Workshop

Nothing is perfect
The quantum mechanics of defects

Congressi Stefano Franscini
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Program

Organizators' slots
Invited talk: 30 min
Contributed talk: 15 min
Poster session
Round table

	Sunday April 26th
18:30 – 19:30	Welcome drink
19:30	Dinner

	Monday April 27th	
7:45	Breakfast	
8:45 - 9:00	Opening words	
9:00 – 9:30	Nieminen	photovoltaics
9:30 - 10:00	Petretto	
10:00 - 10:30	Zhang	
10:30 - 11:00	Break	
11:00 - 11:30	Gali	open-shell, q-bits
11:30 - 12:00	Bockstedte	
12:00 - 14:00	Lunch break	
14:00 – 14:15	Welcome Address FMV & CSF	
14:15 – 14:45	Komsa	correction schemes
14:45 – 15:00	Kumagai	
15:00 - 15:30	Varvenne	
15:30 - 16:00	Break	
16:00 - 16:30	Levchenko	surfaces
16:30 – 17:00	Deak	
17:00 – 19:00	Poster session	
19:30 -	Dinner	

	Tuesday April 28th	
7:45	Breakfast	
9:00 – 9:30	Biermann	correlations
9:30 - 10:00	Chen	
10:00 - 10:30	Kresse	
10:30 - 11:00	Break	
11:00 - 11:30	Ertekin	
11:30 - 12:00	Neugebauer	phonons
12:00 – 14:00	Lunch break	
14:00 – 14:30	Ramprasad	
14:30 – 15:00	Lany	oxides
15:00 – 15:30	Pacchioni	
15:30 – 16:00	Break	
16:00 – 16:15	Skaervo	
16:15 – 16:45	van de Vondele	
16:45 – 17:45	Round table discussion	
19:30 -	Conference dinner	

	Wednesday April 29th	
7:45	Breakfast	
9:00 – 9:30	Schluger	interfaces
9:30 – 9:45	Colleoni	
9:45 – 10:15	van de Walle	When time does matter
10:15 – 10:45	Break	
10:45 – 11:15	Rohlfing	
11:15 – 11:30	Wiktor	
11:30 – 12:00	Alkauskas	
12:00 – 14:00	Lunch break	
14:00 – 14:30	Robertson	2D systems
14:30 – 15:00	Krasheninnikov	
15:00 – 15:30	Break	
15:30 – 16:00	Freysoldt	phonons
16:00 – 16:30	Pantelides	
16:30 – 16:45	Final words / Prize	

Talks

Computational studies of defects and doping in CI(G)S solar-cell materials

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We present a the results of an extensive investigation of native atomic-scale defects in $CuInSe_2$ (CIS) and related materials relevant for solar-cell applications. We provide insight into mass transport during materials processing and examine the influence of defects in solar-cell performance. We also report results for the effects alkali doping of CIS on materials microstructure and properties.

The emergence of additional defect charge states within hybrid functional approximation: the binary compounds' case.

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When dealing with semiconductors, the importance of point defects comes from the possibility of obtaining electronic levels inside the band gap. In particular, to be able to manage the semiconductor's conductivity, defects which provide acceptor and donor levels close to the band edges should be identified. Density-functional theory can be a powerful tool when trying to select the best candidates that satisfy this kind of constraint, but several problems related with calculations and with the defect itself should be considered. In our case, we have focused on the study of defects with positive charge states that can compensate possible shallow defects that are formed in the system. We have thus made use of HSE hybrid functional [1], which is a key tool for its ability to better reproduce experimental band gaps, to study acceptor defects in II-VI and III-V compounds and observed the presence of stable positive charge states close to the top of the valence band. We have explored the relation of these states with the choice of the α parameter, which determines the amount of exact exchange which is added to the exchange-correlation functional, and with the corresponding shift of the band edges. In the particular case of ZnO, we have considered several acceptor defects that show this property, supporting once more the difficulty of obtaining p-type doping in ZnO.

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Defects in Emerging Electronic Materials

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Recent history of electronic materials research has witnessed a rapid development of new materials ranging from (monolayer-thick) two-dimensional (2D) semiconductors to organic-inorganic hybrid perovskite solar-cell materials. In either cases, understanding the defect formation and their electronic properties is crucial for the eventual industrial applications of these important materials. In this talk, I will first discuss how to accurately determine the defect, in particular dopant, ionization energy in 2D systems using the jellium approximation under the periodic boundary condition – a longtime debating question. An analytic expression for the asymptotic behavior of the Coulomb divergence is derived, showing converged ionization energy as the zero jellium density limit. This formulation is combined with first-principles calculations to determine the ionization energy for a number of dopants in h-BN, MoS_2, and black phosphorus. Second, I will discuss intrinsic defects in organic-inorganic hybrid perovskite $MAPbI_3$, where MA = CH_3NH_3. While a recent theory [1] attributes the outstanding performance of this class of materials to defect tolerance as in $CuInSe_2$ [2], we, however, found that the defect physics in $MAPbI_3$ resides heavily on the strong covalency of I and Pb, despite the ionic nature of the iodine. By forming iodine trimers and lead dimers, deep recombination centers do develop in such materials, although a proper choice of the growth condition can usually circumvent their formation [3]. Still, Pb is considered a toxic substance and the $MAPbI_3$ salt is soluble in water and decomposes in moisture. An alternative is proposed to develop earth-abundant chalcogenide perovskites for photovoltaics [4].

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Ab-initio theory of solid state quantum bits

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The idea of utilising quantum systems to perform complicated quantum mechanical simulations and calculations was raised by Richard Feynman in 1982. This basic idea has initiated new directions in many disciplines and influenced different fields of nowadays physics. Research groups at the very frontiers of physics are actively working on explaining the behaviour and creating viable designs of the building blocks, such as quantum bits (qubits), quantum gates, etc. of would-be quantum computers. One of the most promising candidates for the realisation of a qubit is the *spin of a single point defect in semiconductors or insulators*, which can be considered as a good compromise compared to the solution of other contenders, and has great technical advantages because of the large amount of accumulated experiences with materials processing. The extraordinary properties of some defects such as the famous nitrogen-vacancy (NV) centre in diamond [1], allow optical control of the electron and the nuclear spins even at single defect level. Together with applying static and radio/micro-wavelength electromagnetic fields to them, several quantum operations have been carried out with these systems so far. Additionally, thanks to the achieved ultimate control of electron spins, these point defects can be applied as nanoscale sensing tools. This recent field of research is often called as nanometrology [1].

We show on NV centre in diamond what magneto-optical properties should be determined in order to fully understand the underlying mechanism of qubit operations. We developed and implemented *ab initio* methods [2-4] to calculate the coupling between electron and nuclear spins (hyperfine interaction) and electron – electron spins that can be applied to understand the ground and excited states' [5] fine structure and identify qubits [2,6,7]. We proposed based on *ab initio* (time-dependent) density functional theory calculations that divacancy, Si-vacancy and carbon-antisite vacancy pairs in SiC can be excellent candidates to realize single photon emitters or qubits similar to NV centre in diamond [8,9]. Recently, single defect manipulation of these defects has been demonstrated [10], where divacancy may act as sensitive strain and electric field sensors [11]. We show how *ab initio* theories contributed to the rapid development of the field of qubits realized in bulk and nanostructured materials [12].

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A route to the excitation spectra and spin physics of defects from first principles

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Color centers in semiconductors or insulators show a rich photophysics. Possessing a total electron spin they may be utilized to store quantum information and thus pave the way for the development of solid state quantum computing. The nitrogen-vacancy center (NV) in diamond [1] as well as the di-vacancy [2] and the silicon vacancy [3] in silicon carbide have emerged as promising candidates for implementing solid state quantum bits. Optical excitation of the high-spin ground state and subsequent spin-selective recombination via unknown intermediate low-spin states enables spin-initialization mediated by intersystem crossings. Together with spin-dependent luminescence this provides all-optical control of the defect spins.

Although the photo physics of a vast variety of systems, including defects [4], was successfully addressed in the framework of many body perturbation theory (GW and BSE) and time dependent density functional theory, these approaches here do not provide direct access to the important low-spin excited states. As an approach towards the spin physics of defects we propose an ab initio CI-hamiltonian employing a restricted basis of Kohn-Sham orbitals of hybrid density functional theory and an effective screened coulomb interaction obtained within the constrained RPA [5].

With this approach we analyze the negative NV-center in diamond as well as the di-vacancy and the negatively charged silicon vacancy in SiC. The importance of screening for low-spin multiplets isdemonstrated. It is shown that electron-phonon coupling in the excited statesof the three defects results in a qualitatively different spin physics.

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Electrostatic energy corrections for charged defects in low dimensions

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Charged defect calculations in supercells subject to periodic boundary conditions suffer from strong and long-ranged electrostatic interactions of the localized charge with its periodic images and with the neutralizing background charge. This issue is nowadays well understood in cases where the defect is inside a bulk material, and consequently the total energies can be corrected well with *a posteriori* correction schemes. However, in order to obtain reliable results in cases where the defects are introduced to systems exhibiting inhomogeneous dielectric response, the correction schemes need to be modified accordingly.

We recently introduced a computational scheme to correct for the electrostatic energy errors arising from charged defects interacting with their periodic images in systems of inhomogeneous dielectrics, such as in slab calculations [1] or in the case of 2D materials [2]. Here, an overview of the scheme is given and results from benchmark calculations are presented. Technical issues and future challenges related to the application of the scheme, such as in the construction of the dielectric constant profile in various cases, are discussed. Finally, we reflect on how the issues arising from electrostatics may couple to other changes in physical properties when going from bulk system to low-dimensional system.

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Electrostatics-based finite-size corrections for point defects in semiconductors and insulators

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First-principles calculations of point defects in semiconductors and insulators usually adopt three-dimensional periodic boundary conditions. As a result, the energies of charged defects can include huge errors up to several electronvolt. The main error sources are artificial electrostatic interactions between the defect charge, its periodic images, and background charge caused in finite size of supercells. Recently, Freysoldt, Neugebauer, and Van de Walle (FNV) proposed a scheme to accurately construct the finite-size correction energies *a posteriori* without additional first-principles calculations [1, 2]. The great advantage is that it can be used in conjunction with computationally very demanding first-principles calculations, namely those using hybrid functionals and random phase approximation, which can treat only very limited size of supercells. The original FNV correction scheme is, however, suitable to nearly isotropic systems because the long-range Coulomb interaction is assumed to be screened by a dielectric constant. In addition, it adopts a planar-averaged electrostatic potential for determining the potential offset between the defect-induced potential and model charge potential, which can not be readily applied to defects with large atomic relaxation associated with electric-field screening [3].

