3.2 First-Principles Calculation of Material Properties

Simulation of electrochemical interfaces

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The electrochemical interface provides a unique environment for efficient redox reactions. The platinum-electrolyte interface has long been focused on the fuel-cell study because of the efficient oxygen reduction reaction (ORR), but defective TiO₂ has attracted attention for its enhanced reactivity and durability. It was explained in our previous first-principles study that the various adsorption forms taken by the ORR intermediates, such as OH and O₂H, is the reason for the reactivity [1]. This contrasts to the metal electrocatalysts where the variety in the adsorption is quite small and thus the ORR activity is limited thereby [2]. Further investigation of the oxide electrocatalyst is the target of this project.

Together with experimentalists, we modeled a ZrO₂ surface introduced with oxygen vacancies and foreign dopants to study the ORR reactivity. To make the model realistically mimic the experiment, we have performed the firstprinciples Monte Carlo simulation using abICS [2] and obtained equilibrium structures for the interface at the annealing condition. The calculated results are used then to investigate the activity. So far various structures with different stability and activity are obtained and this variety can be recognized as the characteristics of this material. Comparison with experiment is now underway.

Through the abICS calculation, we have constructed a machine learning model of the interface, and we plan to predict the activity after obtaining sufficient number of samplings.

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Mechanisms of Semiconductor Interface Formation and its Electronic Properties based on Quantum Theory

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In the fiscal year of 2020, on the basis of the total-energy electronic-structure calculations and molecular dynamics simulations within the density-functional theory, we have studied the epitaxial growth of power semiconductors, atomic and electronic structures of semiconductorinsulator interfaces, and the complex of line defects and impurities. The main computational tools are our RSDFT (Real Space Density Functional Theory) code and RS-CPMD (Car-Parrinello Molecular Dynamics) code. We have clarified 1) the atom-scale mechanism of GaN epitaxial growth [1], 2) the mechanism of the adatom diffusion on SiC stepped surface[2], 3) the formation of dangling-bond free interface of GaN and a gate insulator[3,4], and 4) atomic and electronic structures of the dislocation-impurity complex in GaN [5].

The group identification codes for the achievements above are k0042 and m0001. The below is the explanation of the issue 1) above.

Step-flow epitaxial growth of GaN

Growth of high-quality epitaxial thin films of GaN is indispensable for the energy-saving power electronics and the clarification of the mechanism of the epitaxial growth is essential to advance nanoscience and technology. We have performed first-principles calculations that elucidate atomic structures and formation energies of the surface steps of GaN (0001) surfaces, unveil atom-scale elementary processes of N incorporation at the step edges, and then provide a microscopic picture of the step-ow epitaxial growth of GaN.



Fig.1: Calculated electron densities near the GN step (a) and the Ga2 step (b). The densities are represented by the yellow isovalue surfaces. The small yellow clouds reflect the presence of the low electron density, indicating that the Ga-Ga weak bonds are formed at the step edges. The Ga, Ga-ad (Ga adatom), and N atoms are represented by the green, pink, and blue balls, respectively.

Epitaxial growth usually takes place on Garich vicinal surfaces in which the (0001) surface is slightly inclined toward [1100] or [11-20] direction. There are five distinct mono-bilayer steps on such vicinal surfaces depending on the atomic species, Ga or N, at the step edges and the inclined directions. We have performed the geometry optimization for all the possible step edges and calculated the step formation energies.

Typical structures of the step edges are shown in Fig. 1 along with the electron density. The characteristics is the presence of Ga-Ga bonds at the step edges. As is clear from the small electron clouds in Fig. 1, the Ga-Ga bonds are relatively weak and thus become hot spots for the epitaxial growth.



Fig. 2: Diffusion pathway and the corresponding energy barrier of an NH unit on the terrace of GaN(0001) surface. (a) The total-energy landscape along the diffusion pathway. The left and the right ends correspond to the initial and the final geometries, respectively. (b) Diffusion pathway in a top view represented by the small red balls which denote the lateral positions of the N atom in the NH during the diffusion. (c) An initial geometry of the NH unit which intervenes in the weak bond between the Ga adatom and the top Ga atom. (d) A final geometry of the NH unit which intervenes in the adjacent Ga-Ga weak bond. Burgandy, green, and blue balls depict Ga adatom, Ga and N atoms, respectively.

We have previously shown that the NH₃ provided in Metal-Organic Vapor Phase Epitaxy (MOVPE) arrives at the terrace of the growing Ga-rich surface and is decomposed into the NH unit [Fig. 2(c)] [6]. Now we have found this NH unit diffuses on the surface terrace with the activation energy of 0.6 eV (Fig. 2).



Fig. 3: The GN step-edge structure with two NH units intervening in the Ga-Ga bonds. Burgandy, green, blue and orange balls depict Ga adatom, Ga, N and H atoms, respectively.

This indicates that the NH units wander on the terrace and occasionally reach the surface step edges. We have indeed examined the energetics of the reaction in which two isolated NH units on the terrace diffuse toward a step edge and intervene into the adjacent Ga-Ga bonds as in Fig. 3. We have found this reaction is exothermic with the energy gain of 0.45 eV.

Then the next step is the incorporation of Ga atom at the step edge. Since the growing surface is Ga rich, it is highly likely that an additional Ga atom approaches the step edge where the two NH units are incorporated [Fig. 4(a)]. We have then examined a reaction in which the two H atoms are desorbed as an H2 molecule and the arriving Ga is incorporated at the step edge [Fig. 4(b)]. We have identified a pathway of this reaction, and calculated the energy profile [Fig. 4(d)]. We have



Fig.4: An elementary process in the stepflow growth of GaN. (a) Stable structure of the GN step edge attached with 2 NH units and an additional Ga atom nearby. (b) Stable structure of the GN step with H2 desorbed from the structure (a). (c) The top view of the stable structure shown in (b). Color code of the balls depicting atoms are the same as in Fig. 3. The additional Ga adatom is shown by purple. (d) Calculated energy profile for the reaction from (a) to (b).

found that the energy cost of this reaction is 1.8 eV. However, by examining the obtained energy profile in Fig. 4(d), this is the cost to make 2H atoms on the surface an H2 molecule in the gas phase. In the gas phase, the H2 molecule gains the free energy owing to its translational, vibrational and rotational motions. We have evaluated such

free-energy gain at growth temperature and under the typical H2 partial pressure. It is evaluated to be 2.1 eV. This certainly compensates the obtained zero-temperature energy cost of 1.8 eV, indicating that this reaction is favorable.

The top view of the final structure is shown in Fig. 4(c). The step edge before this reaction proceeds one unit by incorporating two N atoms from the NH units and a new Ga atom. This is the elementary process of the step-flow epitaxial growth.

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Analyses on electronic structure and magnetoelectric effect in high-performance spintronics and magnetic materials

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We studied the magnetic anisotropy and its electric field (EF) effect in the thin film related with spintronic devices [1]. We obtained an qualitative agreement between theory and experiment on magnetic anisotropy of the magnetic thin film including the Fe/MgO interface with Cr underlayer, by taking into account an alloying effect of Fe-Cr. Without alloying in the theoretical calculation, the total magnetic anisotropy indicates an in-plane magnetization. Such theoretical consequence had been solved in the comparison with the experimental result [2] that showed a perpendicular anisotropy. The introduction of alloying effect may be consistent with the fabrication condition in the experiment. As a result, our first-principles approach reveals a potential to describe magnetic anisotropies of magnetic thin film.

In the computational approach, we employed the plane-wave basis electronic structure calculation with using a scheme of non-collinear spin density and fully relativistic ultra-soft pseudopotential (including spin-orbit coupling). This scheme can provide the magnetocrystalline anisotropy energy (MCAE) from the difference between the total energy calculations for the different magnetization directions. In addition, the noncollinear spin density can estimate the shape magnetic anisotropy energy (SMAE) by using the scheme developed before in our research group [3]. In the present applications, the contributions of MCAE and SAME have different sign in the numerical values. Therefore, an accurate numerical computation is required for obtaining a realistic result.

We used the thin films in the followings; vacuum/Cr(6ML)/Fe(4ML)/MgO(5ML)/vacu um(S-I) and vacuum /Cr(6ML)/Fe(1ML)/Cr (1ML)/Fe(3ML)/MgO(5ML)/vacuum(S-II). The magnetic anisotropy energy (MAE) was calculated from the total energy difference between in-plane magnetization ([100]) and out-of-plane magnetization ([100]), MAE = E[100]-E[001]. To apply an EF, we used the effective screening medium (ESM) method.

Sys.	VCMA (fJ/Vm)	$\frac{\text{MCAE}}{(\text{mJ/m}^2)}$	SMAE (mJ/m ²)	MAE (mJ/m ²)
S-I [1]	85	0.586	-1.336	-0.750
S-II [1]	89	1.280	-1.053	0.227
Exp. [2]	~300	—	—	~ 0.500

Table I. Results of VCMA, MCAE, SMAE, MAE(=MACE+SDA) and comparisons with experimental results.



Figure 1. Atom resolved MCAE in (a)S-I and (b) S-II.

To obtain the EF inside the MgO layer, we took into account the dielectric constant (9.8 for MgO).

As shown in Table 1, the alloying system (S-II) shows a perpendicular anisotropy (positive value for MAE). The most important key for the perpendicular is that the MCAE increases by the alloying of Fe-Cr. As depicted in Fig. 1, the increase appears at the interface with MgO layer. This means that the magnetic anisotropy energy at the Fe/MgO interface is sensitive to the termination of Fe layer in the thin film.

Quasi-particle self-consistent GW (QSGW) ele-ctronic structure calculation [4] was performed in the spinel structures of ternary magnetic compound NiCo₂O₄, using the software *ecalj*. The QSGW method is state-of-the-art on electronic structure investigation without using any empirical parameter. The results were also compared

with those from the density functional theory (DFT) based on generalized gradient approximation (GGA). Half-metallicity was observed, where the band energy gap appears in the majority spin state. Such property at the Fermi level is the reason why the material has been considered as a candidate of spintronics application. The QSGW indicated that the gap is larger than that of the corresponding GGA case. The QSGW may yield more localized 3d-orbitals, compared with those from the GGA. Based on the projected density of states (PDOS) analysis, Co atoms of the octahedral site [Co(oct)] were found to be a nonmagnetic/weak magnetic configuration (low spin state) among them, resulting in a negligible contribution to the total magnetization. The largest contribution to the total magnetization is provided by Co atoms of tetrahedral [Co(tet)] site (high spin state). The QSGW indicated the difference of octahedral crystal fields on the different cation sites of Co(oct) and Ni(oct). The electronic states near the Fermi level consist mainly of Co(tet) 3d eg-orbitals. The comparison with the results of one-shot GW reveals that the self-consistent treatment introduces visible changes in the electronic structures.

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Development of first-principles electronic-structure and transport calculation code RSPACE and simulations for device

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4H-SiC is one of the major enabling materials for advanced high power and high temperature electronics applications. However, the performance of the metal-oxide-semiconductor field-effect-transistor (MOSFET) using SiC is severely limited due to their field-effect mobility being much lower than the ideal electron mobility. SiC based MOSFETs are usually fabricated on the front side of 4H-SiC(0001)wafer (Si face) by the thermal oxidation in dry O_2 ambience. On the other hand, it is reported that MOSFETs fabricated on the C face, which is the back side of the same wafer, by wet oxidation in H₂O ambience contain low density of interface defects and exhibit higher carrier mobility than that on the Si face. Electrically detected magnetic resonance (EDMR) spectroscopy revealed that characteristic defects, which are called "C-face defects", are observed in the wet-oxidized C face[1]. However, the details of the generation of C-face defects are unclear.

In this project, we have conducted firstprinciples study on the formation energy of C-face defects at SiO₂/SiC(0001) interface. RSPACE code[2, 3, 4], which is also developed in this project is used for the first-principles calculations. The lateral lengths of the supercell are chosen to be $2\sqrt{3a}$ and 4a along the [1100] and [1120] directions of the 4H-SiC(0001) surface, where *a* is the lattice constant of SiC, and integration over the Brillouin zone is carried out using a 2 × 2 \vec{k} -point mesh. The surface C atoms are connected to OH groups to imitate oxide and the Si atoms are terminated by H atoms. For comparison, the formation energy of the defects in 4H-SiC bulk is also calculated. The dimension of the supercell is $2\sqrt{3a}$, 4a, and c along the $[1\bar{1}00]$, $[11\bar{2}0]$ and [0001] directions, respectively, with c being the lattice constant of 4H-SiC bulk.

