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제13회 고등과학원

# 전자구조 계산학회

일시 : 2017년 6월 15일 (목) - 6월 16일 (금)

장소 : 고등과학원 1호관 대강당

6월 15일 (목)		6월 16일 (금)	
8:30 - 9:20 등록		8:30 - 9:30 등록	
9:20 - 9:30 환영인사			
<b>Session I: Materials Discovery</b>  좌장: 이재광 (부산대학교)	<b>09:30 - 10:10</b> 장기주 (KAIST)  New carbon and boron allotropes discovered by ab initio materials design	<b>Session V: Electronic and optical properties</b>  좌장: 최윤이 (삼성종합기술원)	<b>9:30 - 10:10</b> 이재동 (대구경북과학기술원)  Energetics and transitions in a nanostructure with few-layer or several-layer semiconductor
	<b>10:10 - 10:50</b> 김덕영 (HPSTAR)  New oxidation states of iron oxides at high pressure and its implication to the state of the deep lower mantle		<b>10:10 - 10:50</b> 민홍기 (서울대학교)  Optical and transport properties of 3D Dirac materials
10:50 - 11:20 휴식		10:50 - 11:20 휴식	
<b>Session II: Development of New Methods 1</b>  좌장: 최형준 (연세대학교)	<b>11:20 - 12:00</b> 김한솔 (KAIST)  Extending constrained density functional theory for non-equilibrium quantum transport calculations	<b>Session VI: Electron-phonon interactions</b>  좌장: 이준희 (UNIST)	<b>11:20 - 12:00</b> 허준석 (성균관대학교)  Quantum simulation of molecular vibronic transitions
	<b>12:00 - 12:40</b> 김형준 (KAIST)  Inclusion of Environment Effect to Electronic Structure Calculations using Grid-based Mean-field Coupling of MD and DFT		<b>12:00 - 12:40</b> 김충현 (기초과학연구원)  Polar octahedral rotation and multiferroicity in the bilayer iridates
12:40 - 14:00 점심식사		12:40 - 14:00 점심식사	
<b>Session III : Development of New Method 2</b>  좌장: 김우연 (KAIST)	<b>14:00 - 14:40</b> 고아라 (기초과학연구원)  Truncated Hilbert Space in the Impurity Solver for the Dynamical Mean-Field Theory	<b>Session VII: Strongly correlated materials</b>  좌장: 이관우 (고려대학교)	<b>14:00 - 14:40</b> 심지훈 (POSTECH)  Evolution of the Kondo lattice electronic structure above the transport coherence temperature
	<b>14:40 - 15:20</b> 민승규 (울산과학기술원)  Coupled electron-nuclear dynamics based on exact factorization: from molecules to solids		<b>14:40 - 15:20</b> 문창연 (표준과학연구원)  Origin of doping-driven suppression and reemergence of magnetism in $\text{LaFeAsO}_{1-x}\text{H}_x$ : A DFT+DMFT study
15:20 - 15:40 휴식		15:20 - 15:40	
<b>Session IV: Topological materials</b>  좌장: 진호섭 (UNIST)	<b>15:40 - 16:20</b> 양범정 (서울대학교)  Unconventional topological phase transition in two-dimensional noncentrosymmetric systems	폐회 및 우수 포스터 시상식	
	<b>16:20 - 17:00</b> 김영국 (성균관대)  $\text{Z}_2\text{Z}_2$ topological Dirac insulators		
17:00 - 20:00			
포스터 세션 + 뱅켓 (홀리데이인 서울 성북 호텔)			

# **New carbon and boron allotropes discovered by *ab initio* materials design**

Kee Joo Chang,<sup>1</sup> Ha-Jun Sung,<sup>1</sup> Woo Hyun Han,<sup>1</sup> Sunghyun Kim,<sup>1</sup> and In-Ho Lee<sup>2</sup>

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Since the Materials Genome Initiative was launched in 2011, much attention has been paid to designing advanced materials in an accelerated way and in a cooperative way of theory, computation, and experiment. Recently, we have developed a protocol for computational materials design, called AMADEUS (*Ab initio* MAterials DEsign Using cSa), in which the conformational space annealing (CSA) algorithm for global optimization is combined with first-principles density functional calculations [1]. The efficiency of AMADEUS has been demonstrated by successful applications to predict Si and C allotropes with optically allowed direct band gaps [1-4]. Here we show the results of applications for exploring new exotic C and B allotropes. We identify that a new carbon allotrope termed  $m\text{-C}_8$  belongs to the class of topological nodal line semimetals, exhibiting the topological nodal line in bulk and the topological surface states at surface boundaries [5]. We find novel metastable B allotropes which can be understood as a three-dimensional buckled hexagonal lattice with B vacancies [6]. We suggest that these non-icosahedral B allotropes play as an intermediate phase on the pressure-induced transition pathway from  $\alpha\text{-B}$  to  $\gamma\text{-B}$  in the framework of the Ostwald rule of steps. Finally, we report a two-dimensional triangular Kagome lattice of boron, which exhibits the exotic electronic properties, such as half-metallic ferromagnetism and anomalous quantum Hall effect in the presence of spin-orbit coupling [7].

## References

1. I.-H. Lee, Y. J. Oh, S. Kim, J. Lee, and K. J. Chang, *Comp. Phys. Commun.* 203, 110 (2016).
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6. W. H. Han, Y. J. Oh, D.-H. Choe, S. Kim, I.-H. Lee, and K. J. Chang, *NPG Asia Materials*, in press (2017).
7. S. Kim, W. H. Han, I.-H. Lee, and K. J. Chang, arXiv: 1704.06842.

# **New oxidation states of iron oxides at high pressure and its implication to the state of the deep lower mantle**

Duck Young Kim<sup>1</sup>

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Computational research using Density Functional Theory (DFT) becomes practical to real materials' study and nowadays can guide experimental synthesis of novel materials, which enables us to have another insight about Nature against our conventional wisdoms. Crystal structure searching strategies combined to DFT have successfully predicted novel phases of elements, binary compounds, and even ternary compounds at high pressures. In this presentation, I will show our recent theoretically predicted and experimentally synthesized new oxidation state of iron, namely a pyrite-structured iron dioxide (FeO<sub>2</sub>) [1] at high pressure conditions. It undergoes a metal-insulator transition [2] and a spin transition induced by pressure, which is relevant to abnormal seismic velocity change at the deep lower mantle (DLM) [3]. Last, interacting with hydrogen, FeO<sub>2</sub> turns into a hydrogen-bearing form, namely FeO<sub>2</sub>H<sub>x</sub> (X <1), reversibly [4]. We propose an alternative scenario of the composition of the DLM based on our theoretical and experimental evidences.

[1] FeO<sub>2</sub>, FeOOH, and the Earth's Oxygen-Hydrogen Cycles, *Nature* **534** 241 (2016)

[2] Metal-insulator transition and the role of electron correlation in FeO<sub>2</sub>, *Phys. Rev. B* **95** 075114 (2017)

[3] Hydrogen-bearing iron peroxide and the origin of ultralow-velocity zones, under review

[4] Dehydrogenation of FeO<sub>2</sub>H at Earth's lower mantle, *Proc. Natl. Acad. Sci.* **114** 1498 (2017)

# **Extending constrained density functional theory for non-equilibrium quantum transport calculations**

Han Seul Kim and Yong-Hoon Kim

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We have been developing a multi-space-constrained density functional theory (mscDFT) approach for the first-principles calculations of nano-scale junctions subjected to non-equilibrium conditions and charge transport through them [1, 2, 3]. In the first part of this presentation, we point out a critical issue of numerical accuracy caused by the non-variational nature (the absence of a minimum principle) of electrical current in non-equilibrium Green's function (NEGF) formalism which is a standard quantum transport calculation method. Then we start the second part by providing the details in theory and implementation of mscDFT which obtains non-equilibrium electronic structure within variational principle. As the application system, we consider the vertically-stacked graphene/hexagonal boron nitride (hBN)/graphene Van der Waals heterostructures in the context of tunneling transistor applications. Bias-dependent changes in energy level alignment, wavefunction hybridization, and current are extracted. In particular, we compare quantum transport properties of single-layer (graphene) and infinite (graphite) electrode limits on the same ground, which is not possible within the traditional NEGF formalism. The origin of anomalous nonlinear current-voltage characteristics will particularly be discussed.

- [1] Kim, H. S. and Kim, Y.-H. Bulletin of the American Physical Society 60, BAPS.2015.MAR.T23.15.
- [2] Kim, H. S. and Kim, Y.-H. Bulletin of the American Physical Society 61, BAPS.2016.MAR.K31.5.
- [3] Kim, H. S. and Kim, Y.-H. Bulletin of the American Physical Society 62, BAPS.2017.MAR.Y32.3.

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# **Inclusion of Environmental Effect to Electronic Structure Calculations using Grid-based Mean-field Coupling of MD and DFT**

Hyung-Kyoo Lim and [Hyungjun Kim](#)

*Graduate School of EEWS, KAIST, Daejeon*

First-principles based electronic structure theory, such as density functional theory (DFT) calculation, has been employed in a variety of complex systems. Notwithstanding its wide applications and successes, the calculation often assumes the system being *in vacuo* due to its relatively high computational cost. To extend the applicability of first-principles calculations, it is therefore important to develop new routes to effectively include dynamic environmental effect of the solvation into electronic structure calculations. In this talk, we discuss about our recent approach of grid-based seamless coupling of classical molecular dynamics simulation (to sample the dynamical environmental effect) with planewave based DFT (to investigate the electronic structure), namely DFT in classical explicit solvent (DFT-CES). By employing mean-field approximation, the computational overhead of DFT-CES is much reduced compared with that of conventional QM/MM methods. Moreover, we coupled the fast and efficient free energy calculation method based on two-phase model (2PT) into our DFT-CES method, which enables the direct and simultaneous computation of solvation free energies as well as the electronic structure changes due to solvation effect. We further discuss how our new multiscale simulation method can be applied to investigate exotic material properties where solid-liquid interface becomes important; e.g., solvation of heterogenous catalyst surface, electrochemical interface, etc.

# **Truncated Hilbert Space in the Impurity Solver for the Dynamical Mean-Field Theory**

Ara Go<sup>1</sup> and Andrew J Millis<sup>2</sup>

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*<sup>2</sup>Department of Physics, Columbia University*

Dynamical mean-field theory (DMFT) has been widely used to investigate various correlated systems in condensed matter physics, such as transition metal oxides and heavy fermion systems. Despite of its impressive performance and success, the application of the DMFT is often limited due to imperfection of impurity solvers. For example, the fermionic sign problem puts inevitable difficulties in quantum Monte Carlo calculations with non-diagonal hybridization functions. On the other hand, the exact diagonalization (ED) suffers from excessively large Hilbert spaces if the number of electronic orbitals is larger than twelve. These are insufficient for most realistic DMFT calculations, if multi-orbital feature plays an important role in the target systems.

We introduce a new implementation of Hilbert space truncation for an impurity solver. The effective Hilbert space is constructed by iterative truncation after particle-hole substitutions are applied to adaptively updated reference states. We benchmark the one- and two-dimensional Hubbard model to test the impurity solver and show how the spectral description is improved by additional orbitals. The new solver is capable to solve the impurity Hamiltonians with twenty-four orbitals, where eight of them are correlated. This is twice as large as the ED limit and the capability is particularly useful for multiband cases. We also discuss potential applications in combination of density functional theory, focusing on spin-orbit coupled multi-orbital systems.

# **Coupled electron-nuclear dynamics based on exact factorization: from molecules to solids**

Seung Kyu Min<sup>1</sup>

*<sup>1</sup>Department of Chemistry, School of Natural Science, Ulsan National Institute of Science and Technology (UNIST), 50, UNIST-gil, Ulsan 44919, Republic of Korea*

Nonadiabatic molecular dynamics plays a major role in photochemical/physical phenomena such as photosynthesis, vision processes, and solar cells. So far various theoretical/computational methods for the excited state dynamics have been developed, and one of the most promising tool for practical calculation is a trajectory-based mixed quantum-classical approach such as trajectory surface hopping or Ehrenfest dynamics. However, the conventional trajectory-based approach has major drawbacks. Trajectory surface hopping method suffers from the lack of electronic decoherence, and Ehrenfest dynamics cannot reproduce the spatial splitting of a nuclear wave packet. The exact factorization[1] provides an alternative tool to understand chemical reactions with a single time-dependent potential energy surface and time-dependent vector potentials. Based on the exact factorization, we have recently developed a new mixed quantum-classical algorithm which can describe a nice nuclear wave packet splitting as well as electronic decoherence[2,3] in various non-adiabatic situations. Here I present a novel quantum-classical approach to nonadiabatic dynamics and its applications to various photochemical reactions. In addition, an algorithm toward condensed matter system will be discussed.