To remedy these problems in practice, we extend the FNV scheme by rewriting the formalism in an anisotropic form using a dielectric matrix and use the atomic site local potential as a potential marker [4]. The corrective capability was systematically assessed for 17 defects in 10 materials including layered β-Li_2TiO_3 and h-BN. It is found that our extended FNV scheme excellently corrects the defect formation energies in diverse materials within the errors of less than 0.2 eV for the supercells containing 64 to 128 atoms. The correction scheme was also applied to the native defects in $ZnSnP_2$ recently, which is an alternative photoabsorber material for solar cells [5].

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Point defect modeling in materials : coupling ab initio and elasticity approaches

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Point defects in crystalline solids play a crucial role in controlling materials properties and their kinetic evolution. This is true for both intrinsic defects such as vacancies, self-interstitials, and their small clusters, and extrinsic defects such as impurities and dopants. As a consequence, a proper understanding and modeling of material properties require a precise knowledge of point defect characteristics, in particular their formation and migration energies. To this end, ab initio calculations based on density functional theory and performed with periodic boundary conditions have become a valuable tool. But they are technically limited to a few hundred atoms, so the long-range elastic fields of the defect induce a spurious interaction energy with the periodic images. Convergence of point defect properties can therefore be out of reach, especially for clusters.

Here, we propose to couple ab initio calculations and linear elasticity to get rid of this limitation [1]. We use elasticity theory to model the interaction of the defect with its periodic images so as to withdraw it from the ab initio results. Properties of the isolated defect are then accessible with reduced supercell size. The reliability and benefit of our approach are demonstrated for three problematic cases: the self-interstitial in hcp zirconium, clusters of self-interstitials in bcc iron and and the neutral vacancy in diamond silicon. In all cases, our coupled approach allows a more accurate description of point defects than what could be achieved with a simple ab initio calculation. The effect of different levels of approximation on the elastic correction, as well as the extension of our corrective scheme to the case of charged point defects will be discussed.

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First-principles modelling of bulk and surface defects at realistic temperature, pressure, and doping conditions

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Point defects in oxides and at oxide surfaces play an important role in many applications, including electronics, photovoltaics, and catalysis. However, experimental determination of the concentration of defects at operational conditions is quite challenging. One important parameter influencing defect concentration and charge state is doping, which can occur both intentionally and unintentionally. The effects of doping can be local and global. The local effects occur due to a local change in electronic structure and lattice relaxation around the dopant, while the global effects include charge-carrier conductivity and charge separation on meso- to macroscopic scales [1,2]. Both effects can have a significant influence on defect formation energies and concentration at realistic (T, p) conditions.

Modeling defects in the bulk and at surfaces, in particular charged defects, is also challenging. Charging involves electron transfer between defects and dopants. This makes an accurate description of electronic level alignment (in particular defect level versus Fermi level) crucial. Density functional theory (DFT) with standard exchange-correlation (XC) functionals (LDA and GGA) fails to describe the level alignment correctly, resulting in errors in formation energy up to several electron-volts. Another challenge is to provide physically reasonable charge compensation and remove spurious electrostatic interactions in periodic models, as well as to include lattice relaxation and long-range polarization effects.

In this work, we introduce a first-principles framework that addresses these problems. The framework successfully combines advantages of both periodic and embedded cluster models. First, an optimal hybrid-functional approximation to DFT that accurately describes properties of interest (in particular level alignment, defect formation energies, and adsorption energies) is identified by comparing DFT and many-body perturbation theory (MBPT) calculations for an embedded cluster model. MBPT for both the eigenvalues (fully perturbative or (partially) self-consistent GW) and the total energies (MP2, CCSD, and CCSD(T)) is used for the validation.

Next, the optimal DFT approximation is employed to calculate defect formation energies in different charge states. The standard uniform compensating background method is not directly applicable to charged defects at surfaces, since it introduces the artificial charge density in the vacuum. Recently, an *a posteriori* correction scheme has been developed to address this problem [3]. An alternative approach is to simulate charge-carrier doping by employing the virtual crystal approximation (VCA) [4]. The advantage of VCA is that it allows to simulate a range of finite charge-carrier concentrations, and avoids the effects of the spurious electric field at the surface created by the charge density in the vacuum during the electronic-structure calculations. Thus, realistic charge compensation is provided for both bulk and surfaces. We have extended the use of VCA to the simulation of doping in an all-electron framework [2], while it has also been recently applied in the same context in pseudopotential calculations [5]. The long-range effects of the electronic and ionic polarization are included by either extrapolation to infinite unit cell sizes or by a polarizable force field in the case of cluster models.

Finally, the thermodynamics of the system with (possibly competing) defects is described based on the calculated formation energies. The vibrational contributions to the Gibbs free energies of defect formation are also estimated. The electronic chemical potential (Fermi level) can be obtained self-consistently as a function of the defect concentrations. Most importantly, the large-scale charge separation, resulting in charge-carrier redistribution effects (such as space-charge formation and band bending), is included in the free-energy calculations via electrostatic modelling which takes into account the geometry (bulk or surface) of the system. Using this approach, we demonstrate in particular that charge-carrier trapping at surface defects can lead to the formation of a depletion layer of up to 100 nm thickness at realistic conditions. A similar scheme has been employed to study the effects of charge-carrier doping on the adsorption energy and electron transfer in a hybrid inorganic-organic system [6].

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The effect of the surface on defect states in TiO_2 and diamond

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The functionality of materials is often connected to point-defects in the bulk, or to the surface, which – from the theoretical point of view – is an extended defect. In some cases the interaction of these two types of defects can have a significant influence on particular applications and, at the same time challenge the theoretical description. In this talk I present two case studies: on the oxygen vacancy (V_O) near the surface of TiO_2, and on the negatively charged nitrogen + vacancy center (NV^-) near the surface of diamond. Both problems are treated in a periodically repeated slab geometry, and the screened hybrid functional HSE06 is used to determine electronic properties. While this approach can be regarded presently as “cutting-edge” for systems with valence electrons in the order of 10^3, I will point out certain methodical problems and suggest some solutions.

TiO_2 is used in photocatalysis, where trapping of one carrier type, after photogeneration of an electron-hole pair in the bulk, is an efficiency determining factor. A possible trapping mechanism is the intrinsic formation of small polaron states. We have shown earlier that in bulk anatase-TiO_2 only hole-polarons are formed [1] and V_O is a shallow donor [2]. On the surface of anatase, however, electron-polarons can form, trapping the electrons donated by bulk V_O [3]. The interplay between V_O and the surface changes not only the charge state of the latter but also influences its location. As in all defect studies, coupling to experiments requires the accurate calculation of electronic transitions, which is possible if the generalized Koopmans theorem (gKT) is satisfied for the chosen exchange functional [4]. In the context of this study, I will address the question, how the HSE06 functional (so successful in this respect in bulk-TiO_2) fulfills the gKT near the surface.

The NV^- center of diamond is being under intense investigation lately due to its potential for application in quantum information technology, nano-sensing and bio-labeling. All these depend on the strong, room-temperature, visible photoluminescence (PL) of NV^- centers very near to the surface. However, blinking or even bleaching of this PL has been observed in connection with various surface terminations. Our calculations could explain these phenomena in terms of stress-induced surface states of strongly oxygenated or fluorinated surfaces (with positive electron affinity), and in terms of image states due to the negative electron affinity of hydrogenated and hydroxilated surfaces, respectively [5]. The interaction of the image states with a near surface NV^- center is of particular interest methodically, pointing out the necessity of self-consistent charge correction schemes.

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Electronic correlations from first principles – Is nothing perfect?

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The field of electronic structure calculations for materials with strong electronic Coulomb correlations has witnessed tremendous progress in recent years due to the development of combined electronic structure and many body theory. We will give an introduction to the field, illustrated by examples of rare earth compounds [1], transition metal oxides [2], and adatom systems on surfaces [3]. On these examples we will discuss the different flavors that the consequences of electronic Coulomb correlations can take, and connect them to current developments and open challenges. In particular, we will outline recent considerations on a double counting-free interfacing of ab initio techniques and many-body theory [4]. These ideas also suggest a new view on the Kohn-Sham band structure of density functional theory for weakly correlated systems [5].

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First-principles determination of defect energy levels through GW

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In this talk, we discuss the theoretical determination of defect energy levels in semiconductors and insulators within the GW scheme [1,2]. Important aspects underlying the GW scheme are addressed, including the finite-size correction, the self-interaction of GW, and the dependence of calculation paths [3]. We demonstrate that for localized defects, defect levels obtained in the GW scheme are in good agreement with those calculated in the total-energy scheme using (semi)local or hybrid density functionals, provided a common potential reference is adopted [3]. This correspondence highlights the critical role of band-edge positions in the determination of defect energy levels within the band gap. The quality of theoretical band-edge positions is further assessed through the calculation of band-offsets at semiconductor heterojunctions [4] and of ionization potentials at semiconductor surfaces [5].

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Cubic scaling algorithm for the random phase approximation: applications to defects

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The random phase approximation (RPA) to the correlation energy is among the most promising methods to obtain accurate correlation energy differences from diagrammatic perturbation theory at modest computational cost. The calculations are, however, usually one to two orders of magnitude more demanding than conventional density functional theory calculations.

Here, we show that a cubic system size scaling can be readily obtained, which reduces the computation time by one to two orders of magnitude for large systems. Furthermore, the scaling with respect to the number of k points used to sample the Brillouin zone can be reduced to linear order. In combination, this allows accurate and very well-converged single-point RPA calculations, with a time complexity that is roughly on par or better than for self-consistent Hartree-Fock and hybrid-functional calculations [1].

The present implementation enables new applications. Here, we apply the RPA to determine the energy difference between diamond Si and β-tin Si, the energetics of the Si self-interstitial defect and the Si vacancy, the latter with up to 256 atom supercells. We show that the RPA predicts Si interstitial and vacancy energies in excellent agreement with experiment and diffusion Monte Carlo results. Si self-interstitial diffusion barriers are also in good agreement with experiment, as opposed to previous calculations based on hybrid functionals or range-separated RPA variants [2].

The talk will also cover a critical discussion of the limitations of the RPA and possibly improvements of the RPA, as well, as of errors introduced by the pseudopotential or related projector augmented wave approximation [3].

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A random walk through point–defect electronic structure: insights from quantum Monte Carlo

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Recently, our group has been exploring the application of quantum Monte Carlo methods to predictive modeling of defect energetics, thermal transition levels, and optical ionization energies in semiconductor materials. Quantum Monte Carlo methods are a suite of stochastic tools for solution of the many-body Schrodinger equation. In principle, thanks to a direct treatment of electron correlation they are capable of providing highly-accurate, parameter-free, and systematically improvable calculation of defect properties. In this presentation, I will give a brief overview of the method, and then discuss some of the successes we have had – and the challenges that we struggle with – in the application of this method. Examples include (i) phase stability in manganese oxide polymorphs, (ii) nitrogen defects in zinc oxide, and (iii) Ga DX center defects in zinc selenide. In most cases, we find that the QMC methodology provides results in agreement with other beyond-DFT methods. Generally we find that the use of a direct, many-body approach gives insights to the challenges underlying defects in semiconductors. Additionally, we are developing some tools for statistical analysis of the QMC many-body wave functions, which can provide some diagnostic assessments to reveal the physics that may be missing from other modeling approaches.