The C face defects are $C_{Si}V_C$ c-axial, $C_{Si}V_C$ basal, $V_{Si}V_C$ c-axial, and $V_{Si}V_C$ basal defects. It has been reported that only $C_{Si}V_C$ c-axial and $V_{Si}V_C$ basal are observed at the wet-oxidized C face among them. The $C_{Si}V_C$ defects are generated by removing a Si atom and moving C atom to V_C site from the neighboring C site. We remove Si atom from the first or second SiC bilayer. In addition, $V_{Si}V_C$ defects are created by removing C atoms at the Si site from the $C_{Si}V_C$ defects. The computational model for the case of the $C_{Si}V_C$ c-axial defect is shown in Fig. 1. Table 1 corrects the formation energies and magnetic moments of the defects.

When Si atom in the first SiC bilayer of the interface is removed, $C_{Si}V_C$ basal, $V_{Si}V_C$ c-axial, and $V_{Si}V_C$ basal defects are hardly generated because the dangling bonds of C atom are passivated by the O atom which comes from the oxide layer. As a result, the formation energy of $C_{Si}V_C$ c-axial defect, in which Si atom at the first bilayer is removed, is the most stable among $C_{Si}V_C$ defects. In the case of the $V_{Si}V_C$ defects, the formation energy

$\frac{\sqrt{S_i}\sqrt{C}}{C}$ at the inerface, and $\sqrt{S_i}\sqrt{C}$ in bulk.				
Defects	Formation energy (eV)	Magnetic moment (μ_B)		
$C_{Si}V_C(+)$ c-axial @ 1st layer	0.0	1		
$C_{Si}V_C(+)$ c-axial @ 2nd layer	+0.92	1		
$C_{Si}V_{C}(+)$ basal @ 2nd layer	+0.49	0		
$C_{Si}V_C(+)$ c-axial @ bulk	+0.10	1		
$C_{Si}V_C(+)$ basal @ bulk	0.0	1		
$V_{Si}V_{C}$ c-axial @ 2nd layer	+0.96	1		
$V_{Si}V_{C}$ basal @ 2nd layer	+0.49	2		
$\mathrm{V_{Si}V_C}$ c-axial @ bulk	0.0	2		
$V_{Si}V_{C}$ basal @ bulk	+0.09	2		

Table 1: Formation energies E_f and magnetic moments of C-face defects. The zero of the formation energy is set at the lowest models among $C_{Si}V_C(+)$ at the interface, $C_{Si}V_C(+)$ in bulk, $V_{Si}V_C$ at the inerface, and $V_{Si}V_C$ in bulk.

of the c-axial structure is lower than that of the basal one. Although this result is not in agreement with the experimental result, the magnetic moment of the basal defect at the interface corresponds with that in bulk while the magnetic moment of the c-axial does not. This indicats that our calculated results support the experimental situation.

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Figure 1: Computational model for SiC/SiO₂ interface with $C_{Si}V_C$ c-axial defect. Blue, brown, and red balls are Si, C, and O atoms, respectively. The supercell contains 95 Si, 96 C, 16 O, and 32 H atoms. H atoms are used for termination of dangling bonds at the surfaces.

Analyses related to atomic structures and atom dynamics at complex structures such as surfaces, interfaces and defects

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1 Introduction

The understanding on structures and dynamics at surfaces, interfaces and defects on nanoscale is crucial to facilitate developments of novel information and energy devices. Firstprinciples calculation has sufficient accuracy of prediction for this purpose, but its computational cost is often too high to model such devices realistically.

Keeping the above in minds, we have been investigating atomic structures and atom dynamics in various systems via first-principles calculations combined with multi-scale or machine-learning approaches. In the following, some of our results in the fiscal year 2020 are described.

2 Phase stability of Au-Li binary systems

Aiming to deepen our understanding on the operation mechanisms of novel memory device named VolRAM [1] and all-solid-state Liion batteries, we examined Li ion distribution at the interfaces between γ -Li₃PO₄ and metal electrodes by combining first-principles data of defect formation energies with a onedimensional continuum model [2] in the previous year. However, we have not achieved thorough understanding because of alloy formation between Au and Li: The Au-Li binary system is known to exhibit various alloy phases over a wide range of compositional ratios. Therefore, in the fiscal year 2020, we have explored the alloying properties of Au and Li [3].

For this purpose, we constructed a high-dimensional neural network potential (HDNNP) [4] based on density functional theory (DFT) calculations. The predictions by the constructed HDNNP on lattice parameters and phonon properties agree well with those obtained by DFT calculations. The predictions on the mixing energy of $Au_{1-x}Li_x$ also show excellent agreement with DFT verifications. The lack of consensus on the Au-Li stable phases in previous studies can be understood from the existence of various compositions with structures on and slightly above the convex hull.

We have also examined the alloying process starting from the phase separated structure to the complete mixing phase by performing molecular dynamics simulations with the constructed HDNNP. Our results reveal that when multiple adjacent Au atoms dissolved into Li, the alloying of the entire Au/Li interface started from the dissolved region.

3 Band alignment tuning via thin-film insertion

Recently, interfacial resistance between the Nb-doped $SrTiO_3$ (STO) metal and a $LiCoO_2$ (LCO) mixed conductor has been found to de-



Figure 1: Calculated local density of states of (A) $\text{LiCoO}_2(104)/\text{SrTiO}_3(001)$ and (B) $\text{LiCoO}_2(104)/\text{three}$ unit cells of $\text{LaAlO}_3/\text{SrTiO}_3(001)$ along the Z-axis direction perpendicular to the interfaces [5].

crease significantly (by more than five orders of magnitude) upon the insertion of a 1 nm thick insulating LaAlO₃ (LAO) layer at the interface [5]. To clarify the origin of this behavior, we have performed DFT+U calculations for LCO/STO and LCO/LAO/STO heterostructures. In our calculation, we have adopted the undoped system for both LCO and STO, considering the fact that Nb-doping shifts only the Fermi level, and the position of the conduction band minimum, measured from the vacuum level, is nearly the same between the undoped and Nb-doped STO.

Figure 1 shows the local density of states of the structurally optimized LCO/STO and LCO/3 unit cells of LAO/STO systems along the Z-axis direction perpendicular to the interface. In the LCO/STO model, upward (downward) band bending of $\sim 0.20 \text{ eV}$ (0.06 eV) near the interface on STO (LCO) is seen. The difference in the valence band maximum energy of LCO and the conduction band minimum energy of STO was ~ 1.8 eV. In contrast, the energy level difference decreased to 0.28 eV when 3 LAO unit cells were inserted at the interface. The linear change in the LAO band level along the Z-axis shows the presence of a built-in electric field. The electric field was 2.2 eV/nm (0.67 eV per LAO unit cell), which is comparable to the values deduced from the experiments [5] (0.4 eV per LAO unit cell). The shift in the energy level via LAO insertion

suggests a reduction in the Schottky barrier height.

We have also performed quantum mechanical calculations for electron tunneling by solving the time-independent one-dimensional Schrödinger equation with a simple model constructed based on the above behavior of band alignment change due to the LAO layer insertion. The result reproduced the observed interfacial resistance change with the LAO layer thickness: The 4 u.c. LAO case had a minimum resistance.

This study provides a proof-of-concept demonstration of an approach to reduce the interfacial resistance by tuning the Schottky barrier at the interfaces of metals and mixed conductors.

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Theoretical Approach to Reduce the Interface-State Density in SiC-MOS Devices

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SiC power MOSFETs have shown remarkable energy-saving effects and have already been commercialized. However, the SiC/SiO2 interface, which plays a fundamental role in SiC power MOSFETs, still has a high interfacial defect density, and most of the inversion layer carriers induced by the gate voltage are trapped in the interfacial defects. In fact, only 10% of the theoretical electron mobility has been achieved in SiC-MOSFETs. In order to reduce the interface-state density, microscopic identification of them is needed.

We have performed density-functional calculations to investigate the microscopic structure of interface defects. One of the most promising candidates of interface defects is the residual carbonrelated defects at the interface. In this study, the stability of carbon-related defects distributed in three regions (SiC bulk, SiO2 film, and SiC/SiO2 just interface) and their dependence on temperature and oxygen partial pressure were clarified by theoretical calculations based on density-functional theory [1].

Theoretical calculations showed that carbon-related defects were generated near the interface under the temperature and oxygen partial pressure conditions used in the actual experiments. In particular, the residual carbon defects distributed just at the interface were found to be stabilized and present in large amounts. This calculation result indicates that the formation of residual carbon defects at the interface is energetically stable and that thermal oxidation inevitably produces residual carbon defects at the interface.

Therefore. we thought that the formation of carbon defects due to thermal oxidation of SiC was unavoidable, and we sought a way to overcome this problem. As a result, we succeeded in forming a high-quality interface by using a process that eliminates the thermal oxidation of SiC and removes the carbon defects near the SiC surface, followed by the formation of an oxide film [2]. In the proposed process, a Si thin film is deposited after hydrogen etching and oxidized to SiO₂ at a temperature where the oxidation of SiC does not proceed. Subsequent nitridation after the oxide film formation is effective in reducing defects. The effectiveness of the proposed method was confirmed experimentally, and a high-quality interfacial structure with an interfacial level density of $(1-4) \times 10^{10}$ cm⁻²eV⁻¹, which is one order of magnitude smaller than the conventional 10^{11} cm⁻²eV⁻¹, was achieved.



Fig. 1: Successful reduction in interface-state density in SiC/SiO₂

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First-Principles Molecular-Dynamics Study of Structural and Electronic Properties of Covalent Liquids and Glasses under Pressure

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For the investigation of the dynamic properties of covalent liquids and glasses under pressure, it is important to consider the stability of materials states under various conditions from the viewpoint of free energy. We have been using the thermodynamic integration (TI) method [1] for this purpose. The first-principles molecular dynamics (FPMD) simulations would be the most powerful and accurate tool to perform TI calculations. Due to the high calculation cost, however, FPMD simulations have been carried out only for small-sized systems. One of the solutions to solve this cost problem is to use machine-learning interatomic potential based on artificial neural networks (ANN) trained from the results of FPMD simulations.

This study aims to establish the training requirements for the ANN potential to reproduce the phase properties of sodium as an example. Figure 1 shows the temperature dependence of calculated volume V. The black circles show V obtained by FPMD. It is seen that, only when the virial stress tensor, as well as the potential energy and atomic forces, is taken into account in the training (EFP-fit), the constructed ANN potential precisely reproduces the FPMD results. The *V*-*T* relation calculated by the ANN potential trained with potential energy only (E-fit) or with potential energy and atomic forces (EF-fit) is completely different from that by FPMD, though the E-fit method gives almost correct V before melting. We also found that the 128-atom system with 4k points for Brillouin zone integration gives nearly converged results for the melting temperature.



Fig. 1: Temperature dependence of volume V of Na obtained by FPMD and ANN-MD simulations.

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Quantum Simulations on Dynamical Heterogeneous Catalysts

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In 2020-2021, we carried out theoretical investigation of chemical processes at surfaces and interfaces, oxidative etching process of diamond [1], multi-scale simulation of Cu adatom diffusion on Cu surfaces [2], formic acid adsorption in polymeric form and decomposition on Cu(111) [3], oxygen vacancy induced metal-insulator transition of LaNiO₃ thin film over SrTiO3 [4].

In this report, we report the oxidative etching process of the diamond (100) surface [1]. Diamond possesses a unique combination of superlative properties that makes it an attractive material for several novel applications. Of all semiconductors, diamond has the highest dielectric breakdown field, saturated electron drift velocity, and thermal conductivity which make it an ideal material for next-generation electronics that will outperform current systems in terms of operating frequency and power handling capacity. In addition, diamond's wide band gap, optical transparency, chemical inertness, hardness, and low thermal expansion have led to a number of specialized photonics applications including spacecraft window, optoelectronic microlens, photodetector, high energy particle detector, UV and infrared LED, and Raman laser. Diamond has color centers that functions as bright single photon source (SPS) at room temperatures and can be potentially implemented in quantum metrology and quantum information science.