## References

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- [2] S. K. Min\*, F. Agostini, E. K. U. Gross, Phys. Rev. Lett., 115, 073001 (2015)
- [3] F. Agostini, S. K. Min\*, A. Abedi, E. K. U. Gross, J. Chem. Theory Comput. 12, 2127 (2016)

# **Unconventional topological phase transition in two-dimensional noncentrosymmetric systems**

Bohm-Jung Yang<sup>1</sup>

<sup>1</sup>*Department of Physics and Astronomy, Seoul National University*

Here I am going to talk about a topological phase transition between a normal insulator and a quantum spin Hall insulator in two-dimensional (2D) systems with time-reversal and two-fold rotation symmetries. Contrary to the case of ordinary time-reversal invariant systems where a direct transition between two insulators is generally predicted, we find that the topological phase transition in systems with an additional two-fold rotation symmetry is mediated by an emergent stable two-dimensional Weyl semimetal phase between two insulators. Here the central role is played by the so-called space-time inversion symmetry, the combination of time-reversal and two-fold rotation symmetries, which guarantees the quantization of the Berry phase around a 2D Weyl point even in the presence of strong spin-orbit coupling. Pair-creation/pair-annihilation of Weyl points accompanying partner exchange between different pairs induces a jump of a 2D  $Z_2$  topological invariant leading to a topological phase transition. According to our theory, the topological phase transition in HgTe/CdTe quantum well structure is mediated by a stable 2D Weyl semimetal phase since the quantum well, lacking inversion symmetry intrinsically, has two-fold rotation about the growth direction. Namely, the HgTe/CdTe quantum well can show 2D Weyl semimetallic behavior within a small but finite interval in the thickness of HgTe layers between a normal insulator and a quantum spin Hall insulator. We also propose that few-layer black phosphorus under perpendicular electric field is another candidate system to observe the unconventional topological phase transition mechanism accompanied by emerging 2D Weyl semimetal phase protected by space-time inversion symmetry.

## **Z<sub>4</sub>xZ<sub>2</sub> topological Dirac insulators**

Youngkuk Kim<sup>1</sup>

<sup>1</sup>*Department of Physics, Sungkyunkwan University, Suwon, Korea*

Since the discovery of topological insulators in 2005 [1,2], topological band theory has been greatly developed, revealing a large variety of symmetry-protected topological insulators and semimetals. Examples include topological crystalline insulators [3,4], Weyl/Dirac semimetals [5,6], and Dirac line node semimetals [7,8]. Here we introduce a new class of topological insulators, which we refer to as a *topological Dirac insulator*. A *topological Dirac insulator* is a bulk insulator with protected metallic surface states, allowed by non-symmorphic space group symmetries. Unlike conventional topological insulators, the surface states of a *topological Dirac insulator* occur as a four-fold degenerate Dirac point, which can be considered as a topological phase boundary between two-dimensional topological and normal insulators. We introduce Z<sub>4</sub>xZ<sub>2</sub> topological invariants and demonstrate how to calculate the topological invariants from the Wilson loop calculations. We also discuss its material realizations based on first-principles calculations.

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# **Energetics and transitions in a nanostructure with few-layer or several-layer semiconductor**

JaeDong Lee<sup>1</sup>

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Many conventional concepts in relation to electronic or optical transition based on the energy level schemes are clearly applied to the bulk system, but not promptly clear in the few-layer or several-layer system because rather complicated layer-by-layer (layer-resolved) band structure is evolved compared to the bulk band structure. To explore a nanostructure with few-layer or several-layer semiconductor, we propose a new physical insight in handling the electronic or optical transition from the layer-resolved band structure. For example studies, using the first-principles electronic structure calculations, we introduce our recent works concerning (i) a determination of the Schottky barrier in few-layer black phosphorous metal contacts and (ii) optical transitions in the Si nanomebrane.

## **Talk 10**

# **Optical and transport properties of 3D Dirac materials**

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In recent years, there have been much interest in Dirac materials such as graphene, topological insulators and Weyl/Dirac semimetals, which are described by the Dirac-like equation at low energies. Interestingly, Dirac materials in condensed matter systems can have a modified form which does not have a particle-physics analogue, such as anisotropic nonlinear energy dispersion and a topological charge larger than one. In this talk, using standard methods such as tight-binding model, Boltzmann transport theory, and linear response theory which appear in undergraduate or graduate level text books, I will discuss electronic structure, optical and transport properties in 3D Dirac materials. Especially, I will focus on 3D multi-Weyl semimetals and nodal line semimetals, which have non-trivial topology compared with conventional Dirac materials with linear dispersion, thus exhibiting a unique quantum response.

# Quantum simulation of molecular vibronic transitions

Joonsuk Huh<sup>1</sup>

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The intrinsic nature of parallelism of quantum states is anticipated to give extraordinary computational power to quantum processors for certain problems. A linear optical network is one of the simplest quantum processors that it could reveal the (computational) quantum supremacy against classical machines. A photon-sampling problem in a linear optical network, so-called Boson Sampling, is a specially designed mathematical problem, which is expected to be intractable for any classical machine. In my talk, I will present what we can do with the photonic quantum simulator (non-universal quantum computer) practically. Boson Sampling is generalized with Gaussian input states to simulate the molecular vibronic spectroscopy [1-5].

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Quantum emulation of molecular force fields: A blueprint for a superconducting architecture  
Preprint: arXiv:1611.08101

[5] B. Peropadre, J. Huh and C. Sabin, Dynamical Casimir effect for boson sampling, Preprint: arXiv:1610.07777

## **Polar octahedral rotation and multiferroicity in the bilayer iridates**

Choong Hyun Kim<sup>1</sup>

<sup>1</sup>*Center for Correlated Electron Systems, Institute for Basic Science, Seoul, Korea*

<sup>2</sup>*Department of Physics and Astronomy, Seoul National University, Seoul, Korea*

Most perovskite oxides undergo octahedral rotation which strongly influence other electronic, magnetic, and orbital degree of freedom in perovskites and related materials. Hybrid improper ferroelectricity is described by trilinear coupling of two types of octahedral rotation in A-site ordered perovskites or  $n=2$  Ruddlesden-Popper structures. Polar octahedral rotation consequently have the potential to realize new multifunctional materials with strong magnetoelectric coupling. Here we propose and demonstrate hybrid improper ferroelectricity appearing in bilayer perovskite iridates  $\text{Ca}_{3-x}\text{Sr}_x\text{Ir}_2\text{O}_7$  from first-principles density-functional-theory calculations. Its similarity to parent compound cuprates of high-temperature superconductor makes iridates a good candidate for exploring unconventional superconductivity upon carrier doping. And  $d$ -wave charge gap by electron doping was observed by several experiments. In this regards, controllability of magnetism could provide a new opportunities to study superconductivity. Our proposal provide novel route to control magnetism via polar octahedral rotation.

## Talk 13

# Evolution of the Kondo lattice electronic structure above the transport coherence temperature

Ji Hoon Shim<sup>1</sup>

*<sup>1</sup>Department of Chemistry & Physics, Division of Advanced Nuclear Engineering, Pohang University of Science and Technology, Pohang 37673, Korea*

The temperature-dependent evolution of the Kondo lattice is a long-standing topic of theoretical and experimental investigation and yet it lacks a truly microscopic description of the relation of the basic f-d hybridization processes to the fundamental temperature scales of Kondo screening and Fermi-liquid lattice coherence. In this talk, the temperature-dependence of f-d hybridized band dispersions and Fermi-energy f spectral weight in the Kondo lattice system CeCoIn<sub>5</sub> is investigated using first principles dynamical mean field theory (DMFT) calculations containing full realism of crystalline electric field states. All the calculated results are directly compared to f-resonant angle-resolved photoemission (ARPES). Our results reveal f participation in the Fermi surface at temperatures much higher than the lattice coherence temperature,  $T^* \approx 45$  K, commonly believed to be the onset for such behavior. The identification of a T-dependent crystalline electric field will be discussed with its contribution to  $T^*$  as well as local Kondo temperature  $T^K$ .

## References

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# **Origin of doping-driven suppression and reemergence of magnetism in $\text{LaFeAsO}_{1-x}\text{H}_x$ : A DFT+DMFT study**

Chang-Youn Moon<sup>1</sup>, Hyowon Park<sup>2</sup>, Kristjan Haule<sup>3</sup>, Ji Hoon Shim<sup>4</sup>

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Recently, hydrogen doped 1111 material,  $\text{LaFeAsO}_{1-x}\text{H}_x$  has been shown to exhibit another superconducting phase followed by a new antiferromagnetic phase at high doping levels [1-3]. In this work [4], we investigate the magnetic and electronic properties of these materials using DFT+DMFT method, which captures the material-specific electronic correlation. Considering changes of both electron occupancy and lattice structure caused by the hydrogen doping which turn out to have the opposite effects on the electron correlation and magnetism, we find that both the magnetic moment and local susceptibility initially decrease to the minimum at around  $x=0.3$  and then increase again up to  $x=0.6$ , in agreement with the experimental phase diagram of two separate AFM phases centered at  $x=0$  and  $0.5$ . More electron occupation at  $d_{xz/yz}$  orbitals with the doping enhances the importance of the  $d_{xy}$  orbital in the static magnetic moment and also in spin dynamics, while reducing the orbital polarization. Our results emphasize the importance of the electron correlation and structural modification in understanding the doping induced evolution of the electronic structure, and also the magnetism as an indispensable ingredient for the emergence of the superconductivity in these materials.

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## 제 13회 고등과학원 전자구조계산 학회

## Poster Session

\* 포스터세션은 banquet 장소 (홀리데이인 서울 성북 호텔)에서 진행됩니다

강기재	1-POS	Board 1
강성우	2-POS	Board 2
강윤구	3-POS	Board 3
고은정	4-POS	Board 4
고재현	5-POS	Board 5
김관우	6-POS	Board 6
김나영	7-POS	Board 7
김선우	8-POS	Board 8
김영재	9-POS	Board 9
김재욱	10-POS	Board 10
김택중	11-POS	Board 11
노민종	12-POS	Board 12
Thekkepat, Krishnamohan	13-POS	Board 13
Leconte, Nicholas	14-POS	Board 14
Liu, Kai	15-POS	Board 15
박가람	16-POS	Board 16
박나영	17-POS	Board 17
박은원	18-POS	Board 18
박재현	19-POS	Board 19
박재홍	20-POS	Board 20
박환열	21-POS	Board 21
성하준	22-POS	Board 22
송영선	23-POS	Board 23
신동재	24-POS	Board 24
심재훈	25-POS	Board 25
여강모	26-POS	Board 26
여인원	27-POS	Board 27
유동선	28-POS	Board 28
윤상문	29-POS	Board 29
윤영필	30-POS	Board 30
윤용	31-POS	Board 31
윤흥기	32-POS	Board 32
이규현	33-POS	Board 33
이동현	34-POS	Board 34
이미소	35-POS	Board 35
이병주	36-POS	Board 36
이성우	37-POS	Board 37
이세호	38-POS	Board 38
이수진	39-POS	Board 39
이승준	40-POS	Board 40
이시현	41-POS	Board 41
이정희	42-POS	Board 42
이준수	43-POS	Board 43
이준호	44-POS	Board 44
장보규	45-POS	Board 45
장승우	46-POS	Board 46
정민용	47-POS	Board 47
진태원	48-POS	Board 48
차선경	49-POS	Board 49
채진웅	50-POS	Board 50
최민	51-POS	Board 51
최지혜	52-POS	Board 52
Chittari, Bheema Lingam	53-POS	Board 53
한규승	54-POS	Board 54
한우현	55-POS	Board 55
Rahman MD Mokhlesur	56-POS	Board 56

## **Ab-initio study on charge trap states in nitrogen-deficient amorphous Si<sub>3</sub>N<sub>4</sub>**

Gijae Kang, Kyeongpung Lee and Seungwu Han\*

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As the non-volatile memory market has grown tremendously, the needs for smaller, low-power memory devices has been increased significantly. However, attempts to overcome the scaling limitation and the reliability problem of conventional floating gate has not been rewarded yet. Tunnel oxide scaling is limited by stress-induced leakage current (SILC) related to charge loss problem. In the conventional floating gate storage, a single oxide trap will cause a complete charge loss when the device scales down to less than 10nm.

One of the most promising alternatives for the floating gate memory is the charge trap memory device in which amorphous silicon nitride (Si<sub>3</sub>N<sub>4</sub>) is used as a charge trapping layer. The high scalability and the retention capability originated from non-itinerant mid-gap states renders the material to be a suitable candidate for the application. Even though the characterization of the charge trap center is crucial for improving the performance of the storage device, the atomic and electronic properties of the trap states are still not fully understood.

