crystals. 2-TH exists as two polymorphs, form A, which is the known stable form1,2 and form B, which is the newly reported form.The intermolecular hydrogen bonds form a finite chain in both the crystal forms and the difference lies in the pattern of hydrogen bond formation.

In the suggested work, the crystal structure of 2-thiohydantoin A and B form was studied for the first time by infrared and Raman spectroscopy and in parallel by X-ray diffraction. We have aimed at explaning the changes that occour in the vibrational spectra as we head from gas phase to solid phase i.e towards a stable configuration, and these changes were interpreted in terms of changes in molecular structure and hydrogen bonding. The geometry optimization of both the forms of TH were performed at the DFT level employing B3LPY using 6-311G(d,p) basis set, The calculated vibrational spectra were analyzed on the basis of potential energy distribution (PED) of each vibrational mode, which allowed us to obtain a quantitative as well as qualitative interpretation of the infrared and Raman spectra.

Main Topic: A9 Chemical Reactions and Kinetics

Surface Precursors and Reaction Mechanisms for the Thermal Reduction of Graphene Basal Surfaces Oxidized by Atomic Oxygen

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The reduction of graphene oxide surfaces yielding molecular CO/CO_2 is studied from first-principles using density functional theory. We find that this reaction can proceed exothermically only from surface precursors containing more oxygen atoms than strictly needed to produce CO/CO_2 in the gas phase. The calculations show that the lowest-energy configurations of multiple O adsorbates do not involve clustering of epoxy groups (the stable form of O adatoms on graphitic surfaces) but always contain lactone groups, either in lactone-ether or ether-lactone-ether form. We identify these lowest-energy structures as the main reaction precursors. The O adatoms near the lactone group catalyze its gasification to CO/CO_2 by reducing the activation energy from above 1.8 eV (from an isolated lactone) to below 0.6 eV (from a lactone-ether). In addition, the residual O adatoms left behind after the lactone gasification, minimize the energy of the graphitic products by saturating the dangling bonds of the resulting defective surface. By analyzing defect-free as well as defective surfaces, we identify a common set of concerted reaction mechanisms in which the formation of the gas products and the saturation of the newly formed C vacancies happen simultaneously. The calculated activation energies are in good agreement with the available experimental data.

Main Topic: T6 Large-Scale and Multiscale Simulations

Atomistic Simulation of Co-doped α-Alumina Interfaces

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Transparent polycrystalline ceramics have many possible promising areas of application form jewelry and the watch industry to wave guides and optical windows. Alumina is particularly interesting because of its high chemical resistance and mechanical properties when compared to other possible ceramic candidates such as yttria and spinel ($MgAl_2O_4$). To achieve high Real Inline Transmittance (RIT) for applications with alumina, fully dense nano crystalline alumina is desired. Doping of alumina with transition elements (e.g. Y, Mg, La) has been an effective tool for controlling the grain size during the sintering step. This is due to the segregation of dopants at the grain boundaries, producing the grain or solute drag effect. In a few studies on creep behavior of alumina, co-doping of alumina has been reported to be even more effective. However, the atomistic mechanisms behind these observations are still not clear and have led to much debate. Harmer et al.[1] explained the additive effect of co-doping by better packing of different sized segregant ions at the boundaries and hence increased site blocking effect. On the other hand, in their DFT calculations, Elsasser et al.[2] observed a favorable coordinative arrangement of dopant ions in the case of co-doping for a very simplified rhombohedral twin boundary of alumina. To extend the preliminary DFT results for more complex interfaces as well as to verify the experimental results, optimization among system size, complexity of the interfaces and computational cost is required. The current simulation study aims to further the understanding of the atomistic mechanisms behind co-doping using atomistic modeling methods. The energy minimization technique[3] based on empirical potentials has been used to create relaxed doped surfaces and grain boundaries. 9 doped surfaces and the same number of grain boundaries were created and allowed to relax to reach a minimum energy configuration and the energy of the relaxed structure was calculated. Results of co-doping studies on these interfaces show an energetically favorable specific coordinative arrangement as well as tendency of co-segregation in case of La and Y co-doped alumina.