At present, a theoretical study that investigates the entire oxidation process, starting from the adsorption of gas phase O_2 up to the desorption of CO and etching of the surface, has never been done. This kind of study is necessary to develop a comprehensive knowledge of diamond oxidation mechanism. For this reason, van der Waals-corrected density functional theory simulations of the oxidation of the C(100) surface have been performed.

Density functional theory (DFT) calculations have been performed using STATE code package (Simulation Tool for Atom TEchnology) with generalized gradient exchangecorrelation functional (GGA) based on the work of Perdew, Burke and Ernzerhof (PBE). Semi-empirical van der Waals correction was implemented. Core electrons were treated using ultra-soft pseudopotentials. Wave functions were expanded using plane-wave basis with wave function and augmentation charges cutoff of 36 Ry and 400 Ry, respectively.

We simulated the succeeding desorption of CO up to the complete etching of the top C layer. The reaction paths and optimized structures are shown in Fig. 1. Following the desorption of the first CO, there are two possible locations where the second CO could desorb, the adjacent CO_{bridge} towards the $[01\bar{1}]$ direction where O is on top site and the CO from the adjacent ether group towards the [011] direction. The former and the latter have $E_{barrier}$ of 4.53 eV and 3.62 eV, respectively. Succeed-

ing CO desorptions along [011] (Fig. 1 B-E) all have lower E_{barrier} compared to $[01\overline{1}]$, suggesting a preferred etching direction. The calculated desorption activation energies vary between 1.01 - 4.68 eV. Initial desorption of CO along a given row in [011] direction has the highest desorption activation energy (reaction $A \rightarrow B$ and $E \rightarrow F$), while succeeding energy barriers are lower (Fig. 1 A-E, E-I). Analysis of the reaction path geometries shows that for these two reactions, the initial CO desorption proceeds by the near-simultaneous breaking of two CObridge-C bond. The point defect left by the initial desorption allows the next CO_{bridge} to break one bond with second layer C and form CO on top (CO_{top}) structure. The non-simultaneous bond breaking reduces the heat released by the reaction and the desorption activation barrier. This suggests that the point defect functions as nucleation point for CO desorption along [011] direction. This nucleation function was first proposed by John et al. based on their observation that the surface roughness of diamond (100) did not increase even after removal of over 5300 atomic layers, suggesting that the removal rate of rows of atoms is more rapid than the removal rate of layers. Our work is the first theoretical study to support their prediction.

In summary, we performed density functional theory calculations with van der Waals corrections to elucidate diamond oxidation mechanism on the atomic-level which could lead to insights that will advance the improvement of nascent nanofabrication technologies. We developed a comprehensive theory of oxidative etching of the diamond (100) surface, from the adsorption of gas phase O₂, including details of metastable adsorption states, intersystem crossing, and induced surface dereconstruction, to the desorption of CO and CO₂, complete etching of the top surface layer and its subsequent stabilization.



Figure 1: Etching of the top-layer atoms of C(100)- (1×1) : O_{bridge} surface through successive CO desorption. The heat of reactions and activation energies in electron-volts are shown in black and blue texts, respectively. Physisorption energies of CO are shown in orange text. Grey and red spheres correspond to carbon and oxygen atoms, respectively, while the dangling bonds are represented by blue cylinder.

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Development and application of first-principles algorithms for long-range electron transport simulation

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In recent years, a lot of first-principles studies on various materials have been energetically performed toward the development of novel First-principles calculations generdevices. ally require a computational cost proportional to the cube of the system size. In order to perform large-scale simulations, the development of $\mathcal{O}(N)$ algorithms and the improvement of parallelization efficiency of parallel calculations have been promoted. So far, great progress has been made in atomic structure calculations and electronic structure calculations, but reducing the computational cost remains a major issue in electron-transport property calculations.

In this subject, an efficient computational procedure based on the real-space finitedifference formalism^[1] was developed to evaluate the electron-transport properties of long systems containing more than 10^5 atoms under the zero temperature and zero bias limits in the steady state without accuracy deterioration. In the procedure, a transition region is represented by arranging multiple parts along the transport direction. The Green's function of the whole transition region extended towards the transport direction was obtained by recursively combining the Green's functions of the adjoining parts one by one. The computational cost for calculating the submatrices of the Green's functions required to estimate the transport properties can be suppressed linearly for the number of the combined parts.

To exemplify the efficiency of the proposed procedure we demonstrate large-scale electrontransport calculations for BN-doped doublewalled carbon nanotubes composed of 196,608 atoms (Fig. 1), which make, to the best of our knowledge, the largest system in the first-principles electron-transport calculation. These works have been performed on System B and System C of the Supercomputer Center, the Institute for Solid State Physics, the University of Tokyo.



Figure 1: Conductance trace of BN-doped double-walled carbon nanotubes consisting of 196,608 atoms.

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"Prediction of hydrogen function by advanced calculation of solids containing hydrogen" "Development of data assimilation method for crystal structure prediction and its application to hydrogencontaining compounds"

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One of the most challenging problems in first-principles simulations of materials is to predict crystal structure by searching the global minimum in multi-dimensional potential energy surface (PES). It takes a sizeable computational cost to calculate the electronic energy of even a single atomic configuration from first principles. It is, therefore, practically difficult to find the most stable crystal structure when the number of atoms in the unit cell is large and when PES has many local minima.

The problem is partially solved by a data assimilation method which we have proposed [1]. In the data assimilation method, we incorporate powder diffraction data to constrain search space based on Bayes' theorem, by which we can drastically accelerate finding a probable crystal structure. The method is valid even if the diffraction data is incomplete and is insufficient for structure determination by ordinary data analysis methods. Typical applications are crystal structure determination of materials found by high-pressure experiments where the range of the diffraction angle is limited or those containing hydrogen atoms whose positions are difficult to be determined by X-ray diffraction. The data assimilation method might accelerate materials exploration in combination with combinatorial synthesis and measurement.

This year, we showed that the method is very robust against noise in the experimental data if we tune the control parameter representing the weight of the data assimilation [2].

We also extended the method to assimilate multiple experimental data, such as X-ray and neutron diffraction data, at the same time. Both reflect the same interlayer distances of the crystal but with different peak intensities, giving us more information. We applied this method to Zn(OH)₂ to confirm that using both sets of data significantly improved the success rate of crystal structure prediction [2].

Then we applied the method to two systems containing a considerable number of atoms in a unit cell. The first one is a Li-ion conductor LiCB9H10. The Li-ion conductivity of this material is known to increase two orders of magnitude at around 330-360K. Still, the mechanism and associated crystal-structure change have not been clarified yet. From our simulation, the difference in the crystal structure below and above the transition temperature is essentially the orientation and rotative motion of the $(CB_9H_{10})^-$ complex ions. Since the diffusive motion of Li ions is strongly correlated with the rotation of a nearby complex ion $(CB_9H_{10})^-$, it is greatly enhanced by its rotation in the hightemperature phase [3].

The second is a metal hydride $Ca_xAl_yH_z$ newly synthesized at high pressure. Although powder X-ray diffraction data is available, the unit cell seems to be quite large, and neither its accurate chemical composition nor the crystal structure is clarified experimentally. We tried its structure determination and found a plausible model containing more than one hundred atoms in a unit cell, as shown in Fig.1 [2,4]



Fig. 1 Top and side views of a theoretically predicted structure of $Ca_xAl_yH_z$. Large, middle and small spheres denote Ca, Al and H atoms.

These works have been done in collaboration with the experimental groups of the Grant-in-Aid for Scientific Research on Innovative Areas "Hydrogenomics: Creation of Innovative Materials, Devices, and Reactive Processes using Higher-Order Hydrogen Functions" (FY 2018-2022).

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First Principles Studies on Atomic and Electronic Structures of Impurity-Screw Dislocation Complexes in GaN

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Recent experiments suggest that Mg condensation at threading screw dislocations (TSD) induces current leakage, leading to degradation of GaN-based power devices. To investigate this, we performed first-principles total-energy calculations for various Mg and dislocation complexes. Figure 1(a) shows an atomistic configuration of a TSD. The dislocation has the Burgers vector of [0001]. To model the TSD, the atoms are initially aligned in a helical manner along the [0001] dislocation line.34,35 A periodic boundary condition is then imposed on all axes of the system. The system contains 812 Ga and N atoms in total, and a vacuum layer is added on lateral planes perpendicular to the [0001] direction [Fig. 1(b)].



Fig. 1. (a) Model of a TSD. The Burgers vector is [0001], and the dislocation line runs along [0001]. Green and blue spheres are Ga and N atoms, respectively. Thelarger spheres highlight the dislocation core. (b) Schematic of the [0001] plane of the unit cell. The green region represents GaN, surrounding which is the fictitioushydrogen. The outermost region is vacuum. The red cross indicates the position of the dislocation line.

We find that threading screw dislocations indeed attract Mg impurities as shown in Fig.2.



Fig. 2. (a) Binding energies of the Mg-TSD complexes of the D<0|2>, S<0|6>, and S<0|3> cores. d_{Mg-dis} is the distance of the Mg from the dislocation line. (b)–(d). The most stable core structures of the Mg–TSD complexes of the D<0|2>, S<0|6>, and S<0|3> cores, respectively. The position of the Mg atom is inindicated by the orange sphere. A red cross denotes the position of a dislocation line.

These findings provide a picture in which the Mg, being a p-type impurity in GaN, diffuses toward the TSD and then locally forms an n-type region. The appearance of this region along the TSD results local formation of an n–n junction and leads to an increase in the reverse leakage current.

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Theoretical Studies on Semiconductor MOVPE Growth Based on Multi-Physics Simulation

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We examined the main reaction pathway of the TMG (Ga(CH₃)₃) decomposition processes [1]. We calculated and compared the decomposition rate from the Gibbs energy of activation and calculated the mole fraction of each chemical species. As a result, in B3LYP, the decomposition pathway of TMG is the sequential reaction with NH3followed by the reaction with H₂. In M062X, the decomposition proceeds through repeated reactions with NH₃ as in the previous study. Using the reaction rates we obtained, we calculated the mole fractions of each chemical species at 1300 K. It was found that GaH₃ was the most abundant species in B3LYPand Ga(NH₂)₃ in M062X. When we tested the difference between the two exchangecorrelation functions using the high precision CCSD method, it was found that the results of the CCSD method were closer to those of B3LYP. Moreover, the experiment also supports the reaction paths obtained byB3LYP. Therefore, the main reaction pathway of TMG decomposition is shown in Fig.1: Ga(CH₃)₃ \rightarrow Ga(CH₃)₂NH₂ \rightarrow $Ga(CH_3)_2H \rightarrow GaCH_3HNH_2 \rightarrow GaCH_3H_2 \rightarrow$ $GaH_2NH_2 \rightarrow GaH_3$. The main reaction pathway

obtained in our study shows that when H₂ is sufficiently present as a carrier gas, amino groups, which are responsible for the formation of a wide variety of polymers, are difficult to form. Therefore, we were able to reduce the number of chemical reactions considered in conventional fluid simulations. GaH₃ molecules must be considered in the surface reaction of GaN MOVPE. Furthermore, it may be effective to decompose TMG at ahigh temperature of about 1300 K for a certain period of timet o control carbon contamination..



Fig. 1: Mole fraction of each chemical species after 1s at 1300 K and main reaction pathway of TMGa decomposition written in red obtained by the first principles calculations. [Ref.1]

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Mechanisms of Chemical Reaction of β-diketones Molecules with a Metallic Nickel Surface in Thermal Atomic Layer Etching Processes

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Thermal atomic layer etching (ALE) is one of the key manufacturing technologies for nano-scale electronic devices [1] as it can be used for precise and damageless etching of metals. Thermal ALE of Ni with hfacH starts with the deprotonation of hfacH molecules after oxidizing the Ni surface. By increasing the surface temperature in the range of $300 \sim 400$ °C, volatile nickel complex Ni(hfac)₂ and water H₂O molecules are formed on the surface and remove the NiO layer. In this process, once a new metallic Ni surface appears, no further etching occurs, which ensures the self-liming nature of the thermal ALE process [2-5]. It has been known experimentally [5,6] that, when hfacH molecules are supplied to a metallic Ni surface, they decompose and form neither Ni(hfac)₂ nor H₂O molecules, and as a result no etching of Ni takes place. The origin of the self-limiting process in the thermal ALE of Ni with hfacH exposure was discussed in an earlier study[4]. The aim of this work is to clarify the mechanisms of decomposition of β -diketones molecules – such as; hexafluoroacetylacetone (hfacH), trifluoroacetylacetone (tfacH), and acetylacetone (acacH) – on a metallic Ni surface and the effect of surface roughness on the decomposition concerning thermal ALE.