In this study, we carried out first-principles calculations to investigate the characteristics of the charge trap states in the nitrogen-deficient amorphous silicon nitride. The ensembles of amorphous Si<sub>3</sub>N<sub>4-x</sub> structures were generated using ab-initio molecular dynamics. The atomistic and electronic characteristics of the trap states are discussed. This study will give a useful insight into designing and optimizing the charge trap devices.

# **Theoretical investigation of MoS<sub>2</sub> van der Waals p-n junction and application as a hydrogen evolution reaction catalyst**

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In past few decades, there have been many efforts to store solar energy into the form of H<sub>2</sub> by water splitting hydrogen evolution reaction (HER) as a replacement of fossil fuels. However, additional bias to the equilibrium voltage, which is called overpotential, should be provided to obtain enough current because of kinetic barrier in the reaction process. Thus, the efficiency of HER importantly depends on the catalytic material. Recently, transition-metal dichalcogenides (TMDs), especially MoS<sub>2</sub>, have been considered as a promising candidate for HER catalyst due to their low cost, large surface area, and stability in acidic environments. There have been extensive attempts to improve catalytic ability of MoS<sub>2</sub> such as increasing edge sites, transforming phase and inducing defects and strain. Despite these efforts, the efficiency did not reach practical level because the overpotential is not reduced enough. One attempt was made to reduce the overpotential by transferring n-MoS<sub>2</sub> on the p-type Silicon. The overpotential was reduced by the built-in potential generated from charge-transfer between p-Si and n-MoS<sub>2</sub>. Also, this research suggested that the overpotential would be more reduced by constructing van der Waals (vdW) TMDs p-n junction whose p-type and n-type parts are both composed of TMDs layers.

In this research, we theoretically investigate the electronic structures of homogeneous vdW MoS<sub>2</sub> p-n junction and explore its potential applications. We first calculate electronic structures and charge-transfer characteristics of bilayer p-n junction. Then, the quadlayer and hexalayer p-n junction are studied. Based on the DFT calculation results, we inductively build a model for N-layer MoS<sub>2</sub> p-n junction to estimate the built-in potential and electronic structures. Our obtained built-in potential values suggest vdW MoS<sub>2</sub> p-n junction as an efficient HER catalyst even in experimentally possible doping levels. Furthermore, our study of electronic structures suggests TMDs p-n junctions as a novel candidate for optoelectronic applications.

## Comment on "Quasi-One-Dimensional Metal-Insulator Transitions in Compound Semiconductor Surfaces"

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Low-dimensional electronic systems are of great interest in contemporary condensed-matter physics because of their susceptibility to charge density wave (CDW) instability, non-Fermi liquid behavior, spin ordering, and superconductivity at low temperatures. Recently, Zhao et al. [1] claimed that one-atom-wide metallic structures formed by selectively bonding of H or Li atoms to GaN(10 $\bar{1}$ 0) and ZnO(10 $\bar{1}$ 0) undergo the Peierls-type metal-insulator (MI) transitions, leading to a charge-density-wave (CDW) formation with periodic lattice distortion. However, using hybrid density functional theory calculations, we demonstrate that the ground state of such quasi-one-dimensional systems exhibits the competition between the CDW state and the antiferromagnetic (AFM) state. It is found that the GaN(10 $\bar{1}$ 0)-1H system prefers the AFM ground state, while ZnO(10 $\bar{1}$ 0)-1H the CDW ground state [2]. These results are confirmed by the exact-exchange plus correlation in the random-phase approximation (EX + cRPA).

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## Tunneling properties through the nanometer-scale oxide in Ge- and Si-based structures

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Germanium (Ge) is a promising channel material due to its high intrinsic mobility in the Ge- based device. One of the key issues for high-performance of the Ge-based device is the tunneling leakage current through Ge/high-k material structures. From inferring from the old Si-based device structure such as Si/a-SiO<sub>2</sub>/poly Si, in Ge/a-GeO<sub>2</sub>/Ge structures, we investigate the effect of the thickness of a-GeO<sub>2</sub> and the Ge orientations on the tunneling property by first-principles transport calculations. We also compare the tunneling property in Ge/a-GeO<sub>2</sub>/Ge structures with that in Si/a-SiO<sub>2</sub>/Si and Si/c-SiO<sub>2</sub>/Si structures. [1] We compute the tunneling spectra and estimate the tunneling current density with respect to the oxide (a-GeO<sub>2</sub>, a-SiO<sub>2</sub>, c-SiO<sub>2</sub>) thickness ranging from 0.6 nm to 2.1 nm and with respect to the Ge orientations such as Ge (100), Ge (110), and Ge (111). We also examine the effects of interfacial structures such as an abrupt interfacial structure with dangling bonds and a passivated interfacial structure with hydrogen atoms on the tunneling property.

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## Atomic Models for Anionic Ligand Passivation of IV-VI, II-VI, and III-V Colloidal Quantum Dots

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Recently, we have reported that ligand-surface coordination affects physicochemical properties such as shape, doping polarity, and air-stability for IV-VI and III-V colloidal quantum dots (CQDs) [1-3]. Despite its tremendous importance, experimental and theoretical studies on ligand-surface coordination at the microscopic level have been limited due to the complexity of CQDs from wet chemistry synthesis, compared to quantum confinement effect of truncated bulk materials. In order to understand the ligand-surface coordination at the microscopic level, we have examined stable ligand-surface coordination between anionic ligands and cation-rich surfaces of IV-VI (PbS), II-VI (CdSe), and III-V (InAs) CQDs based on electron counting model and first-principles density-functional theory calculations. We found that PbS(111) prefers to (1x1) anionic ligand passivation, in which every Pb atom is exactly coordinated with one anionic ligand in the (1x1) surface unit cell; CdSe(100) could have (1x1) anion passivation or (2x1) reconstruction by Cd-Cd dimerization; CdSe(111) could have (2x1) anion passivation or 1:1 amine-anion co-passivation; InAs(100) could have (2x1) anion passivation or 1:1 amine-anion co-passivation after In-In dimerization; finally InAs(111) could have (2x2) three-anions passivation or 1:3 amine-anions co-passivation. Based on our findings, we could rationalize how II-VI and III-V CQDs with tetrahedral shape are stabilized under amine-anion co-passivation conditions [4].

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## **Ab initio study of a water molecule inside a carbon nanotube/ boron nitride nanotube heterostructure**

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In this presentation, we will report a first-principles study of behaviors of a water molecule inside a carbon nanotube/boron nitride nanotube (CNT/BNNT) heterostructure. We investigate structural, energetic, and electronic properties of the system based on density functional theory (DFT).

For the calculations, Vienna Ab initio Simulation Package (VASP) is utilized. The cutoff energy value was 400 eV and the generalized gradient approximation is used for the exchange-correlation functional. We consider the van der Waals interaction, and use Grimme's DFT-D2 method. For model structures, the (7, 7) CNT and BNNT are chosen. The lattice constants of the CNT and BNNT are 2.48 and 2.51 Å, respectively, and the total length of the heterostructure along the tube axis is about 2.5 nm.

We find that the equilibrium distance between a water molecule and the wall of the CNT (BNNT) is 3.1 Å (3.0 Å). In the CNT (BNNT), the energy of the water molecule is 40 meV higher (110 meV lower) at the center of the tube, and is 45 meV lower (225 meV lower) at the equilibrium position in the tube than in vacuum. In the heterostructure, the potential profile along the tube axis shows a dramatic change around the heterojunction. We expect that a velocity change of water flow could occur near the heterojunction.

## **Shape-Controlled Iron Oxide (FeO) Nanoparticles by the Introduction of Rare-Earth Metals: A First-Principles Study**

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Shape- and size-controlled synthesis of nanoparticles are of great importance in utilizing their unique properties. In many previous studies, people have made efforts to develop ways to control the size and shape of nanoparticles, which is employment of various types of additives and surfactants to stabilize selective facets of nanoparticles. The anionic species, halides and organic surfactants, are well-known for controlling the surface energy and the particle shape. However, we reported that the introduction of rare-earth metals induces sphere-to-cube shape changes in iron oxide nanoparticles and this results in oxide nanoparticles covered with rare-earth metals. In this study, we performed first-principles density functional theory (DFT) calculation in order to understand the shape transformation of iron oxide nanoparticles in the presence of gadolinium precursors for various FeO surfaces. The surface formation energy for (100) and (111) surfaces was calculated to determine thermodynamic stability. Our theoretical work suggests that the undecomposed gadolinium complexes can bind selectively to (100) facets and induce the sphere-to-cube shape change.

## **Microscopic Mechanism of Tunable Band Gap in Potassium Doped Few-Layer Black Phosphorous**

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Tuning band gaps in two-dimensional (2D) materials is of great interest in the fundamental and practical aspects of contemporary material sciences. Recently, black phosphorus (BP) consisting of stacked layers of phosphorene was experimentally observed to show a widely tunable band gap by means of the deposition of potassium (K) atoms on the surface, thereby allowing great flexibility in design and optimization of electronic and optoelectronic devices. Here, based on the density-functional theory calculations, we demonstrate that the donated electrons from K dopants are mostly localized at the topmost BP layer and such a surface charging efficiently screens the K ion potential. It is found that, as the K doping increases, the extreme surface charging and its screening of K atoms pull down the conduction bands having more charge near the surface relative to the vacuum level, while little influence the valence bands having more charge in the deeper layers. This explanation for the observed tunable band gap is different from the previously proposed giant Stark effect that presumed the presence of a vertical electric field from the positively ionized K overlayer to the negatively charged BP layers. The present prediction of the conduction band minimum and valence band maximum as a function of the K doping reproduces well the widely tunable band gap, anisotropic Dirac semimetal state, and band-inverted semimetal state, as observed by angle-resolved photoemission spectroscopy experiment. Our findings shed new light on a route for tunable band gap engineering of 2D materials through the surface doping of alkali metals.

## **Petahertz frequency control of spins at light-wave-controlled charge processing**

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Light-wave-controlled petahertz transport of charges being made asymmetric with respect to the spin carried, the spin transport would result at the same speed. This will be materialized by proposing a model of the layered heterostructure of ferromagnetic (FM) transition metal trichalcogenides (TMTC) and nonmagnetic (NM) semiconductor. With a strong FM TMTC, major and minor spins undergo the cross transfer to the NM and FM layer, respectively, whereas with a weak FM TMTC, only major spins are mostly transferred to the NM layer due to the Coulomb blockade for minor spins. These findings introduce prototypes of the petahertz spin devices, broadening horizons of the spintronics up to the subfemtosecond time span.

# Fast and accurate hybridization scheme for real-space based density functional theory programs

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## Abstract

Since the hybrid method[1] was proposed in the 1990s, which suggests mixing the Hartree-Fock exact exchange energy to the pure density functionals, the hybrid functional became a widely used method in various fields. B3LYP[2], PBE0[3], and HSE[4] functional are one of the popular hybrid functionals. The hybrid functional gives more exact thermodynamic quantities such as binding energy and also provides quantitatively better band-gap for various systems.

The calculation of Hartree-Fock exchange kernel requires tremendous computational costs so that the calculations using the Hybrid functional often avoided. Here, we provide the hybrid method who effectively reduce the computation time without losing the accuracy. Using of the local exact exchange potential produced by the optimized effective potential (OEP) method, the exchange integral can be done easier and faster for real-space grid based program.[5] Furthermore, we adopted LC-wPBE(2Gau) functional [6] to our scheme, which approximates  $\text{erf}(r)/r$  as a linear combination of two Gaussian-type functions. In this presentation, we demonstrate how our method is effective for the molecular system.

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## **Magnetic interactions of organic electrides with zigzag channels**

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We report our recent progress in calculating Heisenberg exchange parameter,  $J_{ij}$ , based on linear response magnetic force theory [1, 2]. Our previous implementation within the non-orthogonal pseudoatomic local orbital formalism [3, 4] is now extended to have momentum and orbital dependence ( $J^{\alpha\beta}_{ij}(\mathbf{q})$ ) [5]. We apply this method to study organic electride materials,  $\text{Rb}^+(\text{cryptand-2.2.2})\text{e}^-$  and  $\text{Li}^+(\text{cryptand-2.1.1})\text{e}^-$ . By introducing so-called empty atom technique and using maximally localized Wannier functions method, we successfully calculate the magnetic interactions in between the 'cavity-trapped electrons' which act as anions in electrides. Our result shows that the magnetic interaction in these materials forms a 'zigzag channel' which has not been identified in the previous study.