Point Defects at Finite Temperatures

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The Gibbs free energy of point defect formation is a critical quantity allowing e.g. to include such defects in phase diagrams. However, an accurate determination of defect formation energies over the entire temperature window, i.e. from T=0 K all the way up to the host melting temperature, is challenging both for experiment and theory. Recent methodological advances provide now the opportunity to compute all these excitation mechanisms with high precision on a fully ab initio basis, making it possible to derive free energies for bulk systems and defects up to the melting temperature. Applying these approaches to vacancies in fcc metals we were able to derive vacancy formation energies over the entire temperature range. We find that non-Arrhenius effects are unexpectedly large, are in a temperature region not accessible to experiment and qualitatively affect our understanding of point defect formation energies and entropies. Particularly, it will be shown that hitherto reported defect energies and entropies are off by 10-20% and an order of magnitude, respectively, calling for a revision of commonly used data sets.

Defects in Dielectrics, and Implications for Dielectric Breakdown

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Polyethylene (PE) is an important insulation material that has found widespread use in electrical applications including transmission line cables and capacitors. The electrical performance of PE over the long term is affected by impurities and chemical defects that are originally part of the material, as well as those that are created progressively with time. Such defects can introduce charge carrier (or defect) states within the band gap of PE, can act as "traps" and sources of charge carriers, catalyze further damage, and can deleteriously affect the overall conduction behavior of the insulator.

The best evidence for the presence of chemical defects (especially in PE) is provided by a variety of electro-, photo- and chemi-luminescence measurements. Nevertheless, assignment of the luminescence emission bands to specific defect types is never straightforward, and an alternate check of whether a particular defect will lead to a particular emission peak or band is highly desired. Here, we go beyond the single-particle picture of defect levels in PE. The combination of computations undertaken, including the determination and usage of charge transition levels (rather than the one-electron levels) and the accurate band edge and gap descriptions [1], allow us to directly and quantitatively connect with available luminescence data for PE.

In addition, a microscopic mechanism (based on *ab initio* molecular dynamics simulations) governing the initiating steps in the high-field degradation of PE is proposed that lead to defects most predominant in luminescence measurements [2]. It is assumed that electrons, holes and excitons are present in the system. Their dynamics and recombination lead to bond cleavage and the formation of chemical defects.

Finally, a first principles method for estimating the *intrinsic* breakdown strength of insulating materials will be presented [3]. This method is based on an average electron model and assumes that the breakdown occurs when the average electron energy gain from the electric field exceeds the average energy loss to phonons. The approach is based on the direct integration of electronic scattering probabilities over all possible final states, with no adjustable parameters. The computed intrinsic breakdown field for several prototypical materials compares favorably with available experimental data. This model also provides physical insight into the material properties that affect breakdown and can speed up recent attempts at rational electric field-tolerant dielectrics design [4].

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Defects and doping in semiconductor alloys

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The computational study of defects in semiconductors has so far had a strong focus on prototypical systems, serving to benchmark the computational approaches. Recent advances, leading to the feasibility of hybrid functional and GW supercell calculations, have significantly reduced the uncertainly of predictions for defects. These developments encourage the study of more complex systems beyond prototype systems, and ultimately, to include the defect properties in the computational design of novel materials.

In a recent study [1], we have shown for ionized donor and acceptor defects in various semiconducting oxides and nitrides, that the formation energies of calculated by standard density functionals (GGA) and by hybrid functionals (HSE) come into close agreement, when consistent reference energies for the valence band maximum and for the elemental chemical potential are used. This finding justifies the use of efficient density functionals for large and complex systems, where converged hybrid functional calculations are presently unfeasible.

As an application of defect calculations, we are considering the defect equilibrium in heavily doped wide gap semiconductors, such as ZnO:Ga. In this case, the association of pairs and complexes between dopants and compensating defects is decisive for the quantitative prediction of the carrier concentrations [2]. The dopant-defect interaction is also important for the doping of Ga_2O_3, which receives currently high interest due to its semiconducting properties despite the large band gap close to 5 eV.

Doping beyond the dilute limit leads into the regime of aliovalent alloying, a potentially rich area for design and discovery of novel semiconductor materials, in particular in the thin-film form where compositions outside the thermodynamic phase diagram can be realized. We are considering the alloying of Cu_2O with divalent cations Mg, Zn, Cd, and the isovalent chalcogen anions S, Se [3]. Here, the chemical substitutions change the band gap and band-edge energies considerably, which causes a composition dependence of the defect formation energy. The modeling of a partial defect equilibrium then yields a prediction of both the band gap and electrical properties as a function of the alloy composition.

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Theory of magnetic impurities in oxides. Problems (and solutions?)

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Dopants in insulating and semiconducting oxides are of fundamental importance for the design of new materials and often result in the presence of holes or electrons trapped at particular sites. The proper identification of these paramagnetic centers is crucial for the understanding of the optical, magnetic and transport properties of oxides. Here we discuss two sets of dopants that result in the presence of magnetic impurities. Al and Ga ions replacing a metal cation in SiO_2, TiO_2, ZrO_2, and HfO_2 will be discussed based on DFT calculations using hybrid functionals and the results will be compared with electron paramagnetic resonance, EPR, measurements. This provides a clear clue on the nature of holes in the O 2p valence band in these materials. The second example is related to N-dopants in TiO_2, ZnO and MgO. Here nitrogen can enter as interstitial or can replace an anion in the material leading to isolated magnetic defect centers. Also in this case a comparison with EPR data allows one to assess the accuracy of the DFT calculations. At high N-dopant concentrations the occurrence of a magnetic ordering has been suggested in some of these materials, which implies the existence of magnetic interactions between the isolated defects. While the use of hybrid functionals allows one to properly describe the nature of isolated magnetic defects in oxides, no magnetic ordering is predicted at this level of theory and for the dopant concentrations used in experiments. The problems related to the theoretical treatment within DFT of magnetic impurities in insulating and semiconducting oxides are discussed.

Unconventional oxygen point defects in hexagonal $YMnO_3$

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Hexagonal manganites have attracted considerable attention due to their multiferroic properties [1, 2], but has also recently shown promise for energy technology purposes. Due to their layered crystal structure, the hexagonal manganites can accommodate interstitial oxygen, which are not common in perovskites. Hexagonal $Dy_{1-x}Y_xMnO_{3+\delta}$ can accommodate excess oxygen up to $\delta < 0.35$ at relatively low temperatures of 250-400 ºC [3], opening the possibility for use as oxygen storage materials at much lower temperatures than the present state-of-the-art materials [4, 5]. Oxidation of manganese ions is a possible charge compensating mechanism which could give holes in the valence band of $YMnO_3$, and hence give rise to p-type semiconductivity [6].

Here we investigate the possibilities for accommodation of interstitial oxygen in hexagonal $RMnO_3$ by Density Functional Theory calculations, addressing the defect energetics lattice distortions and electronic structure. The unusual nature of *enthalpy stabilized* defects does not conform with the conventional definition of point defects. The perfect reference structure of hexagonal manganites must thus be redefined in order to fit the usual thermodynamic framework for point defects.

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Polarons and other defects in the bulk and near the surface of TiO2

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Defects in TiO2 are important for various technologically important systems. First, we will revisit the nature of polarons in both anatase and rutile. We will present a careful study of system size effects and show that polarons are stable in anatase even if a standard PBE0 functional (25% Hartree-Fock exchange) is employed.[1] Next, we will report on a RPA investigation of these polarons, and in particular pay attention to the starting orbitals employed. We find that the RPA results are relatively insensitive to the precise nature of the hybrid functional employed, but that GGA starting orbitals are not suitable.[1] Finally, we consider surfaces of TiO2, and discuss the nature of surface bound species. We highlight the important difference between UHV and bulk interface systems.[2,3,4]

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Defect properties in amorphous oxides and at interfaces

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Defects in amorphous oxides, at interfaces of different oxides and at interfaces of oxides with metal substrates are important for a wide range of applications. In this presentation I will discuss how structural disorder and Fermi level position in the system determine the structure and properties of defects, some of which are nonexistent in the crystal phase. First, I will give an example of electron trapping in the bulk amorphous SiO_2 and at interfaces. I will show how using classical and ab initio calculations we demonstrate that extra electrons can be trapped in pure amorphous SiO_2 (a-SiO_2) in deep band gap states and predict the distribution of their properties [1]. The optical and EPR spectra of these centres are calculated using an embedded cluster method and TD-DFT. Next I will explain how slow degradation of MOSFETs can be explained by the relatively slow structural re-arrangements of the defects caused by the captured injected electrons. To help identify these defects we used a realistic $Si/SiO_2/HfO_2$ stack model to calculate the relative energies, thermal activation energies between like charge states, and tunneling barriers for electron trapping/detrapping for oxygen vacancies with one or two additionally trapped electrons. Finally, I will discuss challenges in predicting the electron transfer between metal substrate and point and line defects in oxides. Most of previous theoretical studies of defects at metal/oxide interface used LDA and GGA functionals, which often predict wrong band offsets and electron localization in defects due to self-interaction error. Although hybrid functionals are known to reliably predict band gaps in oxides and electron localization in defects and polarons, accurately predicting the electronic structures of defects at metal/oxide interfaces requires a method which gives equally good descriptions of both metal and oxide. The recently developed auxiliary density matrix method implemented in CP2K code allows us to use a GGA functional to describe the metal and a hybrid functional to describe the oxide in the joint metal/metal oxide interface system [2]. We applied this approach to studying oxygen vacancies in rough MgO layers and clusters on Ag (111). We obtained much more accurate band offset than by using GGA and more accurate electron localization than using GGA+U. Unlike in previous GGA calculations, we were able to predict the relative stabilities of different charge states of oxygen vacancies in MgO as a function of their position with respect to the interface with Ag. This provides a new approach to determining charge transition levels of defect at interfaces.

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Origin of Fermi-level pinning at GaAs surfaces and interfaces

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GaAs shows high electron and hole mobilities and is the prototype channel material for future CMOS technology, but Fermi-level pinning occurring at the interface with typical oxides hinders its widespread use [1]. Through first-principles simulation methods, we assign the origin of Fermi-level pinning at GaAs surfaces and interfaces to the bistability between the As−As dimer and two As dangling bonds (DB), which transform into each other upon charge trapping. We show that the dimer/DB defect can naturally be formed both at GaAs surfaces upon oxygen deposition and in the near-interface substoichiometric oxide. Through the use of the electron counting rule, it is inferred that the two defect configurations represent opposite charge states, lending support to a Fermi-level pinning mechanism based on amphoteric defects. The Fermi-level pinning at both GaAs surfaces and interfaces is described within a unified picture, wherein the role of As antisites is elucidated [2]. The present assignment offers atomistic insight for the design of suitable passivation routes towards the widespread use of III-V materials in electronic-device technology.