My research assistant A. H. Basher has used ISSP supercomputer to study the chemical reaction of hfacH, tfacH, and acacH molecules on flat and rough metallic Ni surfaces. In this study, we employ van der Waals (vdW) inclusive [7] periodic density functional theory (DFT) to investigate the adsorption and reaction of hfacH on a metallic Ni surface, and clarify the surface chemistry in the atomic layer etching (ALE) process of Ni. We used our in-house plane-wave pseudopotential code STATE [8]. In our calculation, we have used 5 nodes for each submitted jobs to run the calculations on 120 processors parallelly and more than 1800 hours has been consumed.

We have investigated several adsorption sites to find the most stable one thermodynamically with and without vdW forces. Second, the dissociation C-F bond in hfacH was investigated using nudged elastic band (NEB) method as well as climbing image NEB (ciNEB) to get more accurate results. Third, the dissociation bond of O-H in hfacH (deprotonation) was studied by two methods: a) checking the deprotonation manually by increasing the distance between O and H atoms. b) using NEB then ciNEB methods that is still running.

It has been found that the of physisorption energies those β -diketones are almost the same while the chemisorption energy is higher for a β -diketone with a higher polarity and the van der Waals forces play a decisive role in determining the adsorption energy. The dissociation processes of β-diketones have been studied with a climbing image nudged elastic band method, which has shown the cleavage of a C-F bond of a β -diketone is more likely to take place than the deprotonation. The surface roughness can also help to form C-Ni bonds, which were also observed in experiments. In this way, our simulations have demonstrated the self-limiting nature of thermal ALE for Ni with β -diketone gases in general, which is consistent with earlier experimental observations [5,6].

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Thermodynamic properties of icy materials in the interior of planets and satellites

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In this study, the equation of state (EOS) of hydrogen sulfide under high pressure is investigated, which is applicable to predicting the internal structure of icy satellites, such as Europa, and icy planets. H_2O , NH_3 , CH_4 and H_2S are thought to be the typical icy materials, reflecting conditions before establishing the planetary system [1]. We focus on thermodynamical properties of hydrogen sulfide as the component, whose property under high pressure and low temperature has been investigated well due to its superconductivity, but there are no studies under a wider range of temperature and pressure.

DFT-MD calculations of hydrogen sulfide systems with a large parameter space with temperature and density were performed using QUANTUM ESPRESSO. As initial configurations, not only typical structures of hydrogen sulfide but also the Cmca and P1 structures, which were obtained by the structure prediction, were selected because they were suggested to be stable under higher pressure [2].

Figure 1 shows self-diffusion coefficients caluculated for the Cmca structure from 500 to 10,000 K, as a function of the density. In high temperature ranges above 5,000K, the diffusion coefficients as well as radial distribution functions starting from different initial structures converged to nearly identical values at given temperature and density. These analyses would be a good basis for further refinement of the new EOS for icy bodies, as the next step of our study.



Figure 1: The self-diffusion coefficient for the hydrogen atom (a) and the sulfur atom (b) as function of the density of the Cmca structure with four different temperatures (500, 1,000, 5,000 and 10,000 K).

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Electrochemical reaction analysis using density functional calculation + implicit solvation model 2

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The rechargeable Li-ion battery (LIB) is a successful energy storage device due to its high energy density and long cycle life. In order to improve its performance, quantitative understanding of elementary reactions in the LIB such as the reaction of Li intercalation from electrolyte solution into graphite and crystal structure change in graphite during the reaction must be a great help. In previous studies, we have studied charge transfer reactions at electrode/solution interfaces in Liion batteries (LIB) using density functional theory (DFT) calculations combined with implicit solvation model. [1-4]

Structure change of Li-intercalated graphite (LIG) during the charge/discharge processes was recently observed by operando X-ray diffraction measurements using a synchrotron radiation at SPring-8. [5, 6] The operando XRD data cannot explained by conventional staging model for LIG. To compare and discuss these experimental results, we conduct first-principles calculations for the phase stability of LIG.

Formation free energy $\Delta F_{\rm f}$ is defined as

 $\Delta F_{\rm f} \left(\text{Li}_x \text{C}_6 \right) = F(\text{Li}_x \text{C}_6) - xF(\text{Li}) - F(\text{C}_6) \quad (1)$

$$F = E_{\rm DFT} + F_{\rm vib} - TS_{\rm conf} \quad (2)$$

where F are the free energies of LIG at composition Li_xC₆, metal Li, and AB stacked graphite C₆. Free energy is represented as the following three terms: DFT total energy E_{DFT} , vibrational free energy F_{vib} , and configurational entropy term TS_{conf} .

Atomic configurations and cell parameters of Li/6C, Li/9C, Li/12C, Li/18C, Li/24C, and Li/36C in-plane structures (see Fig. 1a) were investigated within van-der-Waals (vdW) level DFT calculations. Interlayer configurations were set to AA, AB, and mix stacking (Fig. 1b). Mix stacking is defined that Li-intercalated layers were set to AA stacking and the other layers were AB stacking. We performed spinunpolarized density functional theory (DFT) calculations with Quantum ESPRESSO (QE) package. [7]

The vibrational free energy was approximated by using independent harmonic oscillators representation. In this representation, phonon density of state (DOS) was obtained from density functional perturbation theory (DFPT) implemented in QE. Lattice gas model of suitable constraint was applied to the configurational entropy term.

Figure 1c shows the calculated formation free energies. LiC₆, Li_{1/2}C₆, and Li_{1/3}C₆ stable structures are AA-stack Li/6C stage1, stage2, and AA stack Li/9C stage2, these structures are consistent with experiment. [1] AB stacking is stable at the region of x < 0.05 in Li_xC₆. We emphasize that formation energies using only DFT term failed to describe higher stage region $(C_6 - Li_{1/3}C_6)$ especially $Li_{1/3}C_6$ and AB stacking cannot become convex hull. The calculation also shows the existence of mix stacking at intermediate region (0.05 < x < 0.3). The expected AB-mix phase transition is slightly different from AA-AB phase transition at $x \approx 0.1$ suggested from X-ray diffraction analysis. [1] Finally, the computational ABmix phase transition well explained the entropy behavior comparing with electrochemically observed entropy. [8, 9]

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Figure 1: (a) In-plane configurations of Li/6C, Li/9C, Li/12C, ... structures. (b) Interlayer configurations of AA and AB stackings. (c) Formation free energies (closed circles, diamonds, and crosses) and convex hull (black solid line) obtained from eq. (1).

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Study of ferromagnetism in Pt(100) thin films by firstprinciples calculation

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Recently, It was reported that ferromagnetism appears in an oscillatory manner in the Pt(100) thin films depending on the film thickness[1][2]. However, few studies have focused in the ferromagnetism in Pt(100) thin film and the mechanism for appearance of ferromagnetism in Pt(100) thin film remains unclear. In this study, we performed the firstprinciples calculations of freestanding Pt(100) thin films to understand the mechanism for appearance of ferromagnetism in Pt(100) thin film. We performed first-principles calculations based on the density-functional theory with the generalized gradient approximation. Projector-Augmented Wave method was adopted as the pseudopotential of Pt. We used $88 \times 88 \times 1$ k points (based on Monkhorst-Pack) and a cutoff energy of 36 Rydberg.

We calculated lattice constant that minimizes the energy. Using the obtained lattice constant, we calculated the Pt layer thickness dependence of the magnetic moment of Pt. As a result of the calculations of electronic structures for the free-standing Pt(100) thin films from 2 monolayers(ML) up to 17 ML, it was confirmed that ferromagnetism appeared in an oscillatory manner with a period of 6 ML (Fig. 1). By examining the energy band structure, we found that the flat band near the Γ point composed of $5d_{xz,yz}$ orbitals overlaps with Fermi energy(E_F) when ferromagnetism appears. This flat band is the quantum well band (Fig. 2).

From the phase model, the period at which the quantum well band in Pt(100) thin film overlaps with E_F is 5.7 ML[1]. This is consistent with experimental result of the previous research[2] and calculated results. So, it was concluded that oscillatory magnetic behavior in Pt(100) thin film can be explained by quantum well states.



Fig. 1: Magnetic moment per Pt atom in Pt(100) thin films (circles) and total energy differences between the paramagnetic (para) and ferromagnetic (ferro) states (diamonds).



Fig. 2: Band structure of 3ML Pt(100) thin film.

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Born-Oppenheimer MD Simulations of Excited States for Firefly Oxyluciferin Anions in Aqueous Solutions

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Firefly oxyluciferin anion, known as the light emitter in firefly bioluminescence process, has garnered significant attention because obtaining a deep insight on oxyluciferin anions could be an essential first step towards understanding the mechanism of the firefly bioluminescence process. However, majority of stabilizing and optical properties of oxyluciferin anions in the external environments are still a mystery.

We have performed first-principles Born-Oppenheimer molecular dynamics simulations (BOMD) for three possible isomers of firefly oxyluciferin anions (phenolate-keto, phenolateenol, and phenol-enolate) surrounded by 64 explicit water molecules and elucidated their stabilizing mechanism in the aqueous solutions in the excited states. To attain the equilibrium conditions, we had to run BOMD up to 1.8 ns (corresponding to 3.7 million MD steps). Figure 1 shows the cumulative average for BLYP total energies simulated for phenolatephenolate-enol, and phenol-enolate. keto, Unlike similar level BOMD simulations in the ground state in which the phenolate-enol form was the most stable [1,2], the current excited states BOMD simulations showed that phenolate-keto was the most stable isomers, whose energy was 0.38 eV and 0.57 eV lower than that of the phenolate-enol and phenolenolate, respectively [3]. We analyzed the trajectories in detail and elucidated that the stabilizing mechanism of the oxyluciferin anions in the explicit aqueous solutions is the difference between at the ground and excited states.



Fig. 1. Cumulative average for BLYP total energies.

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Analysis of Thermoelectric Properties of Clathrate Compounds with Ab Initio Calculations

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Clathrate compounds are promising candidates for thermoelectric materials in terms of the "electron-crystal phonon-glass" concept. Clathrate compounds are composed of guest atoms encapsulated in cagelike structures. It is expected that electrons can smoothly transport in the frame work while phonons are scattered by guest atoms. Particularly, in type-I clathrate compounds, guest vibrate in atoms а strong anharmonic potential because they are composed of a Weaire-Phelan structure, which divides a space with the maximum volume with the same cross-sectional area. While offcenter clathrates such as type-I $Ba_8Ga_{16}Sn_{30}$, in which guest atoms vibrate in a double-well anharmonic potential, have low thermal silicon-based conductivity, clathrates are preferable for actual use in terms of the material cost.

In this study, we show that

aluminum substitutions can enhance thermoelectric of silicon-based performance clathrates, type-I Ba₈Ga₁₆Si₃₀ (Fig. 1(a)).Comparing calculated thermoelectric figure of merits (ZT) with those obtained in experiment, we concluded that (a) aluminum additive enhances ZT with lowering and (b) doping level further suppression of doping level can ZΤ enhance significantly. To thermoelectric investigate properties, we obtained possible structures at finite temperatures with using a cluster expansion and Monte Carlo methods [1] and thermoelectric properties were averaged for different possible structures. As shown in Fig. 1(b), formation energies of arbitrary structures can be accurately with the cluster predicted expansion method. Phonon properties of the clathrates were calculated with using а self-

(SCP) consistent phonon theory first-principles based on calculations [2].While experimentally-observed carrier concentrations are around 10^{22} cm⁻³ for Si-based clathrates, our analysis shows that thermoelectric properties of the clathrate can be improved by suppressing carrier

concentration, as shown in Fig. 1(c).

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Fig. 1. Enhancement of thermoelectric properties of Si-based Clathrate. (a) Crystal structure of Ba₈Ga₁₆Si₃₀. (b) Prediction of formation energy with a cluster expansion method. (c) Dimensionless thermoelectric figure-of-merit (ZT) of the clathrate at different carrier concentrations.

First-principles calculation for low-temperature oxygen transfer in metal oxide

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We have studied oxygen storage and release materials experimentally and computationally. This term CeO₂ and Cr-doped CeO₂ were studied with first-principles calculations.