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## Density functional study of the hydrogen evolution reaction activity of cobalt-embedded C<sub>2</sub>N

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### **Abstract:**

A recent experimental study has reported a new type of 2D layered network structure, which possesses the periodical holes and C<sub>2</sub>N stoichiometry in the basal plane: nitrogenated holey two dimensional crystal structure (C<sub>2</sub>N-*h*2D). C<sub>2</sub>N-*h*2D is expected to have great potential for electrode, storage, transistor, and so on. In particular, it is reported that C<sub>2</sub>N-*h*2D network forms a stable complex with cobalt (Co@C<sub>2</sub>N) so that it shows an excellent hydrogen evolution reaction compared with other conventional catalysts. However, the origin of such outstanding catalytic properties has yet to be revealed.

In this presentation, we employ density functional theory (DFT) to thoroughly investigate geometry, energetics, and electronic structure of Co@C<sub>2</sub>N. We find that the cobalt atoms embedded on C<sub>2</sub>N interlayer lead to different stacking order and stability compared pristine C<sub>2</sub>N-*h*2D. Furthermore, the number of cobalt nanoclusters suggests a more sensitive response to high hydrogen evolution reaction (HER) activity. Our results provide a good explanation that a configuration of metal atoms, which embedded on the cavity of 2D layered structure, is very important.

# **Effect of Strain on the Electronic Properties of III-V Semiconductors: A First-principles Study**

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Devices based on III-V semiconductor compounds and alloys exhibit high electron and hole mobility and consume less power in comparison to their Si based counterparts, making them attractive candidates for next-generation electronic devices. Electronic properties of 4 important compound semiconductors GaAs, GaSb, InAs and InSb were investigated using first-principles based hybrid density functional theory method. Properties like band gap, Luttinger parameters and effective masses of electrons and holes along different crystallographic directions were calculated under strained and unstrained conditions. Our calculated values were found to be in good agreement with previous experimental and theoretical reported values<sup>[1,2]</sup> and can be directly used for device process and modeling simulations. Recently, it was also reported that Majorana fermions can be created and manipulated on strained InAs/Sb based heterostructures<sup>[3]</sup>, which takes us one step closer to realization of quantum computers. This is possible due to an electronic topological phase transition under bi-axial strain<sup>[4,5]</sup>. We investigate systematically different types of strain conditions and their efficacy in inducing a topological phase transition in InAs and InSb. In addition to bi-axial strain on the (100) plane (as reported in previous studies), we also study the (110) and (111) planes and find that critical strain required for the topological transition can be lowered. This opens up the possibility of engineering the critical strain by careful selection of crystallographic direction.

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## **Moiré pattern interlayer potentials in van der Waals materials from high level random-phase approximation calculations**

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Stacking-dependent interlayer interactions are important for understanding the structural and electronic properties in incommensurable two dimensional material assemblies where long-range moiré patterns arise due to small lattice constant mismatch or twist angles. We study the stacking-dependent interlayer coupling energies between graphene (G) and hexagonal boron nitride (BN) single layers for different possible combinations such as G/G, G/BN and BN/BN using high-level EXX+RPA *it ab initio* calculations. The total energies differ substantially when compared with conventional LDA, but for stacking-dependent total energy differences we find that the dominance of short-range covalent-type binding over the longer-ranged van der Waals tails near equilibrium geometries renders the LDA as a reasonable starting point for *ab initio* calculation based analyses for the systems we have studied. Our calculations are useful input for study of strains originated by interlayer interactions in incommensurable 2D van der Waals crystals.

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## **Electronic properties for Ge/high-K La<sub>2</sub>O<sub>3</sub> interface structure**

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The challenge of finding a high-quality gate dielectric on germanium, with an interface trap density matched to that of state-of-the-art silicon, has been a fundamental problem in the semiconductor industry for many years [1]. It has been also reported that La<sub>2</sub>O<sub>3</sub> layer can be epitaxially grown on Ge(111) surface without an interfacial GeO<sub>2</sub> layer, making it an attractive candidate among various high-K dielectric materials for Ge-based devices [2,3]. Although there are reports on the electronic properties of La<sub>2</sub>O<sub>3</sub>, the valence band offset (VBO) and conduction-band offset (CBO) of La<sub>2</sub>O<sub>3</sub> to Ge substrates have been rarely discussed [4].

In this study, we construct various types of Ge/La<sub>2</sub>O<sub>3</sub> interface structures for a deep understanding of atomic property and electrical characterization. For Ge(111)/hexagonal La<sub>2</sub>O<sub>3</sub>(001) interface structures, electrical properties, such as interface state density, polarization charge trapping, and effects of the strain, are studied in detail. It is found that the polarization of hexagonal La<sub>2</sub>O<sub>3</sub> could have impact on interfacial properties of Ge/La<sub>2</sub>O<sub>3</sub> supercell and its band offset alignment. Also, supercell model for Ge(100)/amorphous La<sub>2</sub>O<sub>3</sub> is constructed and studied in detail. The electronic structure of Ge(100)/a-La<sub>2</sub>O<sub>3</sub> shows difference in band alignment compared with Ge(111)/crystal La<sub>2</sub>O<sub>3</sub>, which could be related with the non-polarization of amorphous La<sub>2</sub>O<sub>3</sub> structures.

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# Honeycomb Slinky motion: borazine molecule diffusion with hydrogen dissociation on Pt (111)

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## **Abstract:**

Hexagonal boron nitride (hBN) is a wide bandgap material with a high chemical and thermal stability used in devices. In order to use the properties of hBN in devices, it is important to understand how wafer-scale hBN films grow. With strong catalytic effect, the platinum surface is used as a good substrate for growth experiments using chemical vapor deposition (CVD) with borazine gas ( $B_3H_3N_3H_3$ ), a structure similar to benzene molecule ( $C_6H_6$ ), as a precursor. In this study, we investigate the adsorption and diffusion of a borazine molecule on the Pt(111) surface with hydrogen dissociation using the density functional theory. We confirm that borazine on Pt(111) occupies both the hcp hollow and the fcc hollow site, where the molecule lies on the surface. When a borazine molecule migrates from the hcp hollow site to another hcp (or fcc) hollow site, the energy barrier of diffusion is 1.07 eV (or 0.77 eV). The molecule that moved to the fcc hollow site can again migrate to the hcp hollow site with the energy barrier of 0.87 eV. When a hydrogen atom is dissociated from boron and nitrogen of borazine molecule, the energy barriers are 0.08 eV and 1.51 eV, respectively. In this case,  $B_3H_2N_3H_3$  transforms to a vertical structure with the energy barrier of 0.06 eV. And the vertical structure has an energy gain of 0.28 eV compared to the initial parallel structure. By capturing a hydrogen atom,  $B_3H_2N_3H_3$  move to the next hcp (or fcc) hollow site with a low barrier of only 0.31 eV. This sequential process is similar to the way a Slinky toy descends the stairs. As a result, it can be seen that borazine can diffuse easily through the vertical structure after hydrogen dissociation.

# **Structural effect on the defect formation and diffusion in CsPbI<sub>3</sub>**

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Resistive random access memory (RRAM) devices have been considered as promising next generation nonvolatile memory devices due to their high switching speed, endurance, and low power consumption. Much efforts have been devoted to designing advanced materials to enhance the resistive switching effect. In particular, inorganic perovskite materials like CsPbX<sub>3</sub> (X = Cl, Br, and I) with various functionalities are of great interest for RRAM application. To predict new related functional materials, a good understanding of the thermodynamics and kinetics of point defects is required. In this study, we investigated the formation and diffusion of several point defects in CsPbI<sub>3</sub>. Polymorphs of CsPbI<sub>3</sub> were examined in the cubic perovskite structure and the orthorhombic non-perovskite structure. Defect formation energies for V<sub>I</sub>, V<sub>Pb</sub>, V<sub>Cs</sub>, and I<sub>i</sub> were calculated with the standard exchange correlation functionals (PBE) and the migration barrier energies for iodine vacancy were calculated using the nudged elastic band (NEB) method. Our results will serve as a basis for designing advanced materials for RRAM.

# **Atomic and Electronic Structures of the Substitutional W in GaSe Single Tetralayer**

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Since the reproducible separation of graphene from graphite, two-dimensional layered materials have attracted extensive researches. For instance, transition metal dichalcogenides, a compound of transition metal (*e.g.*, Mo and W) and group-VI chalcogens (*e.g.*, S, Se, Te) have been investigated due to their desirable properties such as a high current on/off ratio. Recently, metal monochalcogenides (MMCs), a compound of group-III metal atoms (*e.g.*, Ga and In) and chalcogens, have attracted the academic and the technological interests due to their potential applicability in photoelectronic devices. MMCs consist of stacked tetralayers (TLs). Atoms within a TL form a covalently bonded network (*e.g.*, Se-Ga-Ga-Se), and the stacking of TL is governed by the van der Waals interaction [1]. In this study, we analyzed atomic and electronic structures of W atom substituted in a GaSe single TL (W-GaSe) by performing density functional theory calculations. We used generalized gradient approximation for the exchange-correlation functional and a 4x4 supercell to simulate the isolated W substitutional. The W atom replacing a Ga atom relaxes towards the neighboring Se atoms, resulting in a change in local tetrahedral environment around W atom compared with that around Ga atoms in pristine GaSe. In detail, the interatomic distance between Ga and Se atoms decreases from 4.23 to 4.14Å and the in-plane Se-Se distance increases from 3.75 to 3.91Å. In consequence, the tetrahedral angle of Ga-W-Se decreases from 119° to 112° and that of Se-W-Se increases from 98° to 107°. In short, the W-surrounding tetrahedron in W-GaSe becomes closer to the regular tetrahedron than that in the pristine GaSe. In the electronic structure, we found 5 spin-split defect states within the band gap which are associated with the W atom. Analyzing the wave function characters of the defect states, they are found to be contributed by W(5*d*) orbitals. Due to the spin-split 5*d* orbitals, a magnetic moment of  $3\mu_B$  is developed for each substitutional W atom.

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## Effect of Long-Range Dispersion Correction on Calculation of Elastic Properties of CO<sub>2</sub> Phase II

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Elastic properties of prototypical CO<sub>2</sub> polymorphs under compression are essential to understanding the nature of their pressure-induced structural changes. Despite the fundamental importance in physical chemistry and condensed matter physics and geophysical implications for the nature of fluids in the Earth and planetary interiors, the elastic properties of these polymorphs are not fully understood because of intrinsic uncertainty and difficulties in experimental estimation of elasticity. Theoretical calculations of elastic properties of CO<sub>2</sub> polymorphs allow us to reveal the previously unknown details of elasticity of the diverse polymorphs, particularly, providing useful insight of understand the bonding nature of phase II which has been controversial.

We used the PBE with the long-range dispersion correction by Grimme (PBE-D2) [1] to verify the results for CO<sub>2</sub> – II, in which the role of van der Waals interactions can be significant. However, calculations within PBE and PBE-D2 show little differences on the geometric parameters, elastic constants, bulk modulus, shear modulus, Poisson ratios and acoustic wave velocities of CO<sub>2</sub> – II in the stable pressure region from from 15 to 40 GPa [2]. The effect of D2 correction depends on distances among CO<sub>2</sub> units which are sufficiently small in this region. Our result suggests that CO<sub>2</sub> – II is not purely but faintly molecular. Our report of elasticity of CO<sub>2</sub> phases may hold some promise for studying the elasticity of diverse solids consisting of oxide molecules.

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# Stacking-dependent electric polarization and optical transitions of K valley states in MoS<sub>2</sub>

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Valleytronics utilizes crystal momentum of Bloch electrons as information carrier called valley-index. Monolayer transition metal dichalcogenide (TMDC) is a principal platform where the feasibility of valleytronics has been intensively investigated. The scope has been soon extended to the multilayer TMDC where various effects of the layer stacking on valleytronics have been actively revealed[1-3]. In the multilayer structure, an additional degree of freedom of electron called layer-index can be defined and is associated with electric polarization[4]. However, neither possibility nor demonstration of the control of the layer-index has been reported in both theoretical and experimental perspectives[5]. In this letter, we suggest a prototypical framework of optical control of layer-index in multilayer TMDC based on the analysis of the stacking-dependent electronic properties. First, with MoS<sub>2</sub> as an example, we discuss on the emergence of spontaneous polarization in the layered structure of polar symmetry and development of internal electric field using density functional theory calculations. Second, we discuss the stacking-dependent characteristics of K valley states in the context of double-group theory considering the spin-orbit coupling. Finally, we provide an optical selection rule by which layer- and valley-index can be independently manipulated.