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Defects as nonradiative recombination centers

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Point defects or impurities can act as channels for nonradiative recombination in semiconductors, severely impacting the efficiency of devices such as light-emitting diodes. In spite of a long history (dating back to Shockley-Read-Hall), the quantitative evaluation of nonradiative recombination has proven very challenging. We have developed a first-principles methodology [1] to determine nonradiative carrier capture coefficients, considering transitions that occur via multiphonon emission. All parameters in the theory, including electron-phonon coupling matrix elements, are computed consistently using state-of-the-art electronic structure techniques based on hybrid density functional theory, providing a significantly improved description of bulk band structures as well as defect geometries and wavefunctions. A crucial ingredient to the methodology is the calculation of electron-phonon coupling matrix elements between a defect state and a perturbed bulk state. Carrier capture processes at charged centers are treated with proper inclusion of the impact of long-range Coulomb interaction on scattering states in the framework of supercell calculations. Our approach allows us to produce insight into the physics of defects in wide-band-gap semiconductors, such as the strength of electron-phonon coupling and the role of different phonon modes. Combined with accurate calculations of defect formation energies and charge-state transition levels [2], the calculation of nonradiative capture rates for electrons and holes enables evaluating Shockley-Read-Hall coefficients, thus allowing us to identify specific defects in nitride semiconductors that play a key role in limiting the efficiency of light-emitting diodes for solid-state lighting [3].

Work performed in collaboration with A. Alkauskas, Q. Yan, C. E. Dreyer and J. L. Lyons.

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Optical excitations of defects from many-body perturbation theory

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Optical spectra offer a unique way of probing imperfect condensed matter, including surface states, adsorbates, and point defects. The underlying electronic excitations can be described by many-body perturbation theory, in particular by the Bethe-Salpeter equation for electron-hole pair states on the basis of a preceding GW calculation. This approach includes all relevant effects from electronic exchange and correlation, as well as, from the non-locality of dielectric screening. Furthermore, the localized nature of defect states causes strong interrelation with the geometric structure, leading to spectral broadening and Stokes shifts. We discuss such issues for a number of examples, including point defects in calcium fluoride [1], coupled carbon nanotubes [2], and nanotubes with defects and adatoms [3]. Owing to the complexity of the systems and the required large simulation cells, numerical simplifications and approximations are highly desirable, like a recently developed LDA+GdW approach, which may allow to access larger system size [4].

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Coupled first-principles and experimental positron annihilation study of defects in silicon carbide

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One of the experimental methods that can be used to study open volume defects is positron annihilation spectroscopy (PAS). This non-destructive technique consists in recording the radiation emitted at the beginning and the end of life of positrons in a material and deducing the properties of the positrons and the electrons with which they have annihilated. Vacancies can trap positrons and can therefore be detected by e.g. changes in the lifetime of positrons in the material. To identify the types of defects present in the examined materials, however, comparison with calculated positron lifetimes or with results of other characterization techniques is required.

Positron lifetimes can be calculated using two-component density functional theory [1], which is a modification of the density functional theory. We performed self-consistent calculations of positron lifetimes of fully relaxed monovacancies and vacancy clusters in two polytypes of silicon carbide – $3C$-SiC and $6H$-SiC [2,3]. The calculation results have been used to study the temperature dependence of 12 MeV proton irradiation induced point defects in $6H$-SiC. Coupling of the experiments and calculations enabled the identification of a negative silicon vacancy in the as-irradiated samples, with a positron lifetime of 218 ps. The monovacancy is annealed between 400^{o}C and 700^{o}C. This process involves vacancy migration and formation of the $\mathrm{V_C}+\mathrm{V_{Si}}$ cluster, with a positron lifetime of 235 ps.

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Radiative recombination at defects

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In this work we have developed first-principles techniques to describe and quantify radiative recombination at defects in semiconductors. We have addressed two issues: radiative carrier capture rates (cross sections) and the polarization of luminescence [1], as well as the vibrational structure of defect luminescence bands [2,3]. In order to accurately describe the electronic structure of both the defect and the host material we have employed hybrid functionals.

Using defects in GaAs, GaN, and ZnO as examples, we have demonstrated that in many cases the transition dipole moment depends rather weakly on the geometry of the defect even in the case of large lattice relaxations, enabling the use of the Franck-Condon approximation. The resulting capture coefficients and the polarization of light are in a very good agreement with experimental measurements for defects for which reliable data exists [1].

Concerning the vibrational structure of defect luminescence bands, we have applied different approaches in the case of strong [2] and medium [3] electron-phonon coupling strengths. When the coupling to the lattice is strong (defects in GaN and ZnO), as quantified by Huang-Rhys factors $S>>1$, we have shown numerically that the system can be treated using an effective one-dimensional configuration-coordinate diagram. In all cases calculated luminescence spectra agree closely with experimental data. In the case of intermediate coupling to the lattice ($S\sim1$) all the phonon modes have to be included explicitly. We achieve this using the generating function method. For our test case, the nitrogen-vacancy center in diamond, we describe the fine features of the luminescence lineshape to a very high precision.

Our work thus demonstrates the power of first-principles methods to describe the parameters pertaining to radiative recombination at defects. Such calculations not only provide new insights in the physics of defects, but they will also aid the identification of unknown defects, of which there are plenty.

The work has been performed in collaboration with C. G. Van de Walle, Q. Yan, C. E. Dreyer, and J. L. Lyons.

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Defects and Schottky Barriers in MoS_2 and other Transition Metal Dichalcogenides

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Transition metal dichalcogenides (TMDs) are 2-dimensional semiconductors that have a band gap, unlike graphene. They are therefore of use in field effect transistors (FET), and may be useful in post-CMOS devices such as tunnel FETs (tFETs). However, at present, their devices are limited by high contact resistances, due to Schottky barriers at the contacts. This might be because vacancy states pin the Fermi level within the gap. Also, MoS2 seems to only give n-type devices, whereas both polarities are desired. We show that the anion vacancy is the dominant defect in TMDs. It states lie in the upper gap for MoS2, but can be near midgap for other TMDs like WeSe2. Despite the van der Waals bonding between layers, it is found that TMDs do obey the Metal Induced Gap State model of Schottky barriers, with relatively strong pinning (S~0.3) in the absence of defects. Substitutional impurities are not so effective at doping, some acceptors are shallow but few donors are shallow.

Defects in two-dimensional materials: their production under ion and electron irradiation, evolution and properties from first-principles simulations

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Two-dimensional (2D) materials such as graphene, hexagonal boron nitride, transition metal dichalcogenides (TMDs) and silica bilayers have recently received lots of attention due to their unique properties and numerous potential applications. All these materials have defects, which naturally affect their characteristics. Moreover, defects and impurities can deliberately be introduced by irradiation or chemical treatment to tailor the properties of these systems.

In my talk, I will present the results of our first-principles theoretical studies [1-5] of defects in 2D systems, compare them to the experimental transmission electron microscopy data, and discuss how defect and impurities can be used to engineer the electronic structure of 2D materials. I will also touch upon our simulations of defect production under ion [6,7] and electron [1] irradiation. For the former, the Ehrenfest dynamics and time-dependent density functional theory was shown to be an accurate approach beyond the Born-Oppenheimer approximation to calculate electronic stopping power in graphene [7]. The latter (specifically the knock-on damage) can quantitatively be described [1] by DFT molecular dynamics and McKinley-Feshbach formalism. I will also touch upon Stone-Wales transformations in graphene and silica bilayers [4], 2D materials with the hexagonal symmetry, and address the equivalent transformations in 2D materials with the trigonal symmetry, such as BN or TMDs. I will present the theoretical data on defect evolution, migration and agglomeration and compare the theoretical results to the available experimental data. Besides, I will discuss mixed TMDs, such as MoS_{2x} $\mathrm{Se}_{2(1x)}$, which can be referred to as 2D random alloys. Our simulations [8] predicted that 2D mixed ternary random alloy $\mathrm{MoS}_2/\mathrm{MoSe}_2/\mathrm{MoTe}_2$ compounds are thermodynamically stable at room temperature, so that such materials can be manufactured by CVD or exfoliation techniques. Moreover, our simulations indicated that the direct gap in these materials could continuously be tuned depending on relative component concentration, as confirmed later on by several experimental groups. Finally I will touch upon defects in truly one-dimensional systems ionic crystals, that is chains of CsI [9] and BN [10] atoms.

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The vibrational properties of charged defects

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When wide-gap semiconductors or insulators are grown at elevated temperatures, point defects and impurities are incorporated in non-negligible concentration. The equilibrium concentration can be estimated from theoretically computed formation energies. Yet, these calculations typically exclude explicit temperature effects for simplicity. The common reasoning is that the contribution from vibrational entropy are expected to be only a fraction of kT per degree of freedom.

Yet, in ionic materials, Coulomb interactions are long-ranged, and a point defect may affect a large number of degrees of freedom in its vicinity. Therefore, I will present a theoretical framework to assess the changes in the vibrational density of states due to the presence of the defect. For this, the dynamical matrix of high-level theoretical approaches such as density-functional theory is mapped onto a classical model combining Coulomb terms and short-range harmonic interactions. Special attention is paid to capturing the anisotropy of the Born effective charge tensors, which develop near defects even in otherwise perfectly isotropic host materials.

Using this approach, I will demonstrate that defects induce well-localized changes in the interaction model, which can therefore be parametrized with rather small computational effort. Moreover, the convergence with respect to supercell size is studied, revealing interesting subtleties for charged defects. Applying the scheme to a model defect in MgO shows that the magnitude of vibrational contributions to the finite-temperature formation energy is larger than commonly assumed.

Multiphonon carrier capture and carrier scattering by defects in semiconductors and a novel method to calculate mobilities

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The theory of multiphonon carrier capture by defects in semiconductors was debated extensively in the 1970s, but the issue remained unresolved, with no clear guidance as to how to perform first-principles calculations of capture cross sections. The theory of multiphonon inelastic carrier scattering by defects is nonexistent, but such processes are key to describing hot-electron induced defect activation that is a major cause of power-device degradation. In this talk I will first summarize how, by combining electrical measurements and density functional calculations it has been possible to identify the specific defects and processes that cause hot-electron degradation (primarily through hydrogen release from pre-existing passivated defects or defect reconfiguration) [1]. Engineering-level modeling of device-degradation data requires knowledge of capture cross sections and/or inelastic scattering cross sections as functions of energy, temperature, currents, etc. [2]. I will describe the development of a comprehensive theory of inelastic multiphonon scattering by defects, including carrier capture, and implementation of the theory for carrier capture cross sections for prototype defects [3]. Calculations of carrier mobilities is another related topic that has remained largely unexplored. Engineering-level modeling is based on model mobilities calculated by invoking phenomenological descriptions of scattering in the Born approximation. Defect relaxations, however, cannot be described accurately in this approximation. I will report the development of a new approach based on complex wavevectors within energy band theory ("complex energy bands"), which does not entail the Born approximation [4]. Results for impurity- and phonon-scattering-limited mobilities will be described. Acknowledgements: Collaborators in this work are the coauthors in the cited papers. The work was supported by a U.S. Office of Naval Research MURI grant, the U.S. Air Force Office of Scientific Research Hi-REV program, the Samsung Corporation through the GRO program, and the U S. Department of Energy, Office of Science, Basic Energy Sciences.