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Main Topic: A5 Functional Materials

First principles non-equilibrium Green's function study of Ta_2O_5 atomic switch

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The atomic switches such as Ag_2S, Cu_2S, Ge_xSe_{1-x}, and Ta_2O_5, are promising candidates as resistive-switching devices in both logic and memory circuits[1]. The atomic switches have the M/I/M heterostructure: M is metallic electrodes and I insulator such as oxide, sulfide, or selenide. Appling bias voltages to the structures, low-to-high resistance transition or vice versa occurs, which is the most important property in these switches. Among these switches, Ta_2O_5 is particularly attractive in the light of the compatibility with semiconductor fabrication processes. However, atomistic details of the conduction path in the metallic state have not been clarified yet, as well as the mechanism of the switching from low to high resistance states.

In this work, we have carried out density functional calculations (using VASP) and non-equilibrium Green's function calculations (using ATK) to examine the atomic structures, electronic states and electronic transport properties of the low resistance state of the Ta_2O_5 atomic switch [2]. We mainly considered $Cu/Ta_2O_5/Pt$ heterostructures. Our simulations show that in the case of crystalline Ta_2O_5, Cu atomic chain structures in the solid electrolyte layer work as conduction paths[2]. On the other hand, in the case of amorphous Ta_2O_5, a similar Cu bridge structures has much lower conduction[3]. Structures of conduction paths in the low resistance state and the switching mechanism will be discussed on the basis of the simulation results.

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Main Topic: A11 Other applications

Mechanical properties of icosahedral boron carbide explained *from first principles*

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An exhaustive DFT study of the structural defects of icosahedral B_4C and of their behavior under high pressure has been performed. Among the possible atomic structures, the lowest value of the formation energy with respect to elemental boron and carbon has been found for the *polar* model B_4C^P, which consists of one distorted icosahedron and of one CBC chain. This result, together with the inspection of the vibrational and NMR spectra, has proved that B_4C^P is the proper structural model for B_4C.[1,2] Consequently, B_4C^P has been used as a matrix to isolate the defects. The native defects have been identified and shown to be energetically stable at high pressure. Most vacancy locations in B_4C^P are found to be energetically unstable [3] and only a boron vacancy in the CBC chain is stable. A cluster of these vacancies is shown to induce a dynamical instability of the icosahedra when the pressure is increased, at the onset of the formation of carbon-carbon bonds in the chains. The dynamical failure of shocked B_4C [3] is attributed to the increase in the concentration of these unstable vacancies under plastic deformation [5].

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DFT+U study of oxygen migration processes in nickle doped ceria

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Oxygen migration in ceria-based materials have received extensive attentions due to its application as oxygen donor materials within many types of redox catalysis processes. The motivation of this work is to explore the mechanism of enhanced oxygen migration process of Ni-Ce-O solid solution which possesses strong Ni-Ce interactions at atomic level using GGA+U calculations. Oxygen vacancy migration (six possible pathways) between the nearest neighbors was calculated with activation energies ranging from 0.24 to 0.89 eV. It was found that the most favorable migration path is through the Ni^{2+}-Ce^{4+} pairs. Hubbard-U term have acted on two different sites and sets of orbitals (Ni-d and Ce-f). The main conclusions do not depend substantially on the specific choice of the parameters, as far as they are larger than a minimum value allowing for a correct description of electron localization.

Theory and Methods:
T1 Density-Functional Theory beyond LDA

Applications:
A8 Catalysis and Electrochemistry

Main Topic: A5 Functional Materials

p-type doping and codoping of ZnO based on nitrogen is ineffective: an *ab initio* clue

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While the demand to fabricate p-n homojunctions has made the achievement of p-type ZnO a priority for the photovoltaic industry for many years, the quest for stable and high quality p-type ZnO has still borne no fruit. Nitrogen, the most recommended acceptor, either used in mono- or co-doping only yields frustrating results. We perform first-principles calculations to investigate the p-type nature of boron and nitrogen codoped ZnO [1]. The p-type character can be obtained with the proper clusters, ZnO:(B,N_3). We propose a mechanism that explains the difficulties to synthesize p-type ZnO samples: the formation of N_2 molecules substituting oxygen, which are donors, energetically prevails over any codoping cluster. This mechanism is very general and explains the experimental instability of N-based doping and codoping versus time and temperature.

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