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## Detailed Atomic Reconstruction of Extended Line Defects in Monolayer MoS<sub>2</sub>

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We study the detailed bond reconstructions that occur in S vacancies within monolayer MoS<sub>2</sub> using a combination of aberration-corrected transmission electron microscopy, density functional theory(DFT), and multislice image simulations. Removal of a single S atom causes little perturbation to the surrounding MoS<sub>2</sub> lattice, whereas the loss of two S atoms from the same atomic column causes a measurable local contraction. Aggregation of S vacancies into linear line defects along the zigzag direction results in larger lattice compression that is more pronounced as the length of the line defect increases. For the case of two rows of S line vacancies, we find two different types of S atom reconstructions with different amounts of lattice compression. Increasing the width of line defects leads to nanoscale regions of reconstructed MoS<sub>2</sub> that are shown by DFT to behave as metallic channels. These results provide important insights into how defect structures could be used for creating metallic tracks within semiconducting monolayer MoS<sub>2</sub> films for future applications in electronics and optoelectronics.

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# New topological semimetallic carbon allotrope in mixed $sp^2$ - $sp^3$ bonding networks

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Carbon has a rich variety of structural allotropes due to its ability to form  $sp$ ,  $sp^2$ , and  $sp^3$  hybridized bonds. Two known carbon allotropes, graphite and diamond, are in all  $sp^2$  and  $sp^3$  bonding networks, respectively. Graphene, a single layer of graphite, has all  $sp^2$  bonds and exhibits a linear band dispersion at the Fermi level. Recently, topological semimetals have attracted much attention due to their exotic electronic properties and potential applications. Especially, in topological nodal line semimetals, valence and conduction bands cross each other along lines in momentum space. The nodal line semimetal phase was reported for three-dimensional (3D) carbon networks constructed from graphene, such as Mackay-Terrenes crystal, interpenetrated graphene network, and bco- $C_{16}$ . Due to a negligible spin-orbit coupling in carbon, the nodal lines of these semimetallic carbon allotropes are protected by a combination of inversion and time-reversal symmetries.

In this work, we report a novel 3D carbon allotrope, which belongs to a class of topological nodal line semimetals [1]. We explore new carbon allotropes by using an *ab initio* evolutionary crystal structure search method, as implemented in the AMADEUS code [2]. The new carbon allotrope, termed  $m$ - $C_8$ , consists of five-membered rings with  $sp^3$  hybridized bonds interconnected by  $sp^2$ -graphitic carbon networks. Analyzing the electronic band structure, we confirm that  $m$ - $C_8$  belongs to the class of topological nodal line semimetals. The nodal line is protected by both inversion and time-reversal symmetries in the absence of spin-orbit coupling, and the surface band connecting the projected nodal points is identified. Based on the X-ray diffraction spectra and enthalpy-pressure curves, we propose that the  $m$ - $C_8$  allotrope can be present in experimental detonation soot and a phase transition from graphite to  $m$ - $C_8$  can occur under high pressure.

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# Phonon instability and resonant $p$ -bonds in Ge-Sb-Te compounds

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Ge-Sb-Te (GST) compounds, exhibiting substantial electrical and optical contrast between amorphous and crystalline phases, have attracted great attention for application to non-volatile memory devices. Despite extensive studies of GST compounds, the underlying mechanism for fast transitions between amorphous and crystalline phases is yet to be revealed. In this paper we study the properties of phonons and resonantly bonded  $p$ -orbitals of hexagonal GST compounds using first-principles calculations. By investigating volume-dependent phonon dispersions, we observe the structural instability at elevated temperature due to the spontaneous softening of a specific in-plane vibrational mode ( $E_u$ ). We find that the atomic distortion of the  $E_u$  mode is associated with weakening of resonant  $p$ -bonds. This induces large structural and electrical changes, which is expected to be closely related to the amorphization process. We also discuss how to manipulate the  $E_u$  mode to control the device performance. Our findings would help deepen understanding of the phase-change mechanism and improve the device performance, especially switching power and operating temperature.

# Development of magnetism in armchair graphene nanoribbons with edge functionalizations: A first-principles study

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Graphene nanoribbons with zigzag-shaped edge (zGNRs) are predicted to be magnetic insulator at the ground state, attracting significant interest in view of spintronic applications [1]. On the other hand, although they are energetically and thermodynamically more favored than zGNRs [2], graphene nanoribbons with armchair-shaped edge (aGNRs) have been less spotlighted than zGNRs due to the absence of magnetism. In recent years, we have been systematically studying energetic, electronic, magnetic, and transport properties of edge functionalized GNRs [3]. Herein, based on the combined density functional theory (DFT) and matrix Green's function (MGF) approach, we consider aGNRs functionalized with various molecular groups, and show that the spin polarizations develop for some of the considered aGNR edge functionalization cases. The origin of the induced magnetism will be discussed within the Lieb's theorem [4]. This work will provide a novel guidance for the development of graphene-based spintronic devices.

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# Quantified Degeneracy and Metal Insulator Transition

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While degeneracy can play an important role in determining the material characteristics (e.g. metal-insulator transition), there is no well-defined way to quantify it in real materials having complicated band structure. In this presentation, we suggest a way to quantify 'effective degeneracy' by introducing entropy-like terms. We show that this new quantity well describes the electronic behaviors of real materials. DFT, DFT+U and DFT+DMFT calculations for 3d, 4d, and 5d transition-metal oxides show that the calculated 'effective degeneracy' provides useful insight to understand these systems and their phase transitions.

## **New structure model for the Au/Si(553) surface**

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*(Dated: May 30, 2017)*

Recently, there have been studies about high Miller index silicon surfaces. We expect discover a new physical phenomenon in such systems. The Au/Si(553) surface is a system which is predicted to have spin polarization. The surface electronic structure is important in understanding the spin polarization properties of this surface. The Au/Si(553) surface has a silicon honeycomb structure located at a step edge and two gold-atom chains on the terrace [1]. The calculated electronic structure of the Au/Si(553)1 x 1 show two surface bands originated from the respective gold chains and a band from the silicon honeycomb structure. While in experimental measurements, however, only two gold bands are observed, the band of the honeycomb structure at the step edge is not observed. In this study, using the first-principles method, we calculate the electronic structure of a new model, in which a silicon atom at the step edge is replaced by a gold atom [2]. The electronic structure of the Au/Si(553)1 x 1 of the new model has a band originated from the gold atom at the step edge as well as two bands originated from the respective gold chains, also we find that the band of the silicon, honeycomb structure at the step edge shifts above the Fermi level, which is different from that of the two gold-chain Au/Si(553) model. We compare the electronic structures of both the surfaces and discuss the spin polarization phenomena at the Au/Si(553) surface.

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## Surface morphology of InAs considering entropy effects

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Epitaxial growth of III-V compound semiconductors on Si(001) substrates is important to incorporate III-V materials with outstanding electrical and optical property into the conventional silicon base technology. The epitaxial growth is conducted at a high-temperature and low-pressure conditions where entropy effects become nontrivial. However, the theoretical study of the surface science has usually been conducted on 0 K assuming that the results may not be significantly different from the experimental condition. Therefore, in this study, the thermodynamic effects on the InAs growth was investigated by density functional theory (DFT) calculations including the entropy terms. As the atomic vibrational motion was allowed and configuration was considered, the entropy was found to be important in calculating the high-temperature surface energy. Then, the thermodynamic equilibrium morphology of InAs was determined by Wulff shape as a function of T and P in the region relevant to the experimental growth chamber. By doing so, the change of the surface morphology which is usual process to control the surface properties in experiments could be predicted.

## **Molecular orientation and charge transport in vapor-deposited organic films**

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Organic semiconductors are promising materials for many electronic applications, such as organic light-emitting diodes (OLEDs), organic photovoltaics, and organic thin-film transistors. Vapor-deposition is widely used to prepare these organic films. In the past, it was commonly assumed that the vapor-deposited organic films are isotropic. However, vapor-deposited films can have anisotropic molecular orientation. This is interesting because molecular orientation can improve the light out-coupling efficiency and the charge carrier mobility of the organic electronic devices. Furthermore, vapor-deposited films show exceptional thermal stability compared to ordinary glasses, which helps the device lifetime. In this study, to investigate the effects of vapor-deposition process on film properties, we simulated vapor-deposition process with classical molecular dynamics. The effects of molecular shape and substrate temperature on molecular orientation was shown and it was consistent with previous studies. In the case of doped films, the molecular orientation of dopant molecules was affected by that of host molecules. Also, vapor-deposited films showed higher thermal stability compared to liquid-cooled glass. In addition, we did the charge transport simulation of the deposited films using kinetic Monte Carlo algorithm. Site energies were calculated by using polarizable force fields. The horizontally oriented film showed higher energetic correlation, and higher current density than the isotropic film.

## Importance of Anisotropic Coulomb Interaction in Mn<sub>3</sub>O<sub>4</sub>

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Mixed-valent manganese oxide Mn<sub>3</sub>O<sub>4</sub>, which has attracted much attention not only in fundamental research but also in application fields, is a challenging material to study within the frame of density functional theory (DFT). Mn<sub>3</sub>O<sub>4</sub> has always been yielded as a metal using the conventional DFT calculation, although it has been experimentally observed in an insulating phase. This is due to the spurious self-interaction, which is only partially cancelled under the LDA or GGA exchange-correlation functional. About 10 years ago, a study showed that hybrid functionals would be a better way to describe multivalent manganese oxides within the DFT scheme. [1] On the other hand, it was recently reported that such electronic structures, which are equivalent to those obtained by the hybrid functionals, can be observed by considering the anisotropic Coulomb interactions of localized orbitals within the DFT+U+J calculation. [2] To examine in detail the influence of the anisotropic Coulomb interactions on the electronic structure and magnetic properties of Mn<sub>3</sub>O<sub>4</sub>, we investigated the effects of the valency of manganese ions and the individual roles of the U and J parameters in its electronic structures and magnetic properties. We found that the anisotropic Coulomb interaction between electrons from the trivalent manganese ions affects significantly various physical properties such as band gaps, magnetic moments, canted angles, and exchange coupling constants, whereas that from the divalent manganese ions does not. We further found that these physical properties do directly depend on the occupation of the  $d_{x^2-y^2}$  orbitals of the trivalent manganese ions. Finally we will show that our DFT+U+J calculation with  $U^{\text{Mn}^{2+}} = 4\text{eV}$ ,  $J^{\text{Mn}^{2+}} = 0\text{eV}$ ,  $U^{\text{Mn}^{3+}} = 3\text{eV}$ , and  $J^{\text{Mn}^{3+}} = 1\text{eV}$  verifies the experimentally measured results much better than the previous calculations.

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## **Enhanced Catalytic Behavior of Ni Alloys in Steam Methane Reforming**

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The dissociation process of methane on Ni and Ni alloys are investigated by density functional theory (DFT) in terms of catalytic efficiency and carbon deposition. Examining the dissociation to CH<sub>3</sub>, CH<sub>2</sub>, CH, C, and H is not sufficient to properly predict the catalytic efficiency and carbon deposition, and further investigation of the CO gas-evolving reaction is required to completely understand methane dissociation in steam. The location of alloying element in Ni alloy needed be addressed from the results of *ab-initio* molecular dynamics (MD). The reaction pathway of methane dissociation associated with CO gas evolution is traced by performing first-principles calculations of the adsorption and activation energies of each dissociation step. During the dissociation process, two alternative reaction steps producing adsorbed C and H or adsorbed CO are critically important in determining coking inhibition as well as H<sub>2</sub> gas evolution (i.e., the catalytic efficiency). The theoretical calculations presented here suggest that alloying Ni with Ru is an effective way to reduce carbon deposition and enhance the catalytic efficiency of H<sub>2</sub> fueling in solid oxide fuel cells (SOFCs).

# **First-principles High-throughput Screening of novel p-type Transparent Semiconducting Oxide**

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Transparent semiconducting oxides (TSOs) have been studied for various application, including transparent and flexible electronic devices, and solar cells. While unipolar devices such as oxide thin-film transistor are already commercialized in industry using n-type TSO, there is no practical p-type oxide which is comparable to n-type. It is important to discover p-type TSOs having good performance comparable with n-type TSOs for low-power and low-frequency electronics. However, the existing p-type TSOs such as SnO, Cu<sub>2</sub>O and CuAlO<sub>2</sub> still suffer from low conductivity or low transparency. Recently, as high-throughput screening using density functional theory (DFT) calculation became practicable, several studies screened large number of oxide structures from ICSD to find new p-type TSO using band gap and effective mass as major descriptors.<sup>[1,2]</sup> Although many new candidate materials are suggested that they have promising bulk properties, no materials are verified by experiment to date.

In this work, we suggest a new descriptor for screening p-type oxides and conduct high-throughput calculation. From DFT calculation database of whole binary and ternary oxides in the previous study<sup>[3]</sup>, we calculate hole effective mass for all oxides whose calculated band gap is larger than 2 eV. We use the formation energy of hydrogen interstitial defect as a descriptor for p-type oxides. Through full intrinsic defect calculations, we validate the screened candidates, which is predicted as intrinsic p-type oxide that has large band gap and small hole effective mass.