Plane-wave basis density functional theory (DFT) calculations were conducted to elucidate the Cr doping effects on CeO₂ structure using the VASP code [1,2]. The generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof (PBE) [3] was employed as the exchange correlation energy functional. The DFT+U method introduced by Dudarev et al. [4] was used to treat the electron localization. The parameter, U-J was set as 3.5 eV for Cr3d, 5.0 eV for Ce4f, and 5.5 eV for O2p states, respectively, based on the previous studies of Cr₂O₃ and CeO₂ [5,6]. The valence configurations of the pseudopotentials were $3s^23p^63d^54s^1$ for Cr, $5s^25p^64f^15d^16s^2$ for Ce and $2s^22p^4$ for O. The energy cutoff for the planewave basis was set at 500 eV for all the calculations and provided the convergence of the total energy in the unit cell of CeO_2 (12 atoms). Defect calculations were conducted using the $2 \times 2 \times 2$ extension (96 atoms) of CeO2 unit cell with Monkhorst-Pack k-point mesh of $4 \times 4 \times 4$. Atomic positions were

relaxed within a cubic cell, and the lattice parameters of perfect CeO_2 and Cr-doped CeO_2 were obtained using the Murnaghan equation of state. Forces were converged to 0.01 eV/Å in all calculations.

Nudged elastic band (NEB) calculations were performed to obtain diffusion paths and barrier energies with seven replicas, including five nudged intermediate images. The spring constant linking images was 5.0 eV/Å and the conversion criteria were defined that resultant forces, including the spring forces, were less than 0.01 eV/Å. The energy barrier was obtained by applying the climbing image algorithm [7], which allowed the determination of the saddle point at the transition state.

To elucidate the mobility of oxygen for pure and Cr-doped CeO₂, nudged elastic band calculation was conducted. Figures 1a and 1b show the diffusion path of an oxygen atom to the vacancy site and migration barrier. Compared to pure CeO₂ (0.41 eV), a much lower migration barrier was observed in Crdoped CeO₂ (0.28 eV). In the case of the pure CeO₂, electron polaron (Ce³⁺) exists at the next nearest neighbor of the oxygen vacancy, and diffusion of the polaron accompanied with oxygen diffusion was observed; Rapid polaron diffusion in reduced CeO₂ has been discussed previously [11]. As a result of the NEB calculation, diffusion constants at 400 °C are 5×10^{-11} m² s⁻¹ for CeO₂ and 5×10^{-10} m² s⁻¹ for Cr-doped CeO₂. The high diffusivity of oxygen in Cr-doped CeO₂ is one of the origins to cause high oxygen mobility at low temperature observed in the experiments. This result was published in ref. [12].

(A)



(B)

Figure 1 Energy barrier of oxygen atom diffusion to a vacancy site obtained by NEB calculation for (A) CeO_2 and (B) Cr-doped CeO_2 . Light green, sky blue, dark blue, red, and orange balls represent Ce^{4+} ion, Ce^{3+} ion, Cr, O, and diffusing oxygen, respectively.

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Reduction of Rare Metals in Formic Acid Decomposition Catalysts and Oxygen Storage Materials

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We investigated the catalyst adsorption and diffusion properties on light-element element doped graphene with the aid of the first-principles calculation based on the density functional theory (DFT). Besides, we investigated the oxygen absorption properties of heteroatom-substituted brownmillerite-type oxides.

At first, we investigated the stabilities of Cu atoms embedded in light-element doped graphene. We considered embedded Cu atoms coordinated with various substituted dopants. We performed the total energy and electronic structure calculations using The Vienna Ab initio simulation package (VASP). We installed a parallelized VASP with Intel® MPI Library and Intel® Math Kernel Library. We revealed that the stabilities of Cu atoms embedded in light-element doped graphene strongly depend on the coordinated atoms. In the cases of large coordinated atoms, The Cu atoms protrude from graphene basal planes. We also investigated the catalytic activity using a theoretical volcano plot reported in the previous study.[1] From the adsorption energy of intermediates, we estimated the

reaction activities. We found that the stable Cu atoms embedded in graphene show higher activity than unstable Cu clusters on graphene.

We investigated the oxygen absorption properties of partially substituted Ca₂AlMnO₅. We revealed that rotation of coordination polyhedra of cations releases the distortion induced by heteroatom doping. In addition, we investigated the effects of Pt addition on oxygen storage properties.

We also studied the adsorption properties and catalytic activities [3] and chemical bonding states [4] of Pt sub-nano clusters on light-element element doped graphene.

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Ab initio analysis on the stability of magnetic ternary alloys

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Adding a small amount of third elements in binary systems not only stabilizes system but also changes these physical properties. Recently, a new ternary alloy was discovered by introducing a third element of In into $L1_2$ -FePd₃ by Teranishi's group in Kyoto University [1]. Other interesting example is Nd–Fe amorphous phases which can be crystalized after adding Ga in Nd–Fe–B sintered magnets. Although the physical aspects of these added elements are unclear and cannot be understood deeply only through experiments.

In this study, we conducted theoretical analyses for the stability of an In-doped novel Fe–Pd and Ga-dope Nd–Fe ternary alloys using OpenMX. The model structures for the calculations were based on the chemical composition ratio obtained from experiments.



Figure: Formation energies for $L1_2$ -(Fe, In)Pd₃ and Z3-Fe(Pd, In)₃.

For In-doped Fe–Pd ternary alloys, the In sites were chosen by replacing Fe or Pd sites with a special-quasirandom-structure method implemented in the Alloy Theoretic Automate Toolkit [3]. The figure illustrates the formation energies of L_{12} -(Fe, In)Pd₃ and Z3-Fe(Pd, In)₃ when the number of In in a system takes from 1 to 6. By comparing these formation energies, Z3-Fe(Pd, In)₃ can be more stable than L_{12} -(Fe, In)Pd₃ only in a narrow range of the In content. This tendency can be seen in the experimental results from XRD, EXAFS, and STEM-EDS analyses.

In Ga-doped Nd–Fe ternary alloys, we found that Ga is a key not only to stabilizing the fluorite-type crystal structure but also to suppressing its Curie temperature, which might be one of the reasons to explain why Ga-added Nd–Fe–B sintered magnets have high coercivity [4].

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Fusion of computational material science and data-driven science with massively parallel computation

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The present project was carried out for several topics in the fusion of computational material science and data-driven science on the ISSP supercomputer. The main collaborators are I. Mochizuki, T. Hyodo (KEK-IMSS-SPF), T. Hanada (Tohoku U), K. Hukushima (U Tokyo), K. Yoshimi, Y. Motoyama (ISSP), T. Fujita (IMS), Y. Yamamoto (UEC), Y. Miyatake (U. Tokyo).

The first topic is the development of the data analysis software of total-reflection highenergy positron diffraction (TRHEPD), a novel experimental technique for surface structure determination [1-6]. Experiments are being conducted intensively at the Slow Positron Facility, Institute of Materials Structure Science, High Energy Accelerator Research Organization. Figure 1 shows the structure determination of the Si₄O₅N₃ / 6H-SiC (0001)- $(\sqrt{3} \times \sqrt{3})$ R30° (SiON) surface structure [3]. The software development activity was promoted to Project for Advancement of Software Usability in Materials Science in ISSP (https://www.pasums.issp.u-tokyo.ac.jp) in FY2020 and FY2021. Our software was called '2DMAT' and was published as an open-source software [4,5]. A TRHEPD simulator was

required for the data analysis by 2DMAT and we used the simulator program 'sim-trhepdrheed' originally developed by T. Hanada. [4,6].



Fig.1 (a) Schematic figure of TRHEPD experiment. (b) The side view of Si₄O₅N₃ / 6H-SiC (0001)-($\sqrt{3} \times \sqrt{3}$) R30° (SiON) surface structure. (c) TRHEPD data analysis of the SiON surface structure [3]. The *z*coordinate of the surface atom layers is denoted as $z_1, z_2, ..., z_7$. The color-coded isovalue plots of the R-factor, the residual function between the experimental and calculated data, on the local grid of the $z_1 - z_2$ plane [3].

The second topic is the method and application of large-scale electronic structure calculations for organic and other materials [7-10]. The study was carried out by our original code ELSES (http://www.elses.jp/), an order-*N* electronic state calculation code with an *abinitio*-based tight-binding method and a fragment-molecular-orbital-based method. In
particular, an excited-state theory was constructed for disordered Pentacene/C60 Interfaces [9-10]. The third topic is the development of several fundamental numerical algorithms [11-12].

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Reduction of Rare Metals in Fuel Cell Catalysts and Hydrogen Permeable Membrane

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We investigated the catalytic properties of Pt sub-nano clusters on light-element doped graphene and hydrogen dissolution and diffusion properties in the interfaces of ceramic materials, with the aid of the firstprinciples calculation based on the density functional theory (DFT).

At first, we investigated the adsorption and catalytic properties of Pt single atoms and Pt sub-nano clusters on light-element doped graphene. We performed the total energy and electronic structure calculations using The Vienna Ab initio simulation package (VASP). We installed a parallelized VASP with Intel® MPI Library and Intel® Math Kernel Library. In this study, we focused on oxygen reduction reactions (ORR). In order to evaluate the catalytic properties, we calculated the energy diagrams of whole ORR paths. We also made a volcano-plot to show relationship between the adsorption energy of catalytic activities and intermediate species of chemical reactions.[1] We found that ORR activity of Pt₁ is higher than those of Pt₂ and Pt₃. From the viewpoint of a support effect caused by light-element doped graphene, the catalytic

activity of Pt_1 more strongly depends on the light-element dopants in graphene lattice than those of Pt_2 and Pt_3 . Therefore, Pt single atoms on light-element doped graphene support is a promising candidate for a new catalyst which is better than the current fuel cell catalyst, i.e., bulk Pt catalyst.

We also investigated the chemical bonding between N-doped graphene and Pt single atoms using DFT calculations and transmission electron microscopy combining with electron energy loss spectroscopy, and the hydrogen dissolution and diffusion properties in the interfaces of TiN with residual impurity gasses.

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First-principles study on physics of gap-state control at metal/semiconductor interfaces: II & III

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Due to the break of atomic bonds and the lack of translational symmetry, gap states appear in semiconductor layers around metal/semiconductor interfaces, which have the energy position in the band gap and are localized around the interface. These states induce the electron transfer between metal and semiconductor layers and determine a variety of physical properties at the interface, such as Schottky barrier (SB) and carrier transport. However, it is still unclear how to control these gap states. In this works, we studied the SB and tunneling current at various interfaces and clarify the origins of gap-state generation/annihilation and deformation using the first- principles calculations.

First, we consider metal/Ge interfaces, where Fermi energies of most of simple metals are located around the valence-band top of Ge not depending on the kinds of metals. This is called the Fermi-level (FL) pinning and interrupts desirable low-resistive metal/n-Ge contacts. Although the breakdown of FL pinning was recently observed at the Bi/Ge(001) interface, its origin has not been clarified. To simulate the interfaces, we adopt (2×2) (Bi, Al)/Ge(001) repeated-slab models with various interface structures and calculate their SBs using local potential profiles.

Figure 1 shows calculated SBs for hole carriers ate various interfaces. The SBs at (b) disordered Bi/Ge and (c) plain Al/Ge interfaces are around 0.0eV corresponding to the FL pinning, while the SB at (a) plain Bi/Ge interface has a large value around above 0.3eV, which is in good agreement with experiments. The origin of such SB variation is understood by observing the projected densities of states (PDOS) of interface Ge atoms, which are shown in Fig.2. For (b) and (c) interfaces, the



Fig.1. Left: calculated Schottky barriers for hole carriers at various (Bi, Al)/Ge interfaces. Right: schematic pictures of interface structures. (a): abrupt plain Bi/Ge interface, (b): disordered Bi/Ge interface, and (c): plain Al/Ge interface.

continuous PDOS, thus the gap states, appear around 0.0eV due to the orbital hybridization between metal and Ge atoms, which induces the electron transfer from metal to Ge and realizes the FL pinning. On the other hand, we can see the suppression of gap states in the PDOS of interface Ge for the (a) interface, which realizes the FLdepinning. This suppression occurs due to the weak contact of Bi and Ge layers, which is caused by the lattice mismatch originating from the large atomic radius of Bi and produces the Ge-Ge dimer bonds at the interface as shown in the right of Fig. 1. In this way, the interface Ge-Ge dimer bonds annihilates the gap states in interface Ge layers and produces the large change of the SB values.