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Posters

Charge transition levels of point defects in crystalline materials through thermodynamic integration

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Thermodynamic integration of vertical energy transitions along a fictitious path between reactant and product is commonly used to compute the free energy associated to redox potentials of species in aqueous solution [1]. On the other hand, charge transition levels for charged defects in crystalline materials are usually obtained as a difference between the total-energies of the two involved charge states. In this work, we establish a connection between these two methods focusing on the adiabatic +/0 charge transition level of a chlorine vacancy in NaCl. We obtain the charge transition level from the integration of vertical energy gaps computed on a fictitious trajectory leading from the neutral charged defect to the positively charged one. Hence, the accuracy of this method can be compared to the conventional approach based on total energies [2,3]. The comparison is carried out with both a code based on plane-waves basis sets, such as Quantum-ESPRESSO, and a code based on mixed plane-waves/atomic basis, such as CP2K, which is typically used for free energy calculations. The established link between these two methodologies provides insight into the way detailed knowledge (finite size corrections [4], alignment issues [5]) acquired from the study of charged defects can be transferred to the calculation of redox levels in aqueous solution.

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Calculation of the optical properties of the nitrogen-vacancy center in diamond using a configuration interaction approach

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We present calculations of the optical properties of nitrogen-vacancy (NV) centers in diamond [1]. In particular, the NV center, because of the ability to control and manipulate its charge state, is emerging as a promising candidate in the fields of quantum information, quantum processing and high resolution magnetometry. These applications require a precise prediction, and understanding, of the optical properties of shallow NV centers embedded in nanosized diamonds including their many-body electronic multiplet structure. We utilize a new approach, the atomic effective pseudopotential (AEP) method [2], which is based on the local density approximation (LDA) and an empirical correction to the quasiparticle band structure, to accurately model the NV center in different charge states in the diamond matrix. Starting from the AEP wave functions, we calculate many body effects using a configuration interaction approach that we adapt to the treatment of defects. We highlight the effect of screening in the calculation of the Coulomb and exchange integrals. Our results of the optical spectrum of isolated NV systems, calculated on large supercells, show very good agreement with previous experimental reports, including an accurate reproduction of the experimental zero phonon line.

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Strain-defect interaction in oxides

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We recently established that epitaxial strain in perovskite thin films or heterostructures can not only be accommodated by changes in structural parameters such as bond-lengths or octahedral rotation angles, but also by the formation of point defects [1]. Here we will explore the generality of this concept for perovskite oxides of different compositions and with different functionalities as well as in binary rock-salt oxides. Based on our density functional theory calculations of the strained materials, the resulting point-defect-induced changes in properties such as the electronic conductivity, ferroelectricity and magnetism will be discussed.

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Oxygen Interstitials in Vanadium Sesquioxide Nanocrystals with a Metastable Bixbyite Crystal Struture

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We have recently stabilized a new polymorph of vanadium sesquioxide (V_2O_3) with a bixbyite crystal structure [1]. The bixbyite polymorph was only recently discovered to exist in vanadium oxides, and only a few instances of its formation have been reported, hence there is still much to be learned about its properties [2]. Spontaneous oxidation is observed in bixbyite nanocrystals upon exposure to air, as evidenced by an expansion in lattice coupled with an increase in weight. In nanocrystal form, nonstoichiometry is tolerated up to levels of $\delta=0.5$ (in $V_2O_{3+\delta}$) before transformation to a different phase occurs. Density functional theory is used to understand the energetics of this new polymorph in relation to the stable monoclinic and corundum phases of V_2O_3 as well as to study oxygen interstitial formation in bixbyite and its effect on crystal structure.

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Water Oxidation at Exfoliated Transition Metal Oxides

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A central reaction for the generation of renewable energy carriers is the splitting of water into oxygen and hydrogen. The hydrogen evolution reaction is efficiently catalyzed by a number of electrocatalysts such as Pt[1]. This is in contrast to the oxidation of water to oxygen. This half reaction is indeed the main source of overpotential. Large scale applications of water splitting are further complicated by the fact that state of the art oxygen evolution catalysts are based on rare Ru and Ir oxides. Thus, new efficient catalysts based on more abundant elements are required.

Over the last years numerous new materials were proposed. Among those manganese[2] and cobalt oxides[3] were identified as promising candidates. Improvements beyond the activity of the pure oxides were predicted and found by mixing with other transition metal oxides, i.e. NiFe or CoFe[4,5,6]. A special class of water oxidation catalysts are layered materials such as β-$Co(OH)_2$[6] or Birnesites[2]. These electrocatalysts show already a promising activity as bulk materials[2,6]. Further improvements were reported upon exfoliation[6] and mixing with non inert ions such as Ni[6].

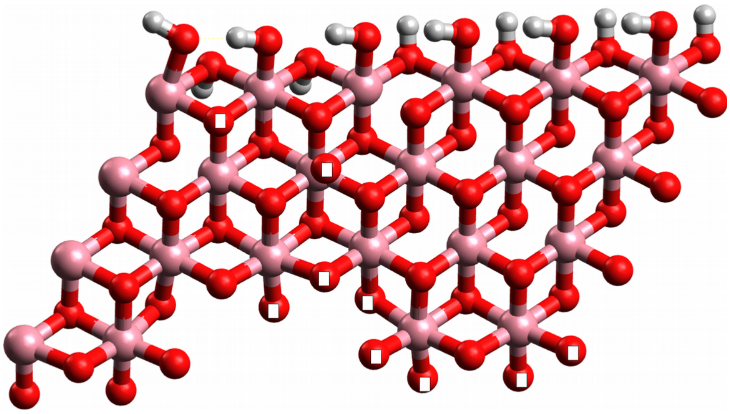
Figure 1:The exfoliated β-CoO_2 model system is depicted. All considered sites are marked by white squares.

The central aims of this work are twofold. First it is aimed at understanding the effects responsible for the improvements found upon exfoliation by means of Density Functional Theory (DFT) calculations. Additionally the influence of doping with non inert ions will be studied. Results obtained for a β-$Co(OH)_2$ test system (see Figure 1) will be presented. The activity of different surface sites present at exfoliated sheets comprising terrace, edge and corner sites will be considered and compared to the activity of multi-layered β-$Co(OH)_2$. A comparison to the activity of more compact cobalt oxides such as Co_3O_4 will be given. Having established a general understanding on the activity of exfoliated cobalt oxide sheets the influence of doping with non-inert ions such as Ni is considered. Indirect influence of the dopants on the stability of the water oxidation intermediates as well as their direct participation through a binuclear[4] or hydrogen transfer mechanism[7] will be discussed.

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Dynamics of impurities in silicon: from DFT to defect engineering

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The highly purified solar-grade silicon is still relatively expensive, and the dominant fraction of silicon is produced by Czochralski(Cz) method. Such material is far from being a clean silicon crystal. Besides dopant atoms added there by purpose to make it n- or p-type semiconductor, it contains impurities naturally included there from the initial melt and crucible. Impurities can interact with each other, with dopants and with structural defects produced by irradiation damage that sometimes results in substantial changes of the formal material's properties.

The structural and dynamical properties of impurities, dopants and complexes play an important role in the material macroscopic properties : boron oxygen complex is responsible for the Light Induced Degradation of the solar cells for instance, or vacancy and oxygen can form A-centres that are recombination centres. We present here two studies that investigate the diffusion properties of oxygen and other light element in silicon.

First, we evidence that p-type doping of silicon leads to an important increase of O monomer diffusivity in low temperature regime. We explain the enhancement 0.4 eV by a charge assisted mechanism [1]. We also exclude other possible sources such as strain or other dopants. Monomers thus become the primary diffusion species in p-type heavily doped silicon, contrary to undoped silicon where dimers diffuse at low temperatures.

Second, we propose an out-of-equilibrium method [3] to study the concentrations of a wide variety of complexes based on an *ab initio* data base of formation and migration energies. Vacancy-oxygen complexes kinetics in presence of carbon and germanium are studied as a model system. Results are in good agreement with experimental data [2]. More importantly, it gives access to the sequence of chain reactions by which oxygen and carbon related complexes are created in silicon. The understanding of these reactions is a key to developing point defect engineering strategies to control such defects and thus semiconductors properties.

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Defect ordering and defect-domain wall interactions in $PbTiO_3$: A first-principles study

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The properties of ferroelectric materials, such as lead zirconate titanate (PZT), are heavily influenced by the interaction of defects with domain walls. These defects are either intrinsic, or are induced by the addition of dopants. We study here $PbTiO_3$ (the end member of a key family of solid solutions) in the presence of acceptor (Fe) and donor (Nb) dopants, and the interactions of the different defects and defect associates with the domain walls. For the case iron acceptors, the calculations point to the formation of defect associates involving an iron substitutional defect and a charged oxygen vacancy (Fe_{Ti} -V_O). This associate exhibits a strong tendency to align in the direction of the bulk polarization; in fact, ordering of defects is also observed in pure $PbTiO_3$ in the form of lead-oxygen divacancies. Conversely, calculations on donor-doped $PbTiO_3$ do not indicate the formation of polar defect complexes involving donor substitutions. Last, it is observed that both isolated defects in donor-doped materials and defect associates in acceptor-doped materials are more stable at 180° domain walls. However, polar defect complexes lead to asymmetric potentials at domain walls due to the interaction of the defect polarization with the bulk polarization. The relative pinning characteristics of different defects are then compared, to develop an understanding of defect-domain wall interactions in both doped and pure $PbTiO_3$. These results may also help understanding hardening and softening mechanisms in PZT.

Tight-binding calculations of intrinsic point-defects levels in chalcopyrite semiconductors

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Cu(In,Ga)Se_2-based solar cells have recently reached a record efficiency of 20.3% and are considered a very promising candidate for high-efficiency and low-cost thin-film solar cells [1]. The presence of defects in these materials leads to intrinsic doping and the formation of trap levels which may act as recombination centers and therefore limit the device efficiency. Therefore, substantial experimental and theoretical research efforts have been directed towards an in-depth understanding of the role of point defects in these devices.

