

## Poster Session B

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# Ab initio study of epitaxial anatase TiO<sub>2</sub> on Si for efficient solar water splitting

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Crystalline metal oxides on silicon have been studied for novel applications ranging from high-k gate devices to solar energy conversion due to the interesting properties at the abrupt oxide interface. In particular, in this work, we investigate the formation of a quasi-2D electron gas (2DEG) at the interface of an epitaxial anatase TiO<sub>2</sub> film on Si for efficient and sustainable solar water splitting. By forming a quasi-2DEG at the interface, electrostatic fields can be induced, thereby separating photo-excited charge carriers and increasing surface reactivity. TiO<sub>2</sub> is known to be a stable photoelectrocatalyst in aqueous solutions. Therefore, by enhancing the charge carrier separation with a quasi-2DEG, solar water splitting can be more efficient. We use ab initio density functional theory calculations to examine the electronic structure and thermodynamic stability of various interface configurations between TiO<sub>2</sub> and Si. We observe the formation of a quasi-2DEG based on the atom-projected density of states, the electronic band structure and charge density. We also observe the induced electrostatic fields and the polarization of TiO<sub>2</sub> monolayers. We further examine the formation energy and diffusion barrier of oxygen vacancies to verify the possibility of kinetically trapped metastable states that forms the quasi-2DEG. Sr-buffered TiO<sub>2</sub> is also evaluated as another possible set of interface configurations.

## A DFT OF MAGNETIC TENDENCIES IN TiAu

WEN FONG GOH, KWAN-WOO LEE, AND WARREN E. PICKETT

TiAu is a rare example of a weak antiferromagnetic, ordering below 36 K. Our interest in this intermetallic compound was piqued by the existence of van Hove singularities (vHs) within 4meV of the Fermi level, reminiscent of the weak ferromagnets ZrZn<sub>2</sub> and TiBe<sub>2</sub>. This fine structure leads to a peak in the density of states and to peculiar behavior in the susceptibility, thus may play a role in creating magnetic fluctuations. The vHs is located, with its quadratic energy dispersion corresponding to effective masses (two positive, one negative) differing in magnitude by a factor of five. Morosan's group (private communication) has found that hole doping, viz. Ti<sub>1-x</sub>Sc<sub>x</sub>Au, causes the magnetic moment to disappear at  $x_{cr}=0.13$ . We apply fixed spin moment calculations and the virtual crystal approximation within DFT to access the tendencies toward ferromagnetism, and among other results find FM instability as well within both LDA and GGA. Several results will be presented and assessed in light of the existing experimental data.

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# Obtaining Excited-State Properties in Doped Two-Dimensional Materials with an Efficient Plasmon-Pole Model

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Determining electronic excitations from first-principles calculations greatly facilitates the designs of functioning materials in electronics and opto-electronics. For systems with medium electron correlations, the key often lies in a successful modeling of the screened Coulomb interactions among the charges. In general, this procedure is formidable since the dielectric screening varies drastically across different length-scales and time-scales. Recently, layered metal dichalcogenides emerge as a novel class of two-dimensional devices, where doping is an important means of controlling their physical properties effectively. From the perspective of first-principles simulations, extra carriers add to the complexity of modeling the dielectric function. In this work, we propose a generic and efficient dielectric model for doped low-dimensional materials [1]. It is found that at commonly seen doping levels, the extra charge carriers only affect the long-wave components of the dielectric function while the other components remain largely intact. The charge carriers contribute to the formation of a lower-energy plasmon, which can be shown to be captured by undemanding computational efforts. Using the GW approximation, we apply our model to the quasiparticle band energies in MoS<sub>2</sub> and MoSe<sub>2</sub> and achieve excellent agreement with recent ARPES experiments. This model can also be further applied to the Bethe-Salpeter Equation for electron-hole excitations.