Next, we consider how the gap states change in electric fields. We consider the tunneling current at indirect-band-gap Si and GaP, and direct-band-gap GaAs and InP p/n junctions, in the cases without



Fig.2. Calculated projected densities of states of interface Ge atoms around (a) plain Bi/Ge, (b) disordered Bi/Ge, and (c) plain Al/Ge interfaces, which respectively correspond to interfaces shown in Fig.1. Orange boxes indicate the band-gap region of Ge.



Fig.3. Calculated tunneling currents at (a) indirect-band-gap Si and GaP, and (b) direct-band-gap GaAs and InP p/n junctions, as a function of electric field. The cases without and with N-atom dopants are shown.

and with N-atom dopants. Figures 3(a) and 3(b) show calculated currents for these interfaces as a function of applied electric field. It is clearly seen that the current is much larger for the latter junctions, which is because the latter system have direct band gap and have larger interband tunneling transitions.

When N-atom dopants are embedded in p/n junctions, the current is markedly enhanced in the cases of indirect band-gap systems, i.e., Si and GaP. This enhancement occurs because the dopant gap state produces the resonance states with the conduction-band states of host Si layers around the junction in electric field as shown in Fig.4(b), and



Fig.4. Calculated transmission spectra of electrons and local density of N-atom dopant states at the Si p/n junction ((a) and (b)), and the GaAs p/n junction ((c) and (d)). The cases of junctions without dopants are also shown by red lines.

such resonance remarkably increases the tunneling probability across the junction as shown in Fig.4(a). On the other hand, in the cases of direct band-gap systems, as seen in Fig.3(b), there is no increase in the current by the dopants. This is because the dopant gap state is strongly localized as in Fig.4(d) and the increase of tunneling is small as in Fig.4(c). By analyzing electronic structures, we found that the difference in the dopant effects on tunneling currents between indirect and direct band-gap systems reflects the characters of conduction-band states in these systems.

All these calculations were performed using the xTAPP, VASP, and our original pspwf codes. In order to realize the calculations for the present interface systems, because the system is made of a large number of atoms (500-2000 atoms), the advanced computing facility having multi-task and higher-speed CPU (more than 1280 cores \times 2.0GHz), larger-size memory (around 256GB), and larger-size strange (more than 2 TB) is indispensable. These conditions are realized only by the present ISSP supercomputing systems.

First-principles Calculations on Magnetism in 2D Magnetic Materials

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We have studied the magnetism in 2D magnetic materials and discussed our current understanding of the mechanisms using the first-principles density functional theory (DFT) calculations.

First, we systematically investigated the magnetocrystalline anisotropy energy (MAE) of the Co-based transition-metal thin films using DFT HiLAPW code at the ISSP seikirei supercomputer. The results show that the large perpendicular MAE can be achieved by tuning atomic-layer stacking in Ni-Co thin film. The MAE is decomposed into single-layer contributions and inter-layer contributions to reveal the fact that not only the on-site SOC of 3d elements but also the strong hybridization between these elements play an important role to determine the MAE. The small effect of electric fields on the magnetocrystalline anisotropy also has been found in Ni-Co thin film, making this system becomes the potential for future spintronics applications [1].

Secondly, we investigated the magnetic stability in 2D magnetic material VI₃ making a comparison with CrI₃ using the VASP code at

the ISSP ohtaka supercomputer. VI₃ is a Mott insulator with an energy band gap is 0.34 eV. In trigonal VI₃, under the crystal field with D_{3d} point group, the t_{2g} orbital state is split into a_{1g} and e_{g} ' states. The a_{1g} orbital state plays an important role in inter-layer magnetic exchange interaction in a bilayer structure. By using Wannier90 code that is interfaced with the VASP code, we estimated the hopping integral and discussed the inter-layer magnetic exchange interaction based on the virtual-hopping mechanism. In the bilayer VI₃ case, we studied two structures corresponding to R3 and C2/cphases in bulk VI₃, namely AB and AB' stacking. The application of electric field enables to switch the magnetic ordering from inter-layer AFM to FM in AB' stacking. This finding may pave a way to the spintronics application with 2D materials [2].

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Band structure calculation based on the group theory

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In the field of spintronics, the spinorbit coupling (SOC) is considered to generate new functions. One of the most important phenomena is concerning

topological insulators. We emphasize that the group theoretical analysis is necessary to deeply understand the SOC effect on electronic structures but the analysis has been insufficient so far. We have developed a method to identify irreducible representations (IR) for the SOC bands which are obtained by using first-principles plane wave base calculations. The identification can be done by using computers and thus misidentification can be avoided.

The IR of the band having the qdegeneracy is determined by using the following expression :

$$Q^{\alpha} = \frac{1}{l} \sum_{j=p}^{p+q-1} \sum_{m=1}^{l} \chi^{\alpha} (C_m)^* < \Psi_{\vec{k}}^{\ j} \mid C_m \mid \Psi_{\vec{k}}^{\ j} >$$

Where l and $\chi^{\alpha}(C_m)$ are the order of the k group and the character for the m-th symmetry

operation $C_{\scriptscriptstyle m}$, respectively. $\Psi_{\scriptscriptstyle ec k}^{\ j}$ is

the Bloch function for the band index *j* and the wavenumber \vec{k} . The wavefunction (does not) belong to the IR of α when $Q^{\alpha} = 1$ ($Q^{\alpha} = 0$).

In this report, we focus on our results on group-IV two dimensional materials.

In the case of graphene, the Dirac cone is found to belong to the twodimensional IR of E" in the D_{3h} group. The SOC is found to split the doubly degenerated level into $E_{1/2}$ and $E_{3/2}$ levels. The former level is found to be higher than the latter level and we clarify the reason for this energetical order by using a tight binding model. We evaluate the topological invariant and confirm that the values for both buckled and non-buckled structures are 1, suggesting the possibility of topological insulators.

Effects of solvents on properties of artificial-retina molecule: ab initio molecular dynamics simulations

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Molecular dyes are attractive great attention because of their application for various optical devices such as solar cell and artificial retina. To improve functionality of the dye molecule, it is used to control the band gap. Therefore, theoretical studies based on the density functional theory tried to understand the structural and photoelectrical properties such as absorption and emission properties in the gas phase. However, the working conditions of such dye molecules in nature and in the industrial applications entail their solvation. We have systematically investigated the effects of solvent, H_2O , tetrahydrofuran, acetonitrile, and chlorobenzene on light-absorption properties in a photoelectric dye (NK-5962) which is better candidate for retinal prostheses by means of ab initio molecular-dynamics simulations. To calculate absorption spectra, we adopted the Time-Dependent Density-Functional linear-Response Theory (TDDFLRT), proposed and formulated by Casida. The simulation reveals that all solvents slightly affect the lightabsorption spectrum but all systems has a main

peak at visible light region. However, the excited charge dynamics after light absorption is influenced a great deal by H₂O. Without H₂O, the generated hole by light-absorption in NK-5962 transfers to counter-ion cite at less than 100 fs. On the other hand, in the case of the system with H₂O, the hole stays in NK-5962 site. Our simulation clarified that these effects are attributed to interaction between H₂O and counterion of NK5962. In addition to retina molecule, we have investigated the dissociation mechanisms from highly charged bromophenol $(C_6H_5OHBr)^{n+}$ (n≤10) by ab initio MD simulations [1]. The charge state dependence of dissociation mechanisms is observed by this simulation. We also investigated the intramolecular charge transfer time by using nonadiabatic quantum-mechanical moleculardynamics with surface hopping approach. It is found that the hole transfer from the Br site to the molecular counterpart in ~ 5 fs.

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Structural and transport properties of multi-component liquid Fe mixtures under high pressure

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We have investigated the effects of light elements (LE) such as H, C, O, Si, and S on the structural and transport properties of liquid Fe under high pressure by ab initio molecular dynamics (MD) simulations. It is believed that Earth's outer core consists of liquid iron (or liquid-nickel alloy) with LE impurities. LE have a strong influence on structural and transport properties of liquid iron under high pressure. However, there are still many uncertainties regarding the influence of LE. For Fe-LE binary systems, we clarified the structural properties and interactions between LE atoms at coremantle boundary condition [1]. The simulations clarify that H, C, and O are incorporated into liquid Fe interstitially while Si and S are "substitutional" type impurities. Under these circumstances, in this study, we have studied structural and transport properties of liquid ternary system consisting of liquid Fe and two types of LE by using ab initio MD simulations. From our simulations, it is found that Si and S atoms show "substitutional" behavior while H and O atoms show "interstitial" behavior even in

ternary systems. For the transport properties, LE in the ternary systems decrease electric conductivity of liquid Fe as same as binary systems. The decreasing rates are between those of binary systems as shown in Fig. 1.



Fig. 1: Change of electrical conductivity of liquid Fe-H-O as a function of concentration of LE. Blue circles show ternary systems. Red and green squares show binary system.

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Impact of the molecular quadrupole moment in the molecularly mixed film of organic semiconductors

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The energy levels of organic semiconductors are primarily determined by the molecular orbital energies of constituent molecules. Recent studies have, however, shown that the energy levels can be changed by the mixing ratio of two molecules which have different permanent quadrupole moments. From the good correlation between the magnitude of the mixed film's energy shift and the constituent molecules' permanent quadrupole moment, it was noted that the molecular quadrupole plays an important role in the energy shift.

In this study, I theoretically examined the mixed films of zinc phthalocyanine (ZnPc) and perfluorinated ZnPc (F₁₆ZnPc), which have permanent quadrupole moments with opposite directions. Here, as was successfully applied to organic semiconductor thin films[1, 2], a combination of the GW approximation suitable in general to solid or bulk systems and a periodic slab approach at the DFT-GGA level was employed. From the theoretical electronic polarization energy D and electrostatic energy S as a function of mixing ratio, ionization energies and electron affinities were estimated.

I performed first-principles electronic structure calculations with the STATE program code to determine the optimized geometries of the pristine crystals as well as 1:1 mixed thin films of ZnPc and F_{16} ZnPc. To check the convergence of the electrostatic energy on the number of the layers in the simulation cell, one, two, and three monolayers (1-3 ML) films were modeled by periodic slabs. For the pristine crystals, I fixed the lattice constants to experimental values of the monoclinic and triclinic forms for ZnPc and F_{16} ZnPc, respectively. The two stable facets are denoted by "edge-on" and "face-on" for each of the crystals, depending on the orientation of the molecules at the surface (see Fig. 1). Since the experimental lattice constants were not available for the mixed film, those of the pristine crystals were used for the mixed films.

The 1 ML slabs for the pristine ZnPc and F_{16} ZnPc films consisted of 2 molecules, and 4 molecules comprised the 1 ML mixed film in the ratio 1:1. The vacuum layer with a thickness of 2.0 nm was inserted. I optimized the geometric structures of the standing 1–3 ML slabs by taking into account the van der Waals forces within PBE-D2. To describe the orientation dependence of the electrostatic interaction, I took the difference in the HOMO or the LUMO energy of ZnPc and F_{16} ZnPc between the slab and an isolated gas-phase molecule.

The electronic polarization energy was described by the many-body perturbation theory, within the G_0W_0 approximation with the GWspace-time code. The fundamental gaps were obtained as the difference between the highest occupied and lowest unoccupied band energies averaged over the Brillouin zone. The numbers of cores used in the calculations were 256~512.

The gaps were determined to be 2.26 eV and 2.19 eV for the monoclinic ZnPc and the triclinic F_{16} ZnPc bulks, respectively. For the gas phase fundamental gap, I estimated the

electron affinity (A_q) and the ionization energy (I_q) at the HSE06/spaug-cc-pVTZ level of theory with the delta self-consistent field approach using Gaussian16 Revision B.01 installed in my own computer resources. I did not use the gas-phase fundamental gap at the $G_0 W_0$ level, since the $G_0 W_0$ treatment tends to over-screen the injected charge in gas-phase molecules [3]. The electrostatic energy S was estimated as the difference in HOMO/LUMO energy between the surface slab and the gas phase estimated with the GGA-PBE level of theory [1, 2]. Based on the bulk fundamental gap obtained with $G_0 W_0$ and the theoretical gas phase ionization energy I_q and electron affinity A_q , the electronic polarization D was obtained.