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## Orbital-resolved exchange interactions combined with QSGW self energy

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We report our recent progress in the magnetic force linear response calculations of exchange parameters [1-3]. Our new implementation calculates  $J^{\vec{j}}(\mathbf{q})_{\alpha\beta}$  (instead of  $J_{ij}$  in the spin Hamiltonian of  $H = \sum J_{ij} S_i \cdot S_j$ ) in  $\mathbf{q}$  space and with  $(\alpha, \beta)$  orbital resolution. This method is combined with two of our software packages, namely, 'OpenMX (<http://www.openmx-square.org>)' and 'ecalj (<https://github.com/tkotani/ecalj>)'. We applied our method to magnetic insulators (MnO, FeO, CoO, NiO) and metals (Mn, Fe, Co, Ni) confirming its reliability and usefulness. In particular, our implementation into 'ecalj' enables us to calculate magnetic interactions within QSGW (Quasiparticle self-consistent GW) framework from which total energy comparison is not feasible.

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## **Development of potential energy surface for SiO<sub>2</sub> system via Artificial Neural Network**

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As the semiconductor devices continued to scale down to 10 nm size, atomistic and quantum mechanical effects become dominant. In this case, the prediction power of conventional device process simulation tools which based on the classical approach began to reduce. Thus, atomic-scale device/process simulation tool is needed for nano-meter-scales devices.

While the molecular dynamics (MD) simulation using density functional theory (DFT) calculation provides highly accurate information about material properties, its high computational cost prohibits real-size device modeling. One can overcome this limitation with classical force fields, However, the accuracy of classical MD simulations critically depends on the interatomic potentials. Although several classical potentials are poised be highly accurate and transferable, optimizing the parameters in the force field requires strenuous efforts.

Recently, artificial neural network (ANN) based potential is gaining attention as an alternative of classical force fields. The potential is constructed through the machine learning on the reference DFT calculation result. Due to its flexible functional form, ANN potential can efficiently represent the DFT result with high accuracy. In this presentation, we tested and developed ANN potential for Si and SiO<sub>2</sub>. The potential generated from various structures not only bulk crystal and amorphous, but also defective structures and surface. We first applied the potential to calculate different SiO<sub>2</sub> crystal phases and check the bulk properties. Finally, we performed an MD simulation to check the validity of generated potential.

# Spin-Singlet Small Bipolaron Revealed in Nonmagnetic $d^0$ Oxides

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Keywords: small polaron, spin-singlet bipolaron, impurity, first-principles calculations

## Abstract

Bipolaron is a dual-polaron-pairing quasiparticle that often explains novel electrical and optical phenomena in solids. However, despite its widespread significance, there is a lack of theoretical study on the bipolaron model in real-level accuracy such as first-principles calculations. Here we show that the electron-lattice coupling mediated by the spin-spin exchange interaction in non-magnetic  $d^0$  oxides can lead to the formation of spin-singlet small bipolaron near impurity. In the prototypical  $\text{TiO}_2$ , we find that small bipolaron near a substitutional hydrogen is not formed in the anatase but is stably formed in the rutile due to antiferromagnetic exchange interaction between two  $\text{Ti}^{3+}$  species bound to the hydrogen. It has been found that this bound small bipolaron is also available in other oxides such as  $\text{HfO}_2$ , as well as other impurities such as fluorine. Our work shows that small bipolaron generated when excess electrons are doped or excited in  $d^0$  oxide can provide a new pathway to understand the distinctive electrical, optical and photocatalytic properties of the oxide.

## **Automated *ab initio* calculations for Screening Non-oxide High-*k* materials**

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As the size of electronic devices has been decreased less than a few nanometers, high gate leakage currents become fatal problem. It leads to high power consumption and reduces device durability. Consequently, many candidates of high-*k* materials such as HfO<sub>2</sub> and ZnO<sub>2</sub> have been suggested to replace conventional SiO<sub>2</sub> as gate dielectric. Recently, high-throughput screening research for high-*k* oxide had been conducted. The research found several candidate materials which have exceeding properties compared t-HfO<sub>2</sub>. However, there are still needs for superb high-*k* materials from non-oxide materials. In future semiconductor technology, the host material might be changed from silicon to higher mobility materials. For example, germanium is outstanding material for next-generation semiconducting industry. But its instability with oxide contact is serious problem to make reliable device. For new material system, new high-*k* materials are required. To screen novel non-oxide high-*k* dielectrics, we conduct high-throughput *ab initio* calculation for non-oxides: binary nitrides, sulfides, phosphides, chloride, and fluorides. We found that nitrides, sulfides, phosphides, chloride usually have lower band gap compared to oxides, so we first extend our screening target to ternary fluorides. As a result, we identified new potential candidates for high-*k* dielectrics.

# Redesign of $\text{Li}_2\text{MP}_2\text{O}_7$ (M = Fe, Mn) by tuning the Li diffusion paths for rechargeable battery electrodes

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## 1. Introduction

The rapidly growing need for reliable power sources stemming from emerging large-scale applications such as electric vehicles requires the development of advanced Li-ion batteries with high performance and low cost.<sup>1-3</sup> To address this issue, many researchers have searched for new electrode materials, the key component determining the performance of batteries. Over several decades, various materials, such as olivines, fluorinated phosphates, silicates, and NASICON-type structures, have been extensively investigated as potential cathode materials to replace the state-of-the-art layered derivatives of  $\text{LiCoO}_2$  for these new large-scale applications. Recently, the pyrophosphate  $\text{Li}_2\text{MP}_2\text{O}_7$  (M = Fe, Mn) has attracted much attention as a potential candidate because of the use of cost-competitive elements (Fe or Mn), the reversible electrochemical reaction at high redox potential, and its easy synthesis via a conventional solid-state reaction.

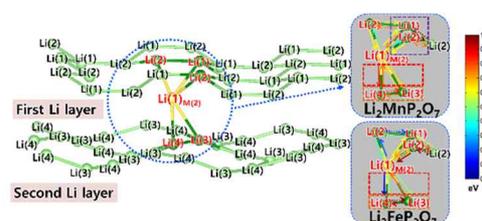


Fig. 1 Li-ion network of  $\text{Li}_2\text{MP}_2\text{O}_7$  with M(2)–Li(1) anti-sites; the corresponding diffusion barriers are designated in the inset.

## 2. Computational detail

First-principle calculations were conducted to estimate the energies of given materials, based on the spin-polarized generalized gradient approximation (GGA) using density functional theory (DFT). We used a plane-wave basis set and the projector-augmented wave (PAW) method which is implemented in the Vienna ab initio simulation package (VASP). PAW potentials have shown good

predictive capability in cathode materials of Li-rechargeable batteries. The Hubbard parameter was added to correct the self-interaction of GGA. U value of 3.9 and 4.0 were used for Mn and Fe in  $\text{Li}_x\text{MP}_2\text{O}_7$  structure. A plane-wave basis with an energy cutoff of 500 eV was used.

### **3. Results and Discussion**

Defects in crystals such as anti-sites generally lead to the deterioration of the ionic conductivity of solid-state ionic conductors. Herein, using first-principles calculations, we demonstrate that the Li diffusion in  $\text{Li}_2\text{MP}_2\text{O}_7$  (M = Fe, Mn), a promising battery material, is sensitively affected by the presence of Li/M anti-sites; however, unexpectedly, the anti-sites significantly promote Li diffusion. The calculations reveal that the presence of anti-sites reduces the barrier of Li hopping and opens up new paths for Li diffusion in the  $\text{Li}_2\text{MP}_2\text{O}_7$  crystal. In our experimental verification, we succeeded in synthesizing crystalline  $\text{Li}_2\text{MnP}_2\text{O}_7$  with varying Li/Mn anti-site contents and demonstrate that the inclusion of anti-sites results in improved power capability with faster Li diffusion for Li-ion battery electrodes. We believe that this unexpected finding of increasing the ionic conductivity by introducing anti-site defects broadens our understanding of solid-state ionic conductors and provides a new strategy to improve Li diffusion in conventional electrode materials for Li rechargeable batteries.

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## **Atomic Structure and Spectroscopy of Single Metal (Cr, V) Substitutional Dopants in Monolayer MoS<sub>2</sub>**

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Dopants in two-dimensional dichalcogenides have a significant role in affecting electronic, mechanical, and interfacial properties. Controllable doping is desired for the intentional modification of such properties to enhance performance; however, unwanted defects and impurity dopants also have a detrimental impact, as often found for chemical vapor deposition (CVD) grown films. The reliable identification, and subsequent characterization, of dopants is therefore of significant importance.

Here, we show that Cr and V impurity atoms are found in CVD grown MoS<sub>2</sub> monolayer 2D crystals as single atom substitutional dopants in place of Mo. We attribute these impurities to trace elements present in the MoO<sub>3</sub> CVD precursor. Simultaneous annular dark field scanning transmission electron microscopy (ADF-STEM) and electron energy loss spectroscopy (EELS) is used to map the location of metal atom substitutions of Cr and V in MoS<sub>2</sub> monolayers with single atom precision. The Cr and V are stable under electron irradiation at 60 to 80 kV, when incorporated into line defects, and when heated to elevated temperatures. The combined ADF-STEM and EELS differentiates these Cr and V dopants from other similar contrast defect structures, such as 2S self- interstitials at the Mo site, preventing misidentification. Density functional theory calculations reveal that the presence of Cr or V causes changes to the density of states, indicating doping of the MoS<sub>2</sub> material. These transferred impurities could help explain the presence of trapped charges in CVD prepared MoS<sub>2</sub>.

# Multivalency-Driven Formation of Te-Based Monolayer Materials: A Combined First-Principles and Experimental Study

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Contemporary science is witnessing a rapid expansion of the two-dimensional (2D) materials family, each member possessing intriguing emergent properties of fundamental and practical importance. Using the particle-swarm optimization method in combination with first-principles density functional theory calculations, here we predict a new category of 2D monolayers named tellurene, composed of the metalloid element Te, with stable 1T-MoS<sub>2</sub>-like ( $\alpha$ -Te), and metastable tetragonal ( $\beta$ -Te) and 2H-MoS<sub>2</sub>-like ( $\gamma$ -Te) structures [1]. The underlying formation mechanism is uniquely rooted in the multivalent nature of Te, with the central-layer Te behaving more metal-like (e.g., Mo), and the two outer layers more semiconductor-like (e.g., S). We also show that the  $\alpha$ -Te phase can be spontaneously obtained from the magic thicknesses truncated along the [001] direction of the trigonal structure of bulk Te, and both the  $\alpha$ - and  $\beta$ -Te phases possess electron and hole mobilities much higher than MoS<sub>2</sub>. Furthermore, we present preliminary but convincing experimental evidence for layering behavior of Te on HOPG substrates, and demonstrate theoretically the importance of multivalency in the layering behavior of Se. These findings effectively extend the realm of 2D materials to group-VI elements.

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## **Alkali metal adsorption on GaSe single tetralayer**

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There have been extensive researches on two-dimensional layered materials like graphene, hexagonal boron nitride, phosphorene, and transition metal dichalcogenides. Metal monochalcogenides (MMC) are also layered two-dimensional material. GaSe is one of the typical MMC. GaSe monolayer consists of stacked tetralayer (Se-Ga-Ga-Se) with covalent bonds. Alkali metal (AM) atoms can act as the electron donor. On the other hand, adsorption of Li atoms are reported to cause a structural transition in MoS<sub>2</sub> monolayer, another family of 2D materials.<sup>1</sup> We investigated adsorption structures and electronic structures of alkali metal adatoms on GaSe single tetralayer by using density functional theory calculations. We found that the most stable adsorption site is the hollow site (H), but on-top of 2<sup>nd</sup>-layer Ga site (T<sub>Ga</sub>) is also locally stable site. The energy difference between H and T<sub>Ga</sub> is smaller than 0.1 eV. In addition, we studied the energy barrier calculation. In Li adatom case, the energy barrier of is 0.13 eV. Na and K adatom case, energy barrier is smaller than Li adatom. In addition, we studied the interaction between two AM adatom. When the distance between adatoms is 4~6Å, the adatoms are under effective attraction mediated by substrate. Also the lowest energy configuration is achieved when the two adatoms are separated by about 5Å. Such an energetic stabilization is accompanied by a characteristic structural modification of GaSe tetralayer in between the two adatoms: the Se atom in-between the two AM adsorbates relaxes towards the adsorbate by breaking a Ga-Se bond. In consequence, a new Ga-Ga dimer is formed. Such structural changes are reflected in the density of states (DOS). From the site-projected DOS, we found the occupied deep defect state within the fundamental gap. The defect state is contributed by the  $p_x$  and the  $p_z$  orbitals of Se atom in-between the AMs and the  $p_x$  and the  $p_y$  orbitals of the Ga atom in the Ga-Ga dimer. This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (No. 2015R1A2A2A01005564).