[1] Yufeng Liang and Li Yang, Phys. Rev. Lett. 114, 063001 (2015)

# Modeling STM contrasts of buried interfaces

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Recently, there has been a lot of activity in applying surface microscopy methods to buried interfaces, which are made by growing thin insulating oxide films on top of metallic substrates. Several studies of buried interfaces suggested that it is possible to probe the interface electronic structure via a low-bias scanning tunneling microscopy (STM). However, in many cases the interpretation of the observed STM images is ambiguous. We propose a theoretical method of low-bias STM simulation based on first-principles calculations that allows one to unambiguously interpret the formation of STM images. The method is based on construction of an *ab initio* tight-binding representation of the states near the Fermi level of the system [1]. We apply our method to a prototypical buried interface system: an ultrathin film of rock-salt MgO on top of an Ag substrate. We show that the formation of the STM contrast in this system is dominated by the surface atoms. We show that the low-bias contrast is formed by the states at the Fermi level that originate in the substrate and propagate evanescently through the atomic orbitals of MgO.

[1] A. Malashevich, E. I. Altman, and S. Ismail-Beigi, Phys. Rev. B **90**, 165426 (2014).

## **Parallel electron-hole conducting gases in monoxide/mononitride multilayers**

ANTIA S. BOTANA, University of California, Davis, VICTOR PARDO, Universidade de Santiago de Compostela, WARREN E. PICKETT, University of California, Davis

An unexplored class of materials for the realization of a two dimensional (2D), two carrier (electron+hole) gas is proposed: heterostructures of a rocksalt oxide (MgO) and nitride (ScN or CrN) grown along the polar (111) direction. For thinner nitride blocks of four unit cells or less, the heterostructures (designed as a superlattice) remain insulating with the band gap defined by states residing at the two separate interfaces. For thicker blocks, the band gap collapses as an insulator-to-metal transition takes place at a critical thickness of 5 layers. First principles calculations indicate that each of the metallic electron and hole layers is confined to its own interface, with negligible overlap, constituting a periodic array of alternating electron and hole 2D gases. Use of the N anion should promote robust two carrier 2D conduction compared to oxides, where holes are prone to localization – recall that most bulk transition metal nitrides are metallic. We additionally propose experimental tests for detecting this peculiar bi-conducting system, i.e. thermopower and Hall effect measurements. Both should display considerable electron-hole compensation, especially for the (essentially vanishing) thermopower that could enable the use these superlattices as a reference material for thermoelectric measurements at the nanoscale.

## Investigation of Thin Cobalt/Nickel/Manganese Oxides Supported on Au(111) and Other Fcc Metals

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In the last decade, a number of experiments have shown that ultra-thin layers of TMOs can be stabilized when interfaced with precious metal supports such as Au(111) and Pt(111) or Ir(100).<sup>1-6</sup> Moreover, gold supported Co/Ni/Mn-based catalysts have been experimentally proven to exhibit higher oxygen evolution reaction (OER) activities than other metal supported oxide catalysts.<sup>7-9</sup> However, the synergistic effect of contact with gold support is yet to be fully understood.

In the first half of my talk, I will report the results of our combined experimental and computational study of ultra-thin layered cobalt oxides.<sup>4</sup> The synthesis of three distinct types of thin-layered cobalt oxide nano-islands supported on a single crystal gold (111) substrate is confirmed by combination of STM, XAS methods. Additionally, DFT+U theoretical investigation of above nano-islands confirms stability of two low-oxygen pressure phases: (a) rock-salt Co-O bilayer and (b) wurtzite Co-O quadlayer and single high-oxygen pressure phase: (c) O-Co-O trilayer. Very importantly, I will discuss the effect of water exposure in these systems, which results in noticeable hydroxylation of the basal planes. The results of the theoretical hydroxylation models will be compared with experiments.

In the second half of my talk, I will present the calculated OER activities of general thin-film Mn/Fe/Co/Ni supported oxides, which are assumed to have the structure of the ultra-thin layered cobalt oxides. In more detail, I will discuss the theoretical overpotentials obtained on basal planes relative to edge sites in these systems as function of different metal support with the goal of elucidating the synergistic effect of gold.