Experimentally, characterization of the defects levels in $CuInSe_2$ takes place with various methods such as : photoluminescence, cathodoluminescence, absorption measurements, Hall measurements, admittance spectroscopy, drive-level capacitance profiling (DLCP), and deep-level transient spectroscopy (DLTS). Nevertheless, the chemical and structural identification of the defect centers producing these levels still remains a challenge.

From a theoretical point of view, first-principles calculations within density functional theory have mostly been used to study the point defects in $CuInSe_2$. Despite the recent progress made in using the hybrid density functional of Heyd, Scuseria and Ernzerhof (HSE06) to study the thermodynamic and electronic properties of intrinsic point defects (see, e.g., [2, 3, 4]) the assignment of the experimentally observed defects levels remains controversial.

Performing hybrid DFT-calculations in supercells of sufficient size is computationally very demanding. We have fitted tight-binding parameters to defect calculations in small supercells (where the defect level is still dispersive). With these parameters, we then perform semi-empirical defect calculations in large supercells where the defect levels become non-dispersive. We present first results for the defect levels in $CuInSe_2$ and discuss the influence of these defects levels on the electronic properties.

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Electronic signatures of stacking solitons in bilayer graphene

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A number of properties of bilayer graphene (BLG) are due to the stacking configuration of its single-layer counterparts. Experiments on BLG show the coexistence of regions of inequivalent stacking order (AB and BA) separated by domain boundaries, topological defects akin to solitons [1-3]. The Frenkel-Kontorova model predicts that in-plane atomic displacements result in stacking domain boundaries of few nanometers width [4]. We show how a hexagonal network of stacking domain boundaries naturally arises in twisted BLG in the limit of small twist angle (below ca. 1°). Equilibrium configurations of twisted BLG have been produced by means of classical force-field simulations. Atomic displacements diminish the area of AA stacking regions and extend the AB and BA stacking regions to form triangular domains separated by boundaries of 7-8 nm width. Large-scale tight-binding simulations unveil the electronic properties of such twisted BLG models. A charge density depletion is the low-energy signature of stacking domain boundaries with electronic states mostly confined in AB and BA domains. Zero-energy states at the network nodes reach an asymptotic localization for vanishing twist angles. We propose scanning tunneling microscopy experiments to confirm our predictions.

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An ab initio investigation of materials relevant to the nuclear fuel cycle

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In the UK, spent fuel from nuclear reactors are transferred to the Sellafield site where it undergoes reprocessing. The first stage of reprocessing is the dissolution of the spent fuel in nitric acid (HNO_3), followed by separation of the plutonium and uranium through solvent extraction. The resultant high level liquid waste is transferred to evaporators where they are reduced to 2-5 % of the original volume. Following evaporation, the waste is then transferred to temporary storage in the Highly Active Storage Tanks (HASTs). Ultimately, the waste will undergo vitrification and permanent storage, however there is currently no confirmed date for these processes to happen. Within the HASTs, formation of metal nitrates is inevitable and it has been shown that two products, barium nitrate, $Ba(NO_3)_2$ and Strontium-90 can co-crystallise to produce the complex $Ba_xSr_{1-x}(NO_3)_2$. This can cause serious storage issues as the complex is fast-settling and produces excessive heat which enhances the rate of corrosion of the tanks.

Due to the highly radioactive nature of the nuclear waste, there is a limited scope of measurements that can be performed and therefore computational techniques have been adopted to help characterised the materials of interest.

Using *ab initio* DFT [1] calculations, we are investigating the properties of barium nitrate, with particular interest in strontium-90 substitution and also general defect properties. Defect calculation techniques, such as finite size scaling [2], and cohesive energy calculations are being explored to help determine the stability and characteristics of possible crystal structures. Following on from this work, it will also be interesting to see whether we can use *ab initio* DFT to improve on Molecular Dynamics force-field potentials of isomorphous nitrates [3].

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Breakdown of the Arrhenius Law in Describing Vacancy Formation Energies: The Importance of Anharmonicity Revealed by Ab initio Thermodynamics

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Conventionally the Gibbs energy of vacancy formation $G^f(T)$ is assumed a linear Arrhenius type function $G^f(T) = H^f - TS^f$ with H^f and S^f being the respective *constant* Enthalpy and Entropy of formation. We explicitly calculate the full temperature dependence of the Gibbs energy of vacancy formation in Al and Cu from $T = 0\,\mathrm{K}$ up to the melting temperature by first principles fully taking into account anharmonic contributions [1]. Our results reveal that $G^f(T)$ is highly nonlinear and the generally applied Arrhenius law breaks down for vacancy type of defects. We show the fully *ab initio* calculated temperature dependence in Al and Cu to naturally consolidate experimental measurements at different temperatures and that in particular anharmonic contributions are essential for an accurate description. Based on a simple local Grüneisen theory (LGT) interpretation of our results—rather than the linear Arrhenius extrapolation that is commonly assumed in analyzing experimental data—revised formation enthalpies are obtained that differ up to 20% from the previously accepted ones as compiled, e.g., in the Landoldt-Börnstein series [2]. The substantial shift between previously accepted and the newly revised $T = 0\,\mathrm{K}$ formation enthalpies has also severe consequences in benchmarking *ab initio* methods against experiments, e.g., in deriving corrections that go beyond commonly used LDA and GGA exchange-correlation functionals such as the AM05 functional. We compare our results to recently computed formation energies using the HSE xc functional [3] and show significant implications on vacancy volume of formation upon inclusion of anharmonic contributions.

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Band offsets and defects at the crystalline / amorphous silicon interface from first-principles

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Silicon heterojunction (SHJ) solar cells combine high-efficiency of c-Si wafer technology with high-throughput and low-cost of hydrogenated amorphous silicon (a-Si:H) solar cells. The interface between crystalline and amorphous silicon lies at the heart of the SHJ solar cell. Since a-Si:H has a larger band gap than c-Si, band offsets are formed at the interface.

Experimentally the band offsets can be determined with techniques such as photoelectron spectroscopy and capacitance-voltage measurements. The reported values scatter in a broad range. This can be due to different deposition conditions of the a-Si:H layer or misinterpretation of the experimental results. On average it appears that the offset at the valence band is larger than at the conduction band [1].

In light of the conflicting reports our goal is to calculate the band offsets at the c-Si/a-Si:H interface from first-principles. To this end we construct a simulations cell with dimensions of $1.5\times1.3\times3.6$ nm^3 and divide it into a crystalline and amorphous part. Periodic boundary conditions are applied in all three dimensions. The crystalline part is terminated with (111) surfaces on both sides. The amorphous structure is generated by simulating an annealing process at 1100 K, with DFT molecular dynamics. Using relatively long annealing times (80 ps) we are able to generate realistic a-Si:H structures.

We use a hybrid functional to calculate the electronic structure of the interface. The position of band edges in the amorphous part is obtained by fitting the calculated density of states to a square root dependence. This is in the spirit of the Tauc band gap often used to interpret optical measurements. Our preliminary results show that the valence offset is larger than the conduction band offset.

In total we prepare 10 interface models. All of them contain a small number of defects. We find three types of defects: 3-fold coordinated Si atoms, 5-fold coordinated Si atoms and 2-fold coordinated H atoms. The over-coordinated Si atom is the most common defect. This is in contrast to the prevailing view that considers the 3-fold coordinated Si atom (dangling bond) as the only defect.

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Investigations on simple copper vacancies and split vacancies in Cu_2O based on density functional theory

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Cuprous oxide (Cu_2O) is a prototypical p-type conducting oxide with applications in photovoltaics, dilute magnetic semiconductors, low cost solar cells, gas sensors, and catalysis[1]. The design and fabrication of high figure of merit p-type transparent conducting oxides (TCOs) is also a major goal for materials scientists, as this will enable invisible electronics based on transparent p-n junctions. An understanding of the defect chemistry and conduction properties of Cu_2O is therefore vital to the optimization of these technologically important Cu(I)-based p-type TCOs[1].

We present investigations on simple copper vacancies V_{Cu} and split vacancies V_{Cu}^{split} in Cu_2O based on density functional theory. Both defects are simulated in a 2x2x2 supercell of Cu_2O. We determine the influence of these defects on structural and electronic properties using the LDA+U functional and compare them with properties of defect free Cu_2O. Since both vacancies come along with an electron hole state, we further investigate the localization of this defect state. In order to do so we calculate Born effective charges, magnetic moments and density-differences for both defect structures. Investigations on both defects show that only simple vancancies contribute to the electronic conductance. In contrast, split vacancies act as trap states for electron holes and do not contribute to electronic conductance.

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Strain controlled oxygen vacancy formation in II-IV manganites

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Control of defect formation through epitaxial strain in functional oxides has caught increasing interest the recent years, potentially serving as a new route to engineering material properties [1,2]. DFT calculations of $\mathrm{CaMnO_3}$ have shown that the stability of oxygen vacancies increases with biaxial tensile strain, suggesting that oxygen vacancies serve as a relaxation mechanism for tensile strain accommodation in epitaxial thin films [3]. Oxygen vacancies in $\mathrm{CaMnO_3}$ create localized charge compensating electrons which leads to reduction of manganese according to:

$$\mathrm{O_O^x} + 2\,\mathrm{Mn_{Mn}^x} \rightleftharpoons \mathrm{V_O^{\bullet\bullet}} + 2\,\mathrm{Mn_{Mn}^{'}} + \frac{1}{2}\mathrm{O_2(g)} \tag{1}$$

The change in ionic radius upon reduction of manganese from $\mathrm{Mn^{4+}}$ (0.54 Å) to $\mathrm{Mn^{3+}}$ (0.645 Å) causes a considerable volume expansion. While it is well established that oxygen vacancies can induce chemical expansion in perovskite oxides [4], an analogous, but reverse, effect is also found in that tensile strain reduces the formation enthalpy of oxygen vacancies in $\mathrm{CaMnO_3}$ [3].

We investigate the stability of oxygen vacancies upon biaxial strain in the (100) and (111) pseudocubic planes and the impact of the tolerance factor by studying the manganites $\mathrm{CaMnO_3}$, $\mathrm{SrMnO_3}$ and $\mathrm{BaMnO_3}$ with first-principles calculations. Strain can be mitigated by a change of bond lengths and bond angles, or formation of point defects like vacancies and planar defects such as dislocations. In this study of epitaxially strained thin films, we disregard dislocations. The investigated hypothesis is that the formation enthalpy of oxygen vacancies is more sensitive to tensile strain when the bond angles are straight and can not change and if the bonds are under tensile stress, due to a high tolerance factor. General correlations between crystal structure, biaxial strain and vacancy formation energy is finally discussed.

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LDA-1/2 method applied for study of defects in semiconductors

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Defects and impurities are often decisive in determining the physical properties of most semiconductor based materials. The process of defect identification and characterization is typically difficult and indirect, usually requiring an ingenious combination of different experimental techniques. First-principles calculations have emerged as a powerful microscopic tool that complements experiments or sometimes even serves as the sole source of atomistic information due to experimental limitations. The ``standard" toolkit includes density functional theory (DFT) combined with supercell band structure calculations. It was long known that DFT methods underestimates band gaps in semiconductors. Since the band gap is the relevant energy scale in the study of defects, this so-called ``band-gap problem" of DFT severely affects the results of defect levels calculations.