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## Low Lattice Thermal Conductivity in Phosphorene Oxide

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Recently-discovered phosphorene, a single layer of black phosphorous, has been paid attention to various scientific and engineering communities due to its potential usage for future applications such as a good thermoelectric material. It has, however, a crucial disadvantage that it may become easily oxidized under normal condition. To make good use of such a disadvantage, we identified the equilibrium structure of phosphorene oxide and investigated its phonon transport property using the Boltzmann transport equation based on first-principles density functional theory. We found that phosphorene oxide has much lower thermal conductivity (1~3 W/mK, at 300K) than its pristine counterpart, phosphorene implying a possibility of higher thermoelectric efficiency. To explore the underlying mechanism of phonon transport in detail, we evaluated the contributions of acoustic and optical phonon modes to the lattice thermal conductivity, phase space of phonon scattering and anharmonic phonon scattering rate. Finally, we found that the a strong anharmonic phonon scattering occurred in phosphorene oxide plays an important role in its low thermal conductivity.

# For Better DFT+U Method: Double counting and Hund's interaction

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LDA (or GGA) + $U$  method has been one of the most successful approaches to describe strongly correlated electron systems within first-principles density functional framework. Despite its great success in describing correlated ground state, some limitations have been noticed such as ambiguity of double-counting functional [1-3]. Here we perform a comparative study for the double-counting functional dependence as well as the Hund's exchange coupling and Coulomb interaction anisotropy. Based on our new implementations into 'OpenMX' software package ([www.openmx-square.org](http://www.openmx-square.org)), we discuss the detailed electronic structure, spin splitting, and the non-collinear spin moment formation depending on the LDA (or GGA) + $U$  formalisms and implementations.

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# First-Principles Study on the Polaronic Behavior in Ca-doped BiFeO<sub>3</sub>

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Bismuth ferrite (BiFeO<sub>3</sub>) has attracted attention as a multiferroic material, which simultaneously exhibits both ferroelectric and antiferromagnetic properties [1]. Cation doping has been used in several experimental studies to improve fundamental properties such as the electronic, magnetic and ferroelectric properties of multiferroic oxides [2]. Particularly, it has been reported that the conductive properties of Ca-doped BiFeO<sub>3</sub> can be reversely controlled by changing the concentration of oxygen vacancy (V<sub>O</sub>) and the applied electric field [3]. Here, Ca doping at the Bi site (Ca<sub>Bi</sub>) that provides a hole carrier in the host BiFeO<sub>3</sub> system becomes an acceptor, meaning that its high doping is essential to promote a high concentration of the compensating donor defect like intrinsic V<sub>O</sub>. In the V<sub>O</sub>-depletion region of the electrically formed Ca-doped BiFeO<sub>3</sub>, the uncompensated hole carrier was suggested to be captured by the formation of a small polaron through strong carrier-lattice interaction [4]. Although there are few DFT studies on doped BiFeO<sub>3</sub> [5-6], there is no theoretical study on the polaronic behavior in Ca-doped BiFeO<sub>3</sub>.

In this study, we perform first-principles hybrid functional calculations to understand the microscopic properties of Ca<sub>Bi</sub> and V<sub>O</sub> in Ca-doped BiFeO<sub>3</sub>. We investigated the thermodynamic stability and electronic structure of V<sub>O</sub> defects in undoped and Ca-doped BiFeO<sub>3</sub>, and we identified that V<sub>O</sub> undergoes deep-to-shallow electronic transition from the (0) -charge state to the (2+) -charge state, similar to the other DFT study [7]. Moreover, the Ca<sub>Bi</sub> dopant induce a deep state in Ca-doped BiFeO<sub>3</sub> without oxygen vacancy. This indicates that the hole-induced trap state can be regarded as a small polaron, which associated with the Bi and O atoms near the Ca dopant. Our theoretical results for Ca dopant and oxygen vacancy in Ca-doped BiFeO<sub>3</sub> can provide an explanation for recent experimental observations.

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# First-principles study of adsorption properties of liquid crystal molecule on two-dimensional transition metal dichalcogenides

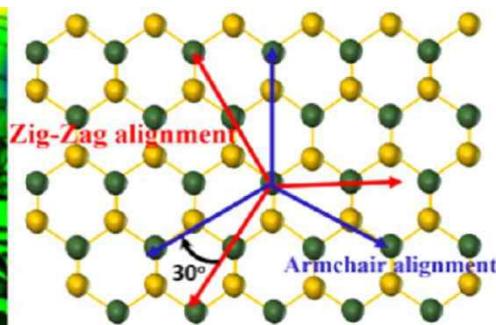
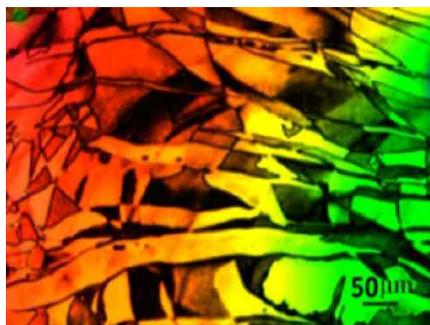
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To modify the electrical and optoelectronic properties of transition metal dichalcogenides (TMDs), direct observation of grains and boundaries is essential. Using a type of liquid crystal molecule, 4-pentyl-4-cyano-biphenyl (5CB), Shehzad *et al.* observed grains and boundaries of the chemical vapor deposition-grown TMDs, molybdenum diselenide (MoSe<sub>2</sub>) and tungsten diselenide (WSe<sub>2</sub>), and also found alignment behavior of 5CB there [1]. To understand this alignment behavior in depth, we have carried out density functional theory calculations, employing the Vienna ab initio simulation package (VASP) [2, 3], and found out discrete preferential orientations and three-fold symmetric alignment of 5CB on the MoSe<sub>2</sub> and WSe<sub>2</sub> surfaces, instead of six-fold symmetry, which is previously reported in the case of another two-dimensional hexagonal lattice, graphene.

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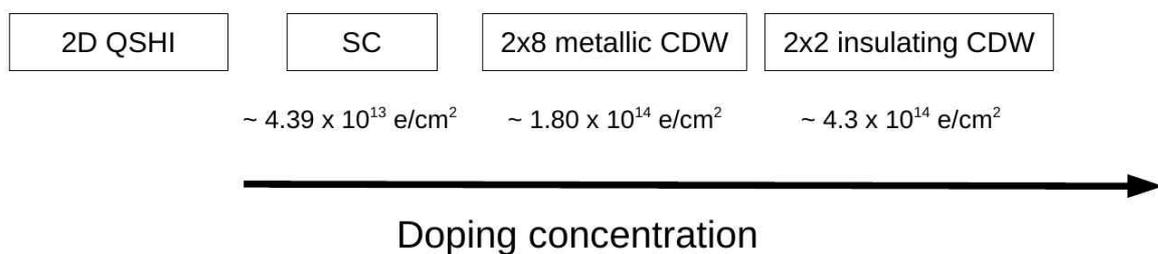
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## Doping-induced phase transitions in single-layer 1T'-TMDs

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We explore doping induced phase transitions in single-layer transition metal dichalcogenides (TMDs) having distorted octahedral phase (1T'),  $MTe_2$  ( $M = Mo$  and  $W$ ), known as a two-dimensional quantum spin Hall insulate (2D QSHI), based on first-principles calculations. We find diverse phase transitions as a function of electron doping. At a low doping region, we obtain a dome-shaped conventional phonon-mediated superconducting (SC) phase by solving anisotropic Eliashberg equation. The transition temperature of SC phase calculated by Allen-Dynes formula reaches around 9 K. At an intermediate doping region, we obtain charge-density wave (CDW) instability at  $\mathbf{q} \approx (0.5/a, 0.375/b, 0) 2\pi$  and find a long-ranged (2x8) CDW phase where the transition metals are clustered each other in zigzag chain of 1T'-TMD. Such peculiar lattice distortions break inversion symmetry and allow a new crystal symmetry which gives rise to a metallic CDW phase. At a high doping region where adatoms are introduced to mimic ionic gating, the metallic CDW phase is transformed into a short-ranged (2x2) insulating CDW phase with the diamond shape chain structure



*Fig. 1. Schematic diagram of phase transitions in single-layer 1T'-TMDs as a function of doping concentration*

## Metal-Insulator and Spin State transition in FeO<sub>2</sub>

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Iron oxide is a key compound to understand the state of the deep Earth. It has been believed that previously known oxides such as FeO and Fe<sub>2</sub>O<sub>3</sub> will be dominant at the mantle conditions. However, the recent observation of FeO<sub>2</sub> shed another light to the composition of the deep lower mantle (DLM) and thus understanding of the physical properties of FeO<sub>2</sub> will be critical to model DLM [1].

Here, we report the electronic structure and structural properties of FeO<sub>2</sub> by using density functional theory (DFT) and dynamic mean field theory (DMFT). The crystal structure of FeO<sub>2</sub> is composed of Fe<sup>2+</sup> and O<sub>2</sub><sup>2-</sup> dimers, where the Fe ions are surrounded by the octahedral O atoms. We found that FeO<sub>2</sub> shows metal-insulator transition (MIT) under high pressure. The MIT is not a Mott type but a band insulator type which is driven by the O<sub>2</sub> dimer bond length change. However, the correlation effect of Fe 3d orbitals should be considered to correctly describe O<sub>2</sub> dimer bond length of FeO<sub>2</sub> and the MIT [2]. Also the spin state transition in FeO<sub>2</sub> under high pressure will be discussed.

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# Thickness-dependent magnetic ground state of $\text{LaMnO}_3$

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$\text{LaMnO}_3$  is one of the prototypical materials in which charge, spin and orbital degree of freedom play together in producing complicated phase diagram. While bulk  $\text{LaMnO}_3$  is known as an A-type antiferromagnetic (AFM) insulator, its thin film is reported to be ferromagnetic (FM) and insulating. Recent experimental studies show an intriguing thickness-dependent AFM-to-FM transition driven by the internal charge transfer at the thickness larger than a critical value [1-3]. To understand these experiments, we performed DFT+ $U$  calculations in combination with constrained random phase approximation (cRPA) method. Our calculations of bulk and the films with thicknesses of 1, 2, and 3 show that the internal charge transfer is occurred even below the experimentally-known critical thickness, which implies that this transfer may not be the main origin of the observed transition.

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## Direct experimental observation of the molecular $J_{\text{eff}}=3/2$ ground state in a lacunar spinel $\text{GaTa}_4\text{Se}_8$

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Strong spin-orbit coupling lifts the orbital degeneracy of  $t_{2g}$  states in  $5d$  transition-metal systems, leaving a Kramers doublet and quartet with effective angular momenta of  $J_{\text{eff}} = 1/2$  and  $3/2$ , respectively. These spin-orbit entangled states can host novel quantum phases such as a topological Mott insulator, unconventional superconductivity, and quantum spin liquid phase. The lacunar spinel compound,  $\text{GaTa}_4\text{Se}_8$ , was theoretically predicted to form the molecular  $J_{\text{eff}} = 3/2$  ground state [1]. Experimental verification of such a novel quantum state is a critical step for exploring and understanding its intriguing physical properties. Here, we report the first direct experimental evidence and theoretical interpretation of the  $J_{\text{eff}} = 3/2$  ground state in  $\text{GaTa}_4\text{Se}_8$ . The excitation spectra collected by resonant inelastic x-ray scattering is compared with the band structure calculations and the cluster model calculations. At the Ta  $L_3$  edge, all low energy orbital excitations were observed, which were assigned to transitions from the occupied molecular orbitals to the unoccupied  $J_{\text{eff}} = 1/2$  and  $3/2$  molecular orbitals. Importantly, however, we found that the excitations involving the  $J_{\text{eff}} = 1/2$  molecular orbital state were totally suppressed at the Ta  $L_2$  edge, directly manifesting the realization of the molecular  $J_{\text{eff}} = 3/2$  ground state in  $\text{GaTa}_4\text{Se}_8$ .

## ***d* electron charge density: predict stable structural phase of transition metal-based magnetic alloy.**

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The existing magnets such as Nd based magnets which are used in the industry show outstanding magnetic properties, but due to the lack of Nd elements on earth and its low Curie temperature ( $T_C$ ), Nd-based magnet is applied only in limited area. Therefore, abundant transition metal based magnets are needed to be investigated to replace Nd-based magnet. As a first step of finding new magnet, the stable crystal structure of the magnet should be predicted, which affects the magnetic properties of the material. Recently, high-throughput method based on the *ab-initio* calculation and data mining approach has been used in various transition metal alloy and collect their magnetic properties [1]. However, there are still a lot of limitation in finding the candidates of new magnet due to lack of understanding of physical parameters which determine properties of the magnet such as stability, maximum energy product ( $(BH)_{max}$ ) and  $T_C$ .