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# Density Functional Theory Calculations of Activation Energies for Carrier Capture by Defects in Semiconductors

N. A. Modine, A. F. Wright, and S. R. Lee

Sandia National Laboratories

Carrier recombination due to defects can have a major impact on device performance. The rate of defect-induced recombination is determined by both defect levels and carrier capture cross-sections. Density functional theory (DFT) has been widely and successfully used to predict defect levels, but only recently has work begun to focus on using DFT to determine carrier capture cross-sections. Lang and Henry worked out the fundamental theory of carrier-capture by multiphonon emission in the 1970s and showed that, above the Debye temperature, carrier-capture cross-sections differ between defects primarily due to differences in their carrier capture activation energies. We present an approach to using DFT to calculate carrier capture activation energies that does not depend on an assumed configuration coordinate and that fully accounts for anharmonic effects, which can substantially modify carrier activation energies. We demonstrate our approach for the  $-3/2$  level of the Ga vacancy in wurtzite GaN.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

# Abstract Submission Template

-title-

Plentiful magnetic moments in oxygen deficient SrTiO<sub>3</sub>

-/title-

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-abstract-

Correlated band theory calculations based on the DFT+U approach are employed to investigate oxygen-deficient SrTiO<sub>3</sub>. We show that the appearance of magnetism in oxygen vacancies is not determined solely by the presence of a single oxygen vacancy, but by the density of free carriers and the relative proximity of the vacant sites. While an isolated vacancy behaves as a non-magnetic double donor, manipulation of the doping conditions allows the stability of a single donor state with emergent local moments. For clusters of vacancies, different kinds of Ti atomic orbital hybridization are described as a function of the doping level and defect geometry. Our description of the charged clusters widens the previous descriptions of mono and multi-vacancies and points out the importance of the controlled formation of defects for the realization of transition metal oxide based devices with a desirable magnetic performance.

-/abstract-

# A tale of three cubic double perovskites: $Ba_2XOsO_6$ , $X=Na, Ca, Y$

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High valent Os based double perovskites are one center of current interest because they display extreme interplay of large spin orbit coupling and strong electronic correlation. We present electronic and magnetic structures of three cubic Os based double perovskites with  $Os^{+7} (d^1), Os^{+6} (d^2), Os^{+5} (d^3)$ . Despite of  $d^1$  and  $d^2$  configuration  $Ba_2NaOsO_6$  shows very little Jahn-Teller distortion, and  $Ba_2CaOsO_6$  also remains cubic. For these first principles based calculation we used an onsite hybrid exchange only on Os(5d), as implemented in Wien2k. While  $Ba_2NaOsO_6$  is a ferromagnetic Mott insulator, the other two show antiferromagnetic ordering. Our approach faithfully reproduce experimental magnetic moments and Mott insulating state for these perovskites.[1] For comparison purposes we have investigated only the ferromagnetic ordered phase of these three materials. A metal-insulator transition by changing spin orbit coupling direction is observed in all three materials, however each double perovskite is metallic for different magnetic directions. In addition to that we are presenting isotropic chemical shielding constants and magnetic susceptibilities for all these three perovskites with respect to different spin orbit coupling directions, Os shows the most perturbation with change of spin orbit coupling directions. Surprises from looking at the radial charge densities will be discussed.

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[1] S. Gangopadhyay and W. E. Pickett, Physical Review B **91**, 045133 (2015).