Figure 1: Theoretical polarization energy Dand electrostatic energy S as a function of molar mixing ratio of F_{16} ZnPc in the mixed film. The calculated results are displayed by dashed lines and the experimental values are by solid lines.

Figure 1 displays the calculated D and S, along with the experimental values[4]. Overall, the theoretical polarization energies are in good agreement with experiments. In case of the electrostatic energies, the qualitative trend depending on the F₁₆ZnPc amount in the mixed film is similar.

It is found that the polarization energies are almost the same in the "edge-on" and "faceon" configurations. The result implies the nature of the electronic polarization originating from the stabilized injected charge surrounded by the induced polarization clouds inside the bulk, and thus does not depend on the molecular orientation at the surface of the films.

On the other hand, the electrostatic energy changes more rapidly as a function of the mixing ratio in the "edge-on" configuration than in "face-on". The different trend comes from the different orientation of the molecules at the surfaces of the mixed thin film: in the "edge-on" configuration in which the constituent molecules are standing on the surface of the film, the orientation angle is very sensitive to the mixing ratio, while in the "face-on" configuration, the molecular planes are parallel to the film surface and the orientation angle does not change significantly with respect to change in the mixing ratio. The change in the electrostatic energy in the molecular crystal film comprised of molecules with appreciable quadrupole moment such as ZnPc and F_{16} ZnPc may be elucidated in terms of the electrostatics [5]. The present finding may lead to the insight into tuning of the charge injection energy levels at the surfaces of organic semiconductors.

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First principles exploration of the metastable phases of hydrides and their superconductivity

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Superhydrides that crystallize under extremely high pressure have attracted lots of interest since the discovery of high temperature superconductivity in solid hydrogen sulfide [1]. Recently, the domain of searching for new hydrides that possibly exhibit higher transition temperatures is getting broadened to ternary hydrides ABH_x , resulting in the discovery of superconductivity in a C-S-H system with record of $T_c = 286$ K [2].

We conducted exploration of the novel (meta)stable hydrides and calculations of superconducting properties of them. In particular, we contributed to an international theoretical-experimental study of a La-Y-H ternary hydride system. In their pure binary compositions LaH_x and YH_x , LaH_{10} and YH_6 have been discovered to form under pressure, both of which exhibit different forms hydrogen cage structures. The inverse, YH_{10} and LaH_6 , are metastable according to simulations. Interestingly, it is predicted that their mixtures $LaYH_{20}$ and $LaYH_{12}$ can become stable at certain conditions, the origin of which may be a synergetic effect of La and Y. This prediction was verified by the experimentally observed diffraction patterns. We calculated their possible values of $T_{\rm c}$, using the density functional theory for superconductors (SCDFT) [3, 4]to compare them with the experimentally observed $T_{\rm c}$.

Here we append the the scheme of calculating T_c on the basis of SCDFT. First, the Kohn-Sham electronic and phononic structure calculations were performed using an open source code package QUANTUM ESPRESSO [5]. The generalized gradient approximation [6] for the exchange-correlation potential was employed. The optimized norm-conserving Vanderbilt pseudopotentials [7] was used for the calculations. Next, the dielectric matrix and matrix elements of the effective electron-electron Coulomb interaction were calculated with an in-house code. Finally using those data, the superconducting transition temperature was evaluated by solving the following SCDFT gap equation[3, 4, 8]

$$\Delta_{n\mathbf{k}} = -\mathcal{Z}_{n\mathbf{k}}\Delta_{n\mathbf{k}} -\frac{1}{2}\sum_{n'\mathbf{k}'}\mathcal{K}_{n\mathbf{k}\mathbf{n}'\mathbf{k}'}\frac{\tanh[(\beta/2)E_{n'\mathbf{k}'}]}{E_{n'\mathbf{k}'}}\Delta_{n'\mathbf{k}'}(1)$$

 β denotes the inverse temperature. The exchange-correlation kernels \mathcal{K} and \mathcal{Z} , which represents the effects of the electron-phonon and electron-electron interactions, are formulated in terms of the Kohn-Sham electronic and phononic properties.

Solutions of the Kohn-Sham equation was parallelized by MPI as implemented in pw.x code of QUANTUM ESPRESSO. The in-house code for calculating the dielectric matrix has been thread-parallelized by openmp. The SCDFT gap equation was solved without parallelization since it was less time-consuming. Calculations were mainly performed in System B.

Various synthesis protocols were executed for the La-Y-H samples and maximum $T_{\rm c}$ of ~ Table 1: Superconducting transition temperature $T_{\rm c}$ calculated with the SCDFT gap equation Eq. (1). Coupling constant λ and typical frequency $\omega_{\rm ln}$ ([9]) of the electron-phonon coupling spectra are also presented.

	$LaYH_{12}$	$LaYH_{20}$
$T_{\rm c}(SCDFT)$ (K)	191	252
λ	2.82	3.87
$\omega_{ m ln}$	847	868

250 K was observed. The calculated superconducting transition temperatures, especially in LYH₂₀, show good agreement with this experiment (Table 1). This shows that the phononmediated pairing mechanism explains the superconductivity in the current ternary system. This result is to be published [10].



Figure 1: Impacts of the charge (plasmon) and spin fluctuations on superconducting T_c in V, Nb, and Al, taken from Ref. [11].

We also developed an extension of the SCDFT scheme to include the spin fluctuation effect, which is a continuous subject since a ISSP project in the fiscal year of 2018 [Project ID: H30-Ca-0046]. We examined the effects of the spin fluctuation and charge fluctuation on $T_{\rm c}$ in elemental metals, V and Nb. We found that the spin fluctuation strongly suppresses $T_{\rm c}$. Experimentally observed $T_{\rm c}$ is smaller in V than in Nb, whereas the degree of the suppression effect depends on the character of atomic

orbitals. This dependence results in correct reproduction of the $T_{\rm c}$ relation in those systems (Fig.1). This result has been published as a paper [11].

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Helical channel at twin boundary of a boron-nitride atomic layer

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Helical channels, which suffer little from backscattering, have attracted much attention in valleytronics and theoretically studied in graphene on a boron nitride substrate [1, 2]and in a boron-nitride atomic layer (BNaL) with a twin boundary [3]. We focus on the BNaL twin boundary which can support a narrower helical channel. Twin boundaries of the BNaL are classified into unpolarized and polarized boundaries such as shown in Fig. 1 in which carbon chains are inserted at each twin boundary to relax the repulsion between cations and that between anions. In this work we have studied differences in electronic properties of helical channels between polarized and unpolarized twin boundaries.

We have made a first-principles calculation of the energy band of helical channels formed along BNaL twin boundaries (Fig. 1). We impose the periodic boundary condition perpendicular to channels so that the unit cell contains two twin boundaries. We have found that polarized and unpolarized twin boundaries have quite different helical channel bands: the distance in k space between helical channels belonging to K and K' valleys is much shorter in the polarized BCCB-NCCN arrangement [Fig. 1(b)] compared to that in the unpolarized NCB arrangement [Fig. 1(a)]. This result suggests a possibility of largely modifying transport properties through a helical channel by changing the atomic arrangement in the vicinity of the channel.

The computation in this work has been done

using the facilities (system B and C) of the Supercomputer Center, the Institute for Solid State Physics, the University of Tokyo.



Figure 1: Helical channels at twin boundaries with (a) unpolarized NCB arrangement (b) polarized BCCB-NCCN arrangement. The periodic boundary condition is imposed in the ydirection with periodicity of one unit cell. The zero of energy is taken at the Fermi energy.

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First-principles study of quantum transport in nanostructures

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Theoretical investigations on transport properties are important not only for the fundamental research of science but also for the applications of electronics. We have developed the nonequilibrium Green's function (NEGF) method, and the O(N) time dependent wavepacket diffusion (TD-WPD) method on the basis of the density functional theory (DFT). By using these methods, we have investigated charge, head and spin transport properties of materials. [1]

We have developed a Simulation code for Atomistic Kohn-sham Equation (SAKE) for the ab-initio electron transport calculation based on the DFT and NEGF formalism. We have applied the method to analyses of thermoelectricity of magnetic semiconductors CuFeS₂. The electronic transport properties, Seebeck coefficient, and the figures of merit are estimated. We theoretically demonstrate the enhancement in the figure of merit by doping, which is in agreement with experimental work, and design doped systems for higher performance. [2]

We developed the O(N) TD-WPD method for the quantum transport calculation of huge systems of up to 100 million atoms a decade ago. It is possible to calculate the conductivity and the mobility of the system with micron-order lengths at room temperature at the atomistic levels. We have proposed a prediction methodology to obtain charge transport properties of organic single crystals from their structural formula using TD-WPD method. We applied the method to C₁₀-DNBDT molecule, and succeeded in quantitative evaluation of charge mobility of the single crystal using our quantum wave-packet dy-



Figure 1: Seebeck coefficient of $CuFeS_2$ as a function of the chemical potential.

namical simulation method. It is shown that the proposed methodology is an effective theoretical design technique for efficiently developing new high-performance organic semiconductors. [3]

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Magnetocaloric Effect of Transition-Metal Alloys

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We study the magnetocaloric effect of transition-metal alloys by combining firstprinciples calculations and Monte-Carlo simulations. The parameters of the Monte-Carlo simulation are estimated from first-principles calculations. Several types of the magnetocaloric effect such as conventional (direct) magnetocaloric effect, giant magnetocaloric effect, anisotropic magnetocaloric effect, and inverse magnetocaloric effect can be considered by using our original $\operatorname{program}[1, 2, 3, 4]$. The isothermal magnetic entropy change of $Mn_{1-x}Cu_xCoGe$ alloy is shown in Fig. 1 (a). Stoichiometric MnCoGe has two phases, the low-temperature phase is orthorhombic while the high-temperature phase is hexagonal. Both the phases are ferromagnetic below different Curie temperatures. When there is a structural coupling between magnetic and structure part, the isothermal magnetic entropy change becomes gigantic as the Mn_{0.89}Cu_{0.11}CoGe case. We also perform speed-up tests for our massively parallel Monte-Carlo program with hybrid MPI and OpenMP in new System B as shown in Fig. 1 (b) and (c). We obtain a good scaling in the tests of OpenMP and MPI, that is quite important for further study such as virtual screening of magnetocaloric materials.

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Figure 1: (a) Isothermal magnetic entropy change of $Mn_{1-x}Cu_xCoGe$ (x = 0.00, 0.11, 0.15) [1]. (b) and (c) Speed-up tests of our Monte-Carlo program in the new System B (Ohtaka).

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Theoretical analysis of molecular motions in protonconducting organic materials

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Anhydrous proton conduction materials have been investigated for use in electrolytes in fuel cells. The composite materials including imidazole have especially gained much attention because of the lack of humidity. Poly(vinylphosphonic acid)-imidazole (PVPAxIm) has shown the increase of proton conductivity with x [1]. Understanding the proton conduction mechanism leads to the improvement of proton conduction materials.

In this study, we discussed the proton conduction mechanism in PVPA-*x*Im in terms of the microscopic characters of the hydrogen bond and imidazole motions as investigated by molecular dynamics simulations. The simulations were performed by the GROMACS package.

We calculated the translational diffusion coefficients of imidazole, imidazolium cation, and PVPA oligomer in PVPA-*x*Im to investigate their translational motion. All diffusion coefficients increased with temperature. The intercalation of imidazole into PVPA reduces the imidazole diffusion, because the diffusion coefficient of imidazole significantly decreased in PVPA-2Im compared to that in pure imidazole system. The diffusion coefficients of imidazoleium cation and PVPA oligomer in PVPA-2Im further decreased and were similar values each other. Therefore, we find that the imidazolium cation motion was interlocked by PVPA because of the strong hydron bond interaction between imidazolium cation and phosphonic acid in PVPA.

We estimated the rotational correlation time of imidazole and imidazolium cation to investigate their internal motions. The obtained results showed the similar dynamical behavior of the translational diffusions. We compared the activation energies of transrational and rotational motions of imidazole. The calculated energies of rotational motions were lower than those of translational motions. Therefore, it is expected that proton conduction obeys Grotthuss-type mechanism.