In this work, as an extension of Skriver's work on predicting stable structure of the pure transition metal using *d* electron density [2], we show that it can be applied to binary transition metal alloy. Using the *d* electron density in various binary transition metal alloy for 3*d*, 4*d*, and 5*d* transition metal elements, we successfully predict the stable crystal structure of the magnetic alloy. We suggest that the *d* electron density can be used to predict stable crystal structure of various magnetic material alloy system.

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# First-Principles Calculations on the Electronic Structures of Metal Monochalcogenides

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After the discovery of two-dimensional (2D) semi-metallic graphene with remarkable electronic properties, interests on 2D materials has been increased to an unprecedented degree. Such interests lead to the discovery of various 2D materials like hexagonal boron nitride, phosphorene, and transition metal dichalcogenides. Recently, metal monochalcogenides (MMCs), made up of group-III metal atoms and chalcogens, has been added to the family of 2D layered materials. MMCs have desirable photoelectronic properties [1] and potential applications in solar cell [2]. Very recently, a high electron mobility was reported in the BN-encapsulated few-layer InSe [3]. The basic building block of MMCs is a tetralayer (TL), which is composed of double metal layers sandwiched by outer chalcogen layers.

In this work, we performed density functional theory (DFT) calculations employing the Perdew-Burke-Ernzerhof exchange-correlation functional and the Grimme's dispersion correction to investigate the electronic structure of MMCs. We obtained band gap alignment of different single TL MMCs by aligning the vacuum level. The thickness dependence of the band structure was examined for GaS and obtained the band gap of 2.58, 1.88, and 1.62 eV for 1 TL, 2TLs, and bulk, respectively. In the case of 1 TL GaS, the lowest conduction band is found to be mainly contributed by Ga(3s), Ga(3p), and S(2p) from the partial density of states analysis. The highest valence band is contributed by Ga(3p<sub>z</sub>), Ga(3s), and S(2p) orbitals. The four lower-lying valence bands exhibiting two-fold degeneracy at the  $\Gamma$  point, are mostly made up of S(2p) orbitals. In the case of 2 TLs and bulk, partial charge densities show similar wave function characters with the 1 TL.

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## **Biaxial strain effects on Diamane, Fluoro-diamane and Half-fluoro-diamane: a first-principles study**

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Diamane is a nanomaterial that is formed when hydrogen atoms are bonded to bilayer graphene with  $sp^3$  hybridization. It looks like a diamond nanofilm. Using ab initio calculations based on density functional theory, we investigate electronic structure changes of diamane under a biaxial strain. In this study, the energy cutoff is 35 Ry, and the wave function is expanded, using the plane wave basis. Perdew-Burke-Ernzerhof-type approximation is utilized for the Exchange-correlation functional. The Quantum ESPRESSO package is used. The energy band gap increases when diamane undergoes biaxial stretching. In contrast, the band gap decreases under biaxial compression. In the case of fluoro-diamane where fluorine atoms are replaced for hydrogen atoms, its band gap change has the same tendency as the case of diamane under biaxial strain. We also consider half-fluoro-diamane. In this system, hydrogen atoms are bonded to one side, and fluorine atoms are attached to the other side. According to our results, the band gap of diamane is 3.4 eV. On the other hand, half-fluoro-diamane has an energy band gap of 1.8 eV. The energy band gap of fluoro-diamane is 3.6 eV.

## **Excited electron dynamics in the 1T/2H heterophase of monolayer MoS<sub>2</sub>: real-time time dependent density functional theory study for photo-catalyst application**

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Monolayer MoS<sub>2</sub>, one of the two-dimensional transition metal dichalcogenide (TMD) materials, has two different phases, 2H and 1T phases. The 2H, the stable phase, is a semiconductor with direct band gap about 2.4 eV, and 1T, the meta-stable phase, has metallic phase. The 2H phase of MoS<sub>2</sub> has been studied and utilized as a hydrogen evolution reaction (HER) catalyst because of its photovoltaic and photo-catalytic features. On the other hand, the 1T phase of MoS<sub>2</sub> has been investigated in the perspective of nanoscale electronic device, such as ultrathin transistor and supercapacitor electrode component. Furthermore, the heterophase boundary of 2H and 1T phases was also synthesized and its microscopic dynamics was investigated in terms of phase boundary or phase transition.

In this study, we investigated geometric and electronic structure of the MoS<sub>2</sub> heterophase. We found that two different types of phase boundary lead to difference in the band alignments at MoS<sub>2</sub> phase boundaries. As a consequence, the excited electrons in the 2H phase region are transferred and accumulated in the 1T phase region, leading to the charging of the 1T phase region. We performed the real-time time dependent density functional theory (rt-TDDFT) calculation for this electron dynamics. We found that, as the 1T phase is charged, the activation barrier of dissociative adsorption of oxygen molecule on the planar surface of 1T phase is decreased. In the acidic condition, the oxygen reduction reaction (ORR) energy profile on the charged 1T phase region shows similar electrochemical properties with that on the platinum (100) surface. We suggest that the MoS<sub>2</sub> heterophase can serve as the novel low-dimensional ORR photo-catalyst.

## **Structural origin of ReS<sub>2</sub> and quasi-1D phase transition in A<sub>x</sub>Re<sub>1-x</sub>S<sub>2</sub> (A; W, Mo)**

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ReS<sub>2</sub> is one of the group 7 TMDCs having distorted 1T structure with  $2a \times 2a$  unit cell (1T''). This can be compared to the 1T' ( $a \times 2a$  unit cell) phase of group 6 TMDCs which are ground or metastable states. In this work, we compared the 1T' and the 1T'' structure of ReS<sub>2</sub> to unveil the origin of ReS<sub>2</sub>. And we investigated phase transition from the 1T' to the 1T'' structure in W<sub>x</sub>Re<sub>1-x</sub>S<sub>2</sub> and Mo<sub>x</sub>Re<sub>1-x</sub>S<sub>2</sub> using virtual crystal approximation (VCA). In result, the 1T' to the 1T'' transition was 1D Peierls-like transition due to quasi-1D dispersed bands of the 1T' structure. And critical point of the transition was near the  $x = 0.5$  for both VCA systems supporting experimental studies. The critical behavior could be explained by Lindhard function.

## **Electronic and magnetic properties of single-layer $MPX_3$ metal phosphorous trichalcogenides**

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We systematically investigate the electronic structure and magnetic properties of two dimensional (2D)  $MPX_3$  (M= V, Cr, Mn, Fe, Co, Ni, Cu, Zn, and X = S, Se, Te) transition metal chalcogenophosphates to examine their potential role as single-layer van der Waals materials that possess magnetic order. Our *ab initio* calculations predict that most of these single-layer materials are antiferromagnetic semiconductors. The band gaps of the antiferromagnetic states decrease as the atomic number of the chalcogen atom increases (from S to Se to Te), leading in some cases to half-metallic ferromagnetic states or to non-magnetic metallic states. We find that the phase transition boundary from antiferromagnetic semiconductor to ferromagnetic half-metal can be substantially influenced by gating or by strain engineering. The sensitive interdependence we find between magnetic, structural, and electronic properties establishes the potential of this 2D materials class for applications in spintronics.

# Atomic configuration and electronic structures of Ga(As,Sb) solid solution using cluster expansion method

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A solid solution is the chemical mixture of some components and forms a single phase in the composition of a certain range. Many physical and electronic properties of the solid solution are related to atomic configuration [1][2]. From this perspective, a solid solution of GaAs and GaSb, i.e., Ga(As,Sb) is the interesting material. Although it has been used in laser device and its prospect as a next generation semiconductor is promising, its atomic configuration is not well known. Some study considered GaAs<sub>0.5</sub>Sb<sub>0.5</sub> as Cu-Au structure [3], while other study treated GaAs<sub>0.5</sub>Sb<sub>0.5</sub> as chalcopyrite structure [4]. When we assume that properties such as energy come from the interaction between atoms, whole interaction in materials can be divided into interactions of some atomic groups, which are called clusters, and contributions of each interaction determined the property of the materials. Cluster expansion method expects the properties of the material from this data. In this study, the most stable configuration of GaAs<sub>x</sub>Sb<sub>1-x</sub> is investigated for the compositions at x=0.25, 0.5, and 0.75 by using density functional theory calculations combined with the cluster expansion method. The stable configuration of GaAs<sub>x</sub>Sb<sub>1-x</sub> without strain is compared with that under biaxial strain.

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## **New metastable boron allotropes on the pressure-induced transition pathway from $\alpha$ -B to $\gamma$ -B**

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Elemental boron is known as one of the fascinating elements due to its variety of allotropes which are attributed to the ability to form multi-center bonds. Most of three-dimensional (3D) boron allotropes contain B<sub>12</sub> icosahedra as structural units. Theoretical calculations and experiments have shown that various 3D allotropes such as  $\alpha$ -B, amorphous B, and  $\beta$ -B transform to a  $\gamma$ -orthorhombic phase of B at high pressure and high temperature. In addition to B<sub>12</sub> icosahedra, the  $\gamma$ -B phase has B<sub>2</sub> dumbbells occupying the octahedral cavities. Due to the different numbers of atoms per unit cell, the structure of  $\gamma$ -B is incompatible with those of other B allotropes. Thus, it is a challenging issue to understand the kinetic pathway toward  $\gamma$ -B.

In this work, we report the discovery of novel metastable boron allotropes using an ab initio crystal structure search method, as implemented in the AMADEUS code. Our crystal structure method is based on the conformational space annealing algorithm for global optimization combined with first-principles electronic structure calculations. This method allows for searching stable as well as metastable configurations. In contrast to the known 3D boron allotropes, the newly discovered allotropes, called hex-B, are composed of buckled honeycomb layers with B vacancies, without containing B<sub>12</sub> icosahedra. The B vacancies in the 3D honeycomb lattice act as scavengers of extra electrons and thus stabilize the hex-B allotropes dynamically and mechanically. Moreover, the structural flexibility of hex-B can bridge the gap between  $\alpha$ -B to  $\gamma$ -B in pressure-induced structural transition. Based on the results, we propose a pressure-induced transition pathway from  $\alpha$ -B to  $\gamma$ -B in which hex-B allotropes act as intermediate phases in the framework of Ostwald's step rule.

## Orbital Selective Ferromagnetism In Pr Doped CeO<sub>2</sub>

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Recent investigations have shown that CeO<sub>2</sub> doped with various elements exhibits ferromagnetism (FM) while the underlying mechanism of the ferromagnetism is still an issue of controversy. We focus to find out the magnetic mechanism on atomic level by means of density functional theory using GGA-PBE +*U* scheme. We investigated Pr doped CeO<sub>2</sub> and the evolution of ferromagnetism. Ferromagnetism of Pr doped CeO<sub>2</sub> depends on the symmetry of occupied *f*-orbitals of both Pr and Ce, and these *f*-orbital occupancies depend on V<sub>O</sub>/Pr ratio. This type of interaction can be explained by Goodenough-Kanamori-Anderson (GKA) rules of super-exchange. In case of the high ratio of V<sub>O</sub>/Pr, both Pr and Ce which are second and first nearest neighbor of oxygen vacancy respectively, acquire electrons from oxygen vacancies. These electrons occupy  $4f^{x(x^2 - 3y^2)}$  and  $4f^{z^3}$  orbitals of Pr and  $4f^{xyz}$  orbital of Ce. These Pr- $4f$  electrons interact with Ce- $4f$  electron via O- $2p$  orbital by means of GKA rules of super-exchange interaction, and consequently enhance the stability of ferromagnetism. For reduced ratio of V<sub>O</sub>/Pr, two Pr ions which are second nearest neighbor of V<sub>O</sub> get the electron from the oxygen vacancies, and  $4f^{y(3x^2 - y^2)}$  and  $4f^{z^3}$  orbitals of Pr become occupied. These two occupied orbitals interact with each other in two different manner via O- $2p$  orbitals: Pr- $4f^{y(3x^2 - y^2)}$ -O- $2p$ -Pr- $4f^{y(3x^2 - y^2)}$  interaction is anti-ferromagnetic while Pr- $4f^{z^3}$ -O- $2p$ -Pr- $4f^{z^3}$  and Pr- $4f^{y(3x^2 - y^2)}$ -O- $2p$ -Pr- $4f^{z^3}$  interactions are ferromagnetic. This spin frustration leads to less stable ferromagnetism, compared to the previous case. In only Pr doped case, two Pr ions stays far apart and super-exchange interaction is too weak, thus Pr doped CeO<sub>2</sub> do not exhibit ferromagnetism.