# Large phonon anharmonicity in complex oxide and thermoelectrics

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Harmonic and quasi-harmonic models of lattice dynamics are widely successful in explaining thermodynamic properties of materials. However, in some cases, strong anharmonicity can critically affect physical properties, therefore it is important to consider the anharmonic effect in the lattice dynamics models. In this talk, we present the results of *ab initio* molecular dynamics studies of strong anharmonicity in long-standing debated VO<sub>2</sub> and record-high thermoelectrics SnSe. Our first-principles simulations provide good agreement with our measurements of phonon dispersions. We established that the entropy driving the metal-insulator transition in VO<sub>2</sub> is dominated by soft, anharmonic phonons of the metallic phase [1]. We revealed that the origin of strong anharmonicity is responsible for the unique properties of SnSe [2]. This understanding of the role of anharmonicity in lattice provides a critical component for developing more complete physical models of functional materials and energy materials.

[1] J. D. Budai\*, J. Hong\*, M. E. Manley, E. D. Specht, C. W. Li, J. Z. Tischler, D. L. Abernathy, A. H. Said, B. M. Leu, L. A. Boatner, R. J. McQueeney and O. Delaire, Metallization of vanadium dioxide driven by large phonon entropy. *Nature*, 515, 535–539 (2014)

[2] C.W. Li,\* J. Hong,\* A.F. May, D. Bansal, S. Chi, G. Ehlers and O. Delaire, submitted to *Nature Physics*.

Theoretical calculations were performed using the NERSC at LBNL and OLCF at ORNL. Modeling of neutron data was performed in CAMM, measurements were funded by the US DOE, BES, Materials Science and Engineering Division.

# Strong electron-phonon interaction in an FeSe monolayer

Sinisa Coh, Marvin L. Cohen, Steven G. Louie

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We show that the electron-phonon coupling in an FeSe monolayer on a SrTiO<sub>3</sub> substrate is significantly larger than in earlier theoretical estimates. The role of the SrTiO<sub>3</sub> substrate is two-fold. First, the interaction of the FeSe and TiO<sub>2</sub> terminated face of SrTiO<sub>3</sub> prevents the FeSe monolayer from undergoing a shearing-type (orthorhombic) structural phase transition. Second, the substrate allows an anti-ferromagnetic ground state of FeSe which opens certain electron-phonon coupling channels within the monolayer that are prevented by symmetry in the non-magnetic phase. The spectral function for the electron-phonon coupling ( $\alpha^2F$ ) in our calculations agrees well with inelastic tunneling data.

This work was supported by NSF Grant No. DMR10-1006184 and the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. Computational resources have been provided by the DOE at Lawrence Berkeley National Laboratory's NERSC facility.

# First-principles interpretation of ultrafast time-resolved core-level spectroscopies investigating photo-induced charge transfer

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Ultrafast time-resolved core-level spectroscopies provide valuable real-time element-specific probes of chemical dynamics and play an ever more prominent role in the characterization of photoelectrochemical (PEC) systems for energy harvesting applications [1]. However an unambiguous interpretation of the observed transient spectroscopic signatures requires theoretical methods capable of connecting these to structural and dynamical models of materials. We present two case studies of first-principles theoretical methods applied in conjunction with experimental time-resolved x-ray photoemission spectroscopy (TRXPS) and time-resolved x-ray absorption spectroscopy (TRXAS) to investigate charge transfer dynamics at organic-inorganic interfaces relevant to PEC technologies. We use a combination of constrained density functional theory (CDFT) and time-dependent density functional theory (TDDFT) to interpret measured transient core-level shifts in femtosecond to picosecond time-resolved XPS/XAS measurements. In the first study, the dynamics of electron injection from a N3 dye molecule chemisorbed onto a ZnO substrate, within the first picosecond after photo-excitation, is investigated. We argue that the core-level shifts observed a few hundred femtoseconds after photo-excitation of the dye are consistent with a charge-separated exciplex state [2]. In the second study, we theoretically interpret spectroscopic signatures of laser-excited Zn-porphyrin based donor-pi-acceptor dyes [3] as observed in TRXAS measurements with 80ps time resolution. These studies illustrate the utility of combined experimental and theoretical studies in achieving an in-depth understanding of dynamical processes in PEC materials.