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Development of molecular crystal structure prediction methods

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We have developed a crystal structure prediction tool, CrySPY as an open source software [1]. CrySPY is interfaced with VASP[2], Quantum ESPRESSO[3], soiap[4], and LAMMPS code for structure optimization. Several searching algorithms are available in CrySPY, such as random search (RS), evolutionary algorithm (EA), Bayesian optimization (BO), and LAQA. RS is a basic algorithm and widely used. EA[5, 6, 7] is currently very popular. Previously we have developed selectiontype algorithms with machine learning. BO can efficiently select potential candidates from a large number of candidate structures by machine learning[8]. LAQA is one of the refinforcement learning, which can reduce the computation time[9]. CrySPY enables us to find stable structures for bulk systems. However, CrySPY did not support molecular crystal, surface and interface structures. The original plan was to develop a method for surface structure prediction, but we changed the plan and developed a method for molecular crystal structure prediction.

We employed the PyXtal library [10] to generate molecular crystal structure generation, and developed the interface between CrySPY and PyXtal. We tested molecular crystal structure prediction for Li₃PS₄ using CrySPY. The most stable structure of Li₃PS₄ is known as γ -Li₃PS₄ [11], which is composed of six Li atoms and two PS₄ molecules shown in Fig. 1. Fifty molecular crystal structures of two



Figure 1: Crystal structure prediction of Li_3PS_4 . The stable structure is $\gamma - Li_3PS_4$.

formula units of Li₃PS₄ were randomly generated. Structure optimizations were performed using the density functional theory with the projector-augmented wave [12] method as implemented in the VASP code [2]. The generalized gradient approximation by Perdew, Burke, and Ernzerhof [13] was employed for exchange-correlation functional. A cutoff energy of 625 eV for the plane-wave expansion of the wave function and k-point mesh density of 80 Å⁻³ were used.

Crystal parameters of the lowest-energy structure perfectly agree with the experimental ones of γ -Li₃PS₄ except for the tiny amount of differences in lattice constants and atomic positions. These results indicate that the molecular structure generation method is quite useful for stable structure predictions of molecular crystals.

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Density Functional Theory and Polarizable Continuum Model for Developing High-Performance Polymer Electret

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Electret is a dielectric material, where trapped charges can generate electrostatic field for tens of years. Vibrational electret energy harvester (VEEH) can convert kinetic energy into electricity efficiently by electrostatic induction. Because the output power can be increased by four times with bipolar (negative and positive) charging, development of high-performance electret material for both positive and negative charging is crucial.

CYTOP (AGC Co. Ltd.) is an amorphous fluorinated polymer, with its chemical structures shown in Figure 1. There are three kinds of commercialized CYTOP, CTX-S, A and M. Recently, S Kim et al. [1] utilized quantum chemical analysis for evaluating charge trap of CYTOP electrets. It is shown that, although number of repeat unit of CYTOP is over 500, the trapped electron is localized at the end group. In addition, the computed electron affinities (EA) for CYTOP with different end groups are in qualitative agreement with surface charge density and charge stability obtained in experiments. Therefore, we investigate charge stability of molecule candidates with free amine functional group which can react with -COOH end group of CTX-A. EA and ionization potential (IP) obtained from DFT calculations with polarizable continuum model (PCM) are used to evaluate the electron trap energy and hole trap energy of possible candidates after dehydration condensation respectively. The above strategy is shown in Figure 2.





Fig. 1. Chemical structure of CYTOP series.

Fig. 2. Framework of simulation (PCM-DFT) guided material development.



Fig. 3. PCM-DFT EA-IP computation of 600 CTX-A/new amines with comparison to CTX-S, A, M, and CTX-A/AEM.



Fig. 4. Singly Occupied Orbital in negatively (left) and positively (right) charged monomer of CTX-A/AEM.

Firstly, EA and IP for monomer CTX-S, A, M are computed with PCM-DFT as follows. EA: 3.52 eV, 4.39 eV, and 4.60 eV, respectively. IP: 11.32 eV, 9.73 eV, and 6.60 eV, respectively. PCM-DFT EA gave good agreement with previous MD-DFT EAs: 3.42 eV, 3.94 eV, and 4.56 eV. It is also shown that EA of CTX-S is in quantitative agreement with experimentally measured value by LEIPS of 3.60 eV [1].

Within the framework of Fig. 2, 600 EA and IP for molecules of CTX-A/Amines are computed by PCM-DFT, as shown in Fig. 3. CYTOP dataset is then built based partially on these calculations.

In addition to using this dataset for machine learning, statistical analysis of the dataset itself extracts several useful information. For example, -O- is an important factor for enhancing the charge stability, while singly-occupied orbital is usually localized at the end-group for highranking molecules (Figure 4). More analysis and experiments are on-going.

This work was partially supported by JST CREST Grant Number JPMJCR15O3 and JPMJCR19Q1. The calculation is performed with SGI ICE XA ISSP system B and every calculation is held with 1 node (24 CPUs). The energy of the molecule is computed mainly by DFT at the level of CAM-B3LYP/6-31+G(d,p), with solvation effect added by PCM, by using quantum chemical simulation software GAUSSIAN [2]. In addition, different basis sets such as and 3-21G STO-3G are used for determining a good balancing point between calculation cost and accuracy. As computation cost, CYTOP for the hexamers: 2500 CPU hours per molecule; CYTOP monomer: 36 hours per molecule.

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First principles calculation of fluorocarbon layer in dry etching process and exciton self-trapping in low-dimensional perovskites

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First principles calculation of fluorocarbon layer in dry etching process–Plasma dry etching using fluorocarbon gas is the most powerful tool to achieve sub-nm high aspect ratio hole contact (HARC) in silicon oxide and nitride which is indispensable for the current semiconductor industry. One of the main obstacle for HARC process is the 'charge-up' effect where accumulated incident ions in the FC layer exerts electrostatic repulsion and bents the ion trajectories, which prominently twists the etching profile of HARC with ultrahigh aspect ratio. Although many attempts of profile simulation in mesoscopic scale for resolving 'charge-up' problem have been devoted, the atomic understanding of FC layer in terms of their bonding character, dielectric property and environment dependence (for instance, flux ratio of ion and FC neutrals and bias power) were hardly known. Here, we report our progress on ab initio simulation of FC layer on silicon under low pressure non equilibrium plasma condition obtained by densityfunctional calculations combined with the reactive force field simulation. [1]

Separation of the FC clusters For DFT simulation from MD results Step1: MD simulation using plasma diagnostic data (neutral/ion flux, ion energy) Size: 40A × 40A # of atoms: C(964), F(1344), Si(4201)



Fig 1. A schematic of the divide-and-conquer approach for split the FC polymer into small atomic clusters.

In Figure 1, we describe a representative result of the silicon etching simulation obtained with the empirical reactive bond order (REBO) method and the divide-and-conquer approach for splitting the obtained FC polymer into atomic clusters. Because the number of atoms in typical FC polymer simulation with REBO is about 10,000~40,000 atoms including carbon, fluorine and silicon atoms, the obtained results are prohibitively large for density-functional calculations. We split the FC layer (~ 4000 atoms) into many atomic clusters with selectively cutting weak and long-range interactions (so called vdW interaction) and creates many atomic clusters combined with

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covalent interaction between 10~200 atoms. The divided clusters are calculated by density-functional theory (DFT) with ω B97XD functional. The results give accurate atomic structures and electronic structures for carbon 1s XPS and dielectric constant presented in Figure 2.



Fig 2. The simulated XPS spectra based on REBO-MD result and DFT optimized structures. The XPS spectra obtained with DFT results typically show better agreement with experimental data.

First principles calculation of exciton selftrapping in low-dimensional perovskites—

Low-dimensional perovskites are found to efficiently exhibit white broad emission with a single material in contrast to conventional threedimensional materials. While white broad emission is attributed to self-trapped exciton (STE), detailed mechanism of STE formation is rarely explored by theoretical studies. In this project, We explored bound exciton formation in two-dimensional halide perovskites for achieving highly efficient light-emitting diode (LED) and photovoltaic devices. From the systematic study of bound exciton formation by using self-interaction corrected constraint occupation Density Functional Theory (c-DFT), electronic and structural feature of bound excitons are revealed and related outcomes such as line shape of broad emission and exciton trapping rate will be evaluated for providing practical clues for experimental design of optoelectrical and photovoltaic materials.

The exciton self-trapping calculations were performed for the $Cs_3Bi_2I_9$ which is representative 0D perovskite used for photosensors and light-emitting diodes [2].



Fig 2. The simulated trapped excitons and their relative stabilities.

In results, we found three different self-trapped excitons in Cs₃Bi₂I₉. While the localized exciton is the ground state of the trapped-exciton state, one-dimensional and two-dimensional exciton states also exist which should be involved in broad emission and photovoltaic behavior of Cs₃Bi₂I₉.

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Improvement and application of all-electron mixed basis program

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Using the all-electron mixed basis program TOMBO, we performed first-principles molecular dynamics simulations of Mo and Au atom vertical bombardments at the center of a six-membered ring of C_{60} to create endohedral fullerenes. With the kinetic energies of 40 eV and 80 eV, Mo and Au atoms successfully penetrated inside the C_{60} , and the endohedral fullerenes, M@C₆₀ (M=Mo, Au), were created. We confirmed that the created M@C₆₀ continues to exist stably without breaking. This result is currently being submitted.

On the other hand, in the Green's function method in many-body perturbation theory, all the effects of the Coulomb interaction between electrons are incorporated in the self-energy function. However, since the self-energy function depends on the energy, the quasiparticle wave functions, i.e., the basis functions, which diagonalize the Green's function, are not only effect of renormalization of the energy dependence of the self-energy has not been discussed much so far in the one-shot G_0W_0 approximation. Therefore, we discussed the effect of renormalization in the one-shot G_0W_0 approximation and the effect of linearization in the scGW approach (the scLGW method [1]) by using TOMBO, and found out that all these effects are to decrease the energy gap. According to our results, the scLGW method can improve the one-shot G_0W_0 results in many cases. Thus, linearization is very powerful and effective. The result will be submitted soon.

Lastly, we have applied our first-principle phase field method to Ti64 ternary alloys [2] and to Ni-Ti binary alloys [3], and succeeded in reproducing the experimental microstructure without introducing any empirical thermodynamic parameter. In the simulation of Ni-Ti alloys, we noticed an important tolerance behavior that the result does not depend on the assumed atomic alignment at all and found that the result does not change even if we used NiTi₃ instead of NiTi₂.

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Study of Efficient Training Data Generation Method for Constructing Artificial Neural Network Force Field I-II

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Interatomic potential using an artificial neural network (ANN potential) can not only provide high accuracy results by training firstprinciples molecular dynamics (FPMD) data but also have low computational cost, which allows for large scale and long-term MD simulations. In this study, we aim to finding how to efficiently generate the training data required to construct the ANN potential. Active Learning (AL) is one of the promising generation methods that we are paying attention to. In AL, firstly, several ANN potentials with different initial values of weight parameters are constructed by training with the same data. Since an output uncertainty (e.g. standard deviation) can be defined using the ANN potentials, the magnitude of the uncertainty provides us an indicator to identify the candidate data to be trained. However, there is still room for consideration of specific indicators. The indicators currently employed for AL are the uncertainty of potential energy and atomic force. This reflects the current training method, standard where ANN potentials learn the potential energy and force obtained from the FPMD.

Considering that accurate pressure is also

important for MD simulations (e.g. simulations under NPT ensemble), we believe that training of pressure is indispensable and uncertainty of pressure should also be added to the indicator. We recently revealed that the pressure training is necessary to accurately calculate thermal conductivity, which is a fundamental physical quantity that characterize the thermal properties of materials [1]. There is a well-known method using long-term equilibrium MD data and Green-Kubo formula, where the thermal conductivity is calculated from the time correlation function of heat flux. It was also found that a clear relation holds between the heat flux formula and the pressure one derived from the virial theorem [1]. Since the current standard training method mentioned above does guarantee pressure accuracy, ANN not potentials with inadequate pressure accuracy are likely to show poor thermal conductivity. This result further emphasizes the importance of pressure training. We are exploring better indicators of AL including pressure uncertainty.

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Refined Metadynamics and Elucidation of Reaction Mechanism of Polyalcohol Dehydration in Hot Acidic Water

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Subcritical water has high solubility of organic molecules and is expected to be applied as a reaction medium. Cyclization dehydration reaction of polyalcohol in hot water has been proven to be efficient method for utilization of biomass materials [1]. In this study