We applied a new band gap correction method, LDA-1/2 [1], to calculate formation energies of self-interstitial silicon defects [2], and charge transitions levels of magnetic impurity manganese in silicon [3]. In comparison with others gap correction methods, this new one do not make use of adjustable parameters like LDA+U [4] and HSE [5], and as the best GW [6] calculations produces very good band gaps and effective masses, but at a very small computational price. This low price allows the use of large supercells, essential condition for a good defect description. The results obtained showed that the correction increase the formation energies and charge transition levels, leading to an excellent agreement with experimental data.

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Role of Mg interstitial in the self-compensation process in p-type GaN

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Gallium nitride, a wide-gap semiconductor, is already an essential component for commercial blue light-emitting-diodes but further progress in device applications is hampered by the limited efficiency in p-doping [1]. So far, the only successful approach for producing p-type GaN is doping with Mg. The ionization energy of this acceptor is about 0.2 eV [2-4]. Such a deep level requires very high Mg-doping concentrations to achieve significant p-type activation. This approach gives rise to heavy doping effects such as self-compensation which may limit the activation.

In this work we use hybrid density functional theory to study defect states susceptible to play a role in the observed compensation effects in p-type GaN. We consider the nitrogen vacancy ($\mathrm{V_N}$) and several Mg-related defects such as the Mg substitutional to Ga ($\mathrm{Mg_{Ga}}$) the Mg-$\mathrm{V_N}$ complex, and the Mg interstitial. The Mg interstitial acts as a double donor for all Fermi energies in the band gap. Unlike in previous studies [5], we find that in p-type conditions the formation energy of the Mg interstitial is significantly lower than that of $\mathrm{Mg_{Ga}}$. This result suggests that in p-type conditions Mg atoms would prefer occupying interstitial sites rather than substitutional sites, thus hampering the p-doping process by self-compensation. Hence, the Mg impurity shows an amphoteric nature, behaving as a single acceptor in n-type condition and as a double donor in p-type condition. Based on our calculated defect formation energies, we discuss different self-compensating models for p-doped GaN.

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Controlling a spin polarized two-dimensional electron gas through layered oxygen vacancy ordering in $La_{0.7}Sr_{0.3}MnO_{3-\delta}$

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Controlling and tuning the properties of advanced electronic materials has been one of the main goals of material research as this is essential for developing device technology. Functional interfaces between perovskite oxides, with general formula ABO_3, are known for their strong structure property coupling, allowing them to support many interesting properties such as magnetism, ferroelectricity and high temperature superconductivity[1]. One interesting prospect is to rely vacancy ordering to tune these functional properties[2].

It has recently been shown that oxygen vacancies in thin films of $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ can accumulate close to interfaces and form ordered layered structures. One example of such a layered structure is the brownmillerite phase, with general formula $ABO_{2.5}$; this structure have alternating oxygen BO_6 octahedral layers and BO_4 tetrahedral layers along the stacking direction[3,4]. We manipulate the oxygen stoichiometry by including additional octahedral layers in between every tetrahedral layer. In this work, we rely on density functional theory calculations to reveal how it is possible to control the magnetism and electronic transport through oxygen vacancy ordering.

The calculations of the layered structures show that the tetrahedral layers are not spin polarized, while the octahedral layers are spin polarized, similar to bulk $La_{0.7}Sr_{0.3}MnO_3$. We further show that the oxygen deficient tetrahedral layers have a band gap of 1.5 eV. This is in contrast to the octahedral layers which is either metallic if there is more than one octahedral layer between every tetrahedral layer or semiconducting with that a band gap of 0.5 eV if there is only one octahedral layer between them. Band structure calculations show that there is considerable dispersion parallel to the layers, while orthogonal to the layers the bands are relatively flat, this implies a higher mobility along the layers. These results implies that layered oxygen vacancies reduces the coupling between the octahedral layers giving a spin polarized two-dimensional electron gas in these layers. The results further demonstrates that defect engineering is a valuable tool to tune and induce new properties in these material systems.

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Comparative study of isolated Li defects and Li–V_{Zn} defect complexes in ZnO

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A recent experimental study on proton-implanted Li-doped ZnO microwires is found to have room temperature ferromagnetic properties. By matching the X-ray magnetic circular dichroism (XMCD) spectra with the theoretical spectra derived from first-principles method for different defect models, it has been concluded that the magnetic signal is mainly due to presence of Zn vacancies (V_{Zn}) in the sample [1]. Similar conclusion has been derived earlier [2]. This gives rise to the hypothesis that Li point defects help in stabilizing V_{Zn}. In order to verify the hypothesis we are carrying out density functional theory (DFT) calculations on Li-doped ZnO system. The analysis of the stability of defects is done by estimating the formation energy of defects under various growth conditions (see Ref. [3]). In order to overcome the limitations of DFT and make a comparative study, we use the empirical post-processing treatment [4] and the DFT-based hybrid functional approach in our analysis. Our preliminary results from the generalized gradient approximation in DFT suggest that Li in ZnO favors an interstitial site compared to substitutional positions. The charge transition level (+2/+) of the Li interstitial is found to be in the band gap and 50 meV above the valence band maximum. This suggests that a *p*-type condition is possible in Li-doped ZnO samples. Further analysis of charge defects dependence on the chemical potentials and their comparison with Li–V_{Zn} defect complex are ongoing.

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Cation-vacancy and electron-hole relaxation in single-walled aluminosilicate nanotubes: a linear-scaling Density Functional Theory study.

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We report a linear-scaling Density Functional Theory (DFT) study of cation-vacancy related defects in single-walled aluminosilicate nanotubes (AlSi NTs), based on the structures derived from solid-state Nuclear Magnetic Resonance [1]. Defect geometry optimization leads to water condensation and modifications to the AlSi NT hydrogen network around the defect sites, leaving no dangling bond. Electronic structure analysis indicates that defect-states are highly localized in real-space and energy, with appearance of shallow and deep occupied defect states above the valence band (VB) edge of the pristine-NT. Electrostatic alignment of the defect states suggests energetically favorable separation of photo-generated electrons and holes on different defects, which may promote defect-centered photochemistry. The peculiar energy alignment of the defect-states is found to be qualitative unaffected by protonation of the defect-sites. These results should be a useful complement to ongoing experimental research in the potential of (alumino)silicate-based nano-porous materials for photocatalysis [2].

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Spin-polarized transport across line defects in monolayer $\mathrm{MoS_2}$

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Materials with strong spin-orbit interactions present an opportunity for generating spin-polarized charge carriers in non-magnetic media. In our study, we investigate spin transport in prototypical models of experimentally observed line defects in monolayer $\mathrm{MoS_2}$ [1-5]. The ballistic regime transport properties were studied within the Landauer-Buttiker formalism using a non-equilibrium Green's function self-consistent procedure. Our investigation reveals the strong dependence of charge-carrier transmission probability on both the quasiparticle spin and incidence angle. The obtained spin polarization of current reaches 100% for certain model configurations, which highlights the value of monolayer transition metal dichalcogenides as prospective materials for spintronics.

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Raman spectra of point defects in Silicon Carbide : limitations and opportunities to compare with experiments

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The caracterization of materials under irradiation, or after irradiation, has traditionally been performed with a variety of techniques. One can probe macroscopic properties, like mechanical response, thermal or electrical conductivities, optical or magnetic responses, or one can try to observe directly features at the nanoscale, like, e.g., dislocation loops, with local probes like STM or hrTEM. In the former case the observed signals depend on the type of defects induced by irradiation, their concentration, their spatial distribution and their time evolution. Raman spectroscopy has been increasingly used in the last few years for irradiated materials, including silicon carbide [1]; however, the interpretation of spectra is not always an easy task. We have considered silicon carbide not only because of recent experimental works, but also because it is a material for which a lot of knowledge on point defects has been gathered in the last two decades; we have calculated the Raman intensities of defect containing supercells in the framework of linear response theory [2] with the goal of providing tools for the interpretations of experimental spectra. We present a few examples and discuss the limitations and opportunities of our approach, also in connection with the prediction of the time evolution of defect concentrations under irradiation.

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p-type conductivity of N-doped ZnO: a closer look at the V_{Zn}-$\mathrm{N_O}$ and V_{Zn}-$\mathrm{N_O}$-H complexes

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Past research efforts aiming at obtaining stable p-type ZnO have been based on complexes involving nitrogen doping. Recently, significant (10^18 cm^{-3}) p-type behavior was reported in N-doped ZnO films after annealing [1]. The p-type conductivity was attributed to a V_{Zn}-$\mathrm{N_O}$-H shallow acceptor complex, formed by a Zn vacancy, N substituting O, and H interstitial. We present here a first principles hybrid functional study of this complex, as well as of V_{Zn}-$\mathrm{N_O}$, which was also previously reported to originate p-type conductivity in N-doped ZnO [2]. We find that the V_{Zn}-$\mathrm{N_O}$-H complex acts indeed as an acceptor in ZnO. It is however, a deep acceptor. Our results show that H plays an important role, because it lowers the formation energy of the complex with respect to V_{Zn}-$\mathrm{N_O}$. We find that the latter is a shallow acceptor, but with a formation energy higher than that of compensating defects, and so is unstable. The H atom unfortunately also acts as a donor, compensating the hole level at the origin of the shallow behavior of V_{Zn}-$\mathrm{N_O}$ and leaving only two states empty higher in the band gap, thus turning the V_{Zn}-$\mathrm{N_O}$-H complex into a deep acceptor. We conclude that the cause of the observed p-type conductivity in Ref. 1 is not the presence of the V_{Zn}-$\mathrm{N_O}$-H complex, but probably the formation of the V_{Zn}-$\mathrm{N_O}$ complex during the annealing process.

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Defect clusters and photoluminescence lines in crystalline silicon

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The photoluminescence (PL) spectra of c-Si shows radiative recombination pathways associated to defects [1], which would enable PL as a non-destructive technique for defect identification [2]. Nevertheless, not all defects responsible for PL lines in c-Si have been identified. For example, the W and X PL lines, with photon energies of 1018 meV and 1039 meV respectively, are generated during ion implantation and annealing and are associated to small interstitial defect clusters [1, 3]. Different defect configurations have been proposed for these PL centers, and analyzed using ab initio simulations [4, 5]. These studies revealed contradictory results, and the configuration of the W and X centers is not clear yet. In addition, X and W PL lines have gained great interest in Si photonics [6]. The knowledge of the defects responsible for the X and W PL lines can help to optimize the fabrication processes of devices to enhance their presence.