## References:

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# Parallel Eigensolver for Electronic Structure Calculations

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We describe a parallel eigensolver designed for electronic structure calculations. For large problems, diagonalization becomes computationally dominant in all standard Kohn-Sham DFT codes. While universal packages such as LAPACK and ScaLapack are widely used in electronic structure, they fail to take advantage of specific characteristics of the problem. Our new diagonalizer, a partitioned folded spectrum method (PFSM), executes up to an order of magnitude faster than the standard solvers while achieving the same level of accuracy and convergence. It is currently implemented in the Real Space Multigrid (RMG) code developed at NCSU, but it is not specific to this code. RMG is open source and runs on Linux, Windows and Macintosh systems. It has achieved over 6.5 PFLOPS running on 18k nodes of a Cray XK7, and can be downloaded at [sourceforge.net/projects/rmgdft/](http://sourceforge.net/projects/rmgdft/). For more information about PFSM, see the preprint at [arxiv.org/abs/1502.07806](http://arxiv.org/abs/1502.07806). A stand-alone implementation of PFSM will also be distributed as open-source software.

# Developing a machine-learned band gap density functional to facilitate high-throughput searches for optical materials

Brian Kolb and Alexie M. Kolpak

Density functional theory (DFT) is built on the idea that the ground-state electronic charge density is a fundamental variable for an atomic system, meaning that properties of the system can be determined by functionals of this density. Approximations to the total energy functional, for example, have been extremely successful, and are the cornerstone of much materials research. Some key properties, such as the electronic band gap, are not well treated in a Kohn-Sham scheme, and require expensive higher-order methods such as GW or TD-DFT to compute accurately. Such difficulties can preclude high-throughput screening for these properties, or their computation in large complex systems such as heterostructures or systems with dilute defects. While, in principle, properties other than energy can be written as density functionals, this remains a largely unexplored possibility since the form of these functionals is completely unknown *a priori*. Progress can be made, however, by computing densities via DFT and band gap via the GW method for a set of materials and leveraging machine learning techniques to find a connection between these. Such a connection would allow the band gap to be predicted with accuracy nearing GW, but at the computational cost of DFT. Solving such a problem (*i.e.* finding predictive relationships within large and complex data sets) is the forte of machine learning approaches, which have already proven their utility in similar problems. In this work, we construct a training set of  $\approx 1000$  small non-metallic systems for which we compute the ground-state charge density within DFT and the electronic band gap within the GW approximation. We use an in-house developed code to train a neural-network-based density functional to predict the GW band gap from the ground-state density. The aim of this approach is to provide a cheap alternative to expensive GW calculations for use in high-throughput searches for optical materials.

# Electronic, magnetic and topological properties of semi-Dirac dispersion with strongly broken particle-hole symmetry

Yundi Quan and Warren E. Pickett

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**ABSTRACT:** The recently discovered semi-Dirac (semi-Weyl) point in  $\text{TiO}_2/\text{VO}_2$  with massless dispersion along the diagonal of the Brillouin zone and massive dispersion in the perpendicular direction is an important development towards achieving highly anisotropic topologically non-trivial states by engineering complex electronic structures from easily available materials. This model is extended from previous studies on a two-dimensional square lattice to a three orbital model. The electronic, magnetic and topological aspects of the system are explored by varying experimentally tunable parameters, viz. on-site energies, hopping amplitudes, and inter-orbital coupling strengths. With moderate inter-orbital interactions, the middle band has a flat contour and touches the lower band at four semi-Dirac points. When subject to an external magnetic field perpendicular to the lattice, the energy spectrum exhibits fractal structure with respect to the fractional part of the number of magnetic flux quanta per unit cell (Hofstadter spectrum) and each subband has a well defined Chern number which we have calculated numerically.

# Strain-tunable topological quantum phase transition in buckled honeycomb lattices

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(Dated: May 15, 2015)

Low-buckled silicene is a prototypical quantum spin Hall insulator with the topological quantum phase transition controlled by an out-of-plane electric field. We show that this field-induced electronic transition can be further tuned by an in-plane biaxial strain  $\varepsilon$ , owing to the curvature-dependent spin-orbit coupling (SOC): There is a  $Z_2 = 1$  topological insulator phase for biaxial strain  $|\varepsilon|$  smaller than 0.07, and the band gap can be tuned from 0.7 meV for  $\varepsilon = +0.07$  up to 3.0 meV for  $\varepsilon = -0.07$ . First-principles calculations also show that the critical field strength  $E_c$  can be tuned by more than 113%, with the absolute values nearly 10 times stronger than the theoretical predictions based on a tight-binding model. The buckling structure of the honeycomb lattice thus enhances the tunability of both the quantum phase transition and the SOC-induced band gap, which are crucial for the design of topological field-effect transistors based on two-dimensional materials.

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Abstract for a poster for the ES2015 of APS

Adsorption and dissociation of H<sub>2</sub>O monomer on ceria(111): Density functional theory calculations

Shuang-Xi Wang, Ping Zhang, Shu-Shen Li

The adsorption properties of isolated H<sub>2</sub>O molecule on stoichiometric and reduced ceria(111) surfaces are theoretically investigated by first-principles calculations and molecular dynamics simulations. We find that the most stable adsorption configurations form two hydrogen bonds between the adsorbate and substrate. The water molecule is very inert on the stoichiometric surface unless up to a high temperature of 600 K. For the reduced surface, we find that the oxygen vacancy enhances the interaction. Moreover, simulations at low temperature 100 K confirm that it is facilitated for water to dissociate into H and OH species.

Supported by Science Foundation of China University of Petroleum, Beijing (No.YJRC-2013-15) and NSFC(No.11347177).

# Quasiparticle and optical band gaps of $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ from *ab initio* many-body perturbation theory

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The Ruddlesden-Popper (RP) homologous series  $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$  provides a unique opportunity to study the effect of dimensionality and confinement on the band gap and band edges states of the complex oxide  $\text{SrTiO}_3$  [1]. The structure of the  $n$ -th member of the RP series consists of a periodic stacking of  $n$  perovskite  $\text{SrTiO}_3$  monolayers separated by single SrO planes along one axis. As  $n$  becomes large, the structure converges toward bulk  $\text{SrTiO}_3$ . Experimental measurements have shown a decrease in the direct and indirect optical gaps, composed primarily of transitions between occupied O 2p and unoccupied Ti 3d states, as a function of  $n$ . Previous theoretical work [1] focused on the indirect gap and used density functional theory to reproduce the qualitative decrease of band gap as a function of  $n$ . In this work, we study the electronic and optical properties of selected members of the series ( $n=1-5$  and  $\infty$ ) quantitatively, calculating their direct and indirect quasiparticle band gaps using hybrid functionals and many-body perturbation theory within the  $GW$  approximation. Our  $GW$  calculations are in good agreement with measured direct optical gaps ( $\Gamma \rightarrow \Gamma$ ), suggesting that excitonic effects are modest in these materials. Our computed indirect  $GW$  gaps ( $M \rightarrow \Gamma$ ) overestimate reported optical gaps for small values of  $n$  but converge to experimental values at large  $n$ . Accounting for the electron-hole interaction via the Bethe-Salpeter equation approach for selected  $n$ , we compute *ab initio* optical gaps and spectra, and compare with experiment.

[1] Lee *et al.*, APL **102**, 122901 (2013).