Here we propose a systematic procedure for identifying defects that can be responsible for PL lines in c-Si:

i) We used classical Molecular Dynamics (MD) simulations of implantation recoils, and thermal annealing of isolated defects to obtain defect configurations from atom dynamics, rather than presupposing configurations as it was done in previous works [4, 5].

ii) Performed MD simulations resulted in a wide collection of defect configurations. Among them, we selected those having the known symmetry of W and X PL centers in c-Si.

iii) We used ab initio simulations to evaluate the following properties of considered defects:
  - The (0/+) donor levels, from total energy differences between the neutral and the positively charged configurations.
  - The band structure modifications induced by defects.

The combined analysis of previous properties highlights the suitability of two of the defect configurations found as W and X PL centers in c-Si in the following points:

- Donor levels agree quite well with experimental measurements of the W and X PL centers.
- Band diagrams show the appearance of a new occupied band on top of the valence in addition to some modifications at the bottom of the conduction band. These band modifications significantly reduce the energy gap for direct transitions in high symmetry k-points, and turn the gap into direct for case of the defect candidate for the X PL center. In addition, the band alignment with the crystalline matrix in this latter case seems to be favorable for carrier trapping at the defect.

In order to provide further evidences for the identification of the atomic defect configuration of the W and X PL centers in c-Si, we intend to incorporate to our analysis:

i) The evaluation of the phonon frequencies associated to defects, to relate these frequencies with the local vibrational modes observed in PL experiments,

ii) The calculation of the imaginary part of the frequency dependent dielectric matrix by means of RPA or more advanced techniques, to investigate the modifications induced by defects at the energies associated to carrier transitions between band edges.

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Point defects and phase stability in hexagonal $InMnO_3$

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Hexagonal manganites have recieved much attention the last decade due to their intriguing features like multiferroicity, novel domain walls [1] and special symmetry breaking at the ferroelectric transition from $P6_3/mmc$ to $P6_3cm$ [2]. While $YMnO_3$ is the prototypical hexagonal manganite with the polar space group $P6_3/cm$ as its ground state, the space group of hexagonal $InMnO_3$ is currently subject to debate. DFT calculations and second harmonic generation (SHG) measurements have shown that $InMnO_3$ single crystals are non-polar with the most likely space group being P-3c [3], while a ferroelectric ground state with space group $P6_3cm$ has also been reported [4]. Even polar and non-polar regions co-existing in the same sample has also been demonstrated [5].

Here we investigate the hypothesis that the competing stabilities of polar $P6_3cm$ and non-polar P-3c ground states in $InMnO_3$ can be explained by the influence of point defects by performing first principles calculations using the VASP code. We show that point defects which can be reversibly introduced by annealing in different atmospheres, like oxygen vacancies and interstitials, have only a subtle effect on the relative phase stabilities, while non-reversible defects like cation vacancies favour a non-polar ground state. Climbing image Nudged Elastic Band (cNEB) calculations show that different point defects can reduce, or completely remove, the energy barrier between the polar and non-polar ground states compared to perfect stoichiometric crystals. Experimental implications are also briefly discussed.

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Yttrium deficiency in hexagonal $YMnO_3$ by *ab initio* calculations.

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Hexagonal manganites display multiferroicity[1], complex domain wall properties[1,2] and spontaneous symmetry breaking at the trimerization transition enabling testing of the Kibble-Zurek scenario of cosmic string formation in the early universe[3].

While neither of the cations in $YMnO_3$ are volataile, cation non-stoichiometry can still arise during material synthesis[4]. In charge neutral cells, the possible cation vacancies $V_{Y1}^{'''}$, $V_{Y2}^{'''}$ and $V_{Mn}^{'''}$ (in Kröger-Vink notation) can be charge compensated by either oxygen vacancies under oxygen poor conditions or by oxidation of three Mn cations from Mn^{3+} to Mn^{4+} under oxygen rich conditions.

The energetics and local structural distortions of cation vacancies in the dilute limit are investigated. As hexagonal manganites have been shown to tolerate substantial rare earth metal deficiencies, large concentrations of yttrium vacancies are also studied in order to simulate finite non-stoichiometry. Yttrium vacancies in oxygen rich conditions are shown to destroy the ferroelectric polarization as supercells with initial $P63cm$ symmetry relax to the non-polar $P\bar{3}c$ symmetry upon introduction of $V_{Y}^{'''}$. Finitie yttrium deficiency is also demonstrated to induce a transition from an insulating to a conducting state and possible applications of this observation are discussed.

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Ab initio calculations of oxygen vacancies in MgO structure for spintronics applications

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Tunnel magnetoresistance (TMR) effect is key to developing magnetoresistive random access memories, magnetic sensors and novel logic devices [1]. The increase of interest in magnetic tunnel junctions (MTJs) with crystalline MgO barrier is due to the predicted high TMR ratio up to a 1000% when compared with standard amorphous Al_2O_3 barrier where the TMR ratio does not exceed 70%. This high TMR ratio is due to coherent spin and symmetry preserving tunnelling of electrons through the crystalline barrier [2]. Experimental results, however, show values of TMR one order of magnitude below prediction. One of possible causes for this discrepancy is attributed to the existence of defects in the MgO barrier. Defects create additional energy levels within the insulator energy band gap which effectively reduce the barrier hight and affect the coherent spin-polarized transport. Thus, understanding and controlling the behavior of defects in the MgO barrier structure is of a crucial importance.

Defects in MgO may appear as single magnesium or oxygen vacancies (V and F centers, respectively), oxygen divacancies (F^2 or M centers) and neighboring oxygen-magnesium vacancies (P centers). Additionally, oxygen and magnesium vacancies (F and V) can exist in neutral states, as well as in charged or doubly charged states (denoted as F^+, F^{2+}, V^-, V^{2-} respectively). The formation energies for oxygen vacancies are the lowest and this implies that such defects are more likely to occur [3]. Single oxygen vacancies were studied extensively in [4–7]. A removal of one oxygen atom produces doubly occupied localized *s* states and unoccupied resonant *p* states. Thus, the symmetry of the defect state is a mixture of valence and conduction band symmetries. As suggested by recent experiments conducted by *Schleicher et al.* [8], M centers can also affect the electron tunnelling through MgO. Theoretical support is therefore needed to understand the behavior and the influence of double oxygen vacancies on spin–polarized electron transport in Fe/MgO/Fe system.

In our work, we investigate the properties of double oxygen vacancies in MgO structure and their impact on spin polarized transport through the insulating barrier. The calculations is carried out using density functional theory as implemented in VASP package within the projector augmented wave (PAW) method. To simulate defect states in MgO we used supercells of 64 atoms in simple cubic structure. Supercells beyond this size are computationally expensive and may not necessarily add any additional qualitative understanding of defect states in MgO. However, a value of the energy band gap closer to the experimental value of 7.8 eV ensures a good positioning of defect levels within the gap. To this end, we used several types of exchange–correlation functionals: generalized gradient approximation (GGA), metaGGA (MBJ) and hybrid functionals. By adjusting the parameters of MBJ functional or HSE06 hybrid functional the exact value of the band gap can be obtained, and use these parameters to determine the positioning of the defect states. Even though GGA underestimates the band gap of MgO (4.76 eV instead of 7.8 eV), it provides nevertheless appropriate qualitative results of defect levels as compared to those obtained using hybrid functionals. The main disadvantage of hybrid functionals is that they are computationally costly compared to semilocal functionals. On the other hand, MBJ functional provides values of band gaps as good as in case of hybrid functionals but with computational time comparable to semilocal approximations. The only drawback is that sometimes the total energy calculated using MBJ does not converge, which forces us to make most of the calculations within the GGA. We studied oxygen vacancies located up to a distance of 6 Å from each other, which should preserve coherent transport [7]. Based on charge density analysis for the energy range where defect levels appear, we found that only for the closest lying defects states (distance below 3 Å) hybridize with each other. The density of states for this type of defects shows creation of two additional peaks below the Fermi level (E_F) and also new energy levels near the minimum of the conduction bands. It seems that the interaction between occupied levels of neighboring F centres results in creation of two doubly occupied energy levels below E_F for M centre and the interaction between unoccupied F levels gives rise to excited states for M center. To make contact with future experimental results, we computed the complex dielectric function within the electric dipole approximation. We show that the oxygen vacancy peaks in the dielectric function, which emanate from interband transitions between MgO electronic structure and defect levels, are visible within the band gap.

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The color centers in alkali halides revisited: Comparison of GW+BSE and an embedded-cluster quantum-chemistry approach

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F-type color centers in alkali-halide crystals are known since the 1920s. The absorption energy ΔE in different alkali-halides scales roughly with the lattice constant a as $\Delta E \propto 1/a^2$ (Mollwo-Ivey relation [1]). The easiest model considers the active electron at the site of the missing anion to be trapped in a 3-dimensional square-well (box) potential. In this model, the $1/a^2$ scaling follows immediately from the analytic solutions of the Schrödinger Equation.

We perform a numerical study of the Mollwo-Ivey relation by using two quite complementary approaches: (i) quantum-chemistry calculations for an embedded cluster around the anion-vacancy (ii) post-DFT (GW+Bethe-Salpeter) calculations for a periodic supercell containing the point defect. These alternative approaches yield results in good agreement with each other and with the experimental data [2]. Even though the effective potential in which the active electron is moving is quite different from a square-well potential, we obtain for the different alkali-halides results that are very close to the $1/a^2$ curve.

We elucidate the role of cation- and anion size effects on the exponent of the Mollwo-Ivey relation. The quantum-chemistry calculations furthermore enable us to calculate the relaxation of the system in the excited state and to provide a straightforward estimate of the electron-phonon induced line broadening and of the Stokes-shift between emission and absorption lines.

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Cation vacancies in epitaxially strained $BiFeO_3$

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$BiFeO_3$ (BFO) is well known for its room temperature multiferroic properties and its sensitivity to epitaxial strain makes it promising for the new generation lead-free piezoelectrics in device engineering [1]. In epitaxially strained BFO thin films an isosymmetric phase transition occurs at about 4.5% compressive strain accompanied by a 9% change in volume [2]. Point defects is one possible mechanism for accommodating epitaxial strain where the oxygen vacancies are charge compensated by a reduction of Fe^{3+} to Fe^{2+} [3], while the excess oxygen is charge compensated by cation vacancies which are also related to the chemical expansion and contraction. Besides, the low energy-barrier between the R and T phases implites a reversible phase coexistence also needs further studies.

Here we investigate the effect of epitaxial strain on the electronic ordering and symmetry of $BiFeO_3$ with Bi vacancies and Bi-O vacancy pairs. We find that the defect formation energies for both oxygen and cation vacancies depend on the sign and magnitude of the epitaxial strain. Moreover, bi-axial strain in the pseudo-cubic (001) and (111) planes causes different modulations of the defect formation energies. A consequence of these findings is that different epitaxial orientations give rise to specific strain dependent defect chemistries. This opens an opportunity for controlling interfacial defect populations.

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