## Abstract Submitted

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Structure Theory

**Geometrical structures and electronic properties of Sm, K-doped chrysene** XIAO-HUI WANG, Beijing Computational Science Research Center, Beijing, 100094, China, GUO-HUA ZHONG, Center for Photovoltaics and Solar Energy, Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, Shenzhen, 518055, China —The discovery of superconductivity in potassium-doped picene ( $K_xC_{22}H_{14}$ ) has revitalized the research interest in polycyclic aromatic hydrocarbons (PAHs), and a large variety of PAHs superconductors have been reported afterwards, such as phenanthrene, coronene and 1,2;8, 9-dibenzopentacene. Recently a new PAHs superconductor, Sm-doped chrysene, with  $T_c \sim 5$  K was reported experimentally whose precise nature is still unknown. In this work, crystal structure search and electronic structure of A-doped chrysene,  $A_x-C_{18}H_{12}$  ( $A=Sm, K$ ), have been studied by the first-principles density-functional theory using the projector augmented wave method based on the generalized gradient approximation implemented in the VASP package. We also include the van der Waals (vdW) corrections in the calculations, thus clarifying the dopant atoms positions and crystal structures of doped superconducting chrysene. Our findings represent a significant step toward the understanding of superconductivity of PAHs.

# Rashba Spin-Orbit Coupling Enhanced Carrier Lifetime in Organometal Halide Perovskites

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Organometal halide perovskites are promising solar-cell materials for next-generation photovoltaic applications. The long carrier lifetime and diffusion length of these materials make them very attractive for use in light absorbers and carrier transporters. Previous studies reported a relatively low defect concentration in  $\text{CH}_3\text{NH}_3\text{PbI}_3$ , which reduces the scattering centers for nonradiative charge carrier recombination. Recently, it has been suggested that the spatial carrier segregation caused by disorder-induced localization or domains acting as internal  $p$ - $n$  junctions may reduce the recombination rate. While these aspects of organometal halide perovskites have attracted a great deal of attention, the consequences of the Rashba effect [1], driven by strong spin-orbit coupling on the photovoltaic properties of these materials are largely unexplored. In this work, taking the electronic structure of methylammonium lead iodide as an example, we propose an intrinsic mechanism for enhanced carrier lifetime in 3D Rashba materials. Based on first-principles calculations and a Rashba spin-orbit model, we demonstrate that the recombination rate is reduced due to the spin-forbidden transition. These results are important for understanding the fundamental physics of organometal halide perovskites and for optimizing and designing the materials with better performance. The proposed mechanism including spin degrees of freedom offers a new paradigm of using 3D Rashba materials for photovoltaic applications.

[1] M. Kim, J. Im, A. J. Freeman, J. Ihm, and H. Jin, Proc. Natl. Acad. Sci. 111, 6900 (2014).

# First principles study of reaction voltage of metal-fluoride cathodes in Li-ion rechargeable battery

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Binary metal compounds have been widely investigated for their potential applications in conversion reaction of Li-ion rechargeable batteries as they have high Li storage capacity compared to commercialized electrode materials of intercalation reaction. Metal fluorides,  $\text{MF}_2$  (M=Fe, Ni, Cu) especially show a relatively higher reaction voltage among binary metal compounds and thus, can be considered as promising cathode materials for Li-ion rechargeable batteries. The deviation between conventionally obtained theoretical voltage and experimentally observed voltage is the key issue and is still not understood well, however. In this study, we combined first principles calculations and experiments to analyse the conversion reaction voltage for  $\text{MF}_2$  (M=Fe, Ni, Cu) in Li-ion battery. We developed a new method to gain theoretical voltage of conversion reaction as a function of metal nanoparticle size. This methodology is different from conventional way of attaining voltage which adopts the Gibbs free energy of bulk metal. In order to calculate the reaction voltage, model systems of metal nanoparticles in different sizes are adopted with cuboctahedron and icosahedron morphologies. Based strictly on thermodynamics, the result points toward strongly size-dependent voltage. The property of voltage becomes similar to the voltage calculated from bulk metal, as the size of metal nanoparticle increases. The reaction voltage measured from PITT experiment supports the calculation results, indicating lower values compared to the voltage of bulk metal formation. It is remarkable that we proposed the excessive energy on the surface of a metal nanoparticle is an energy penalty, which leads the reaction voltage drop with respect to the voltage of bulk metal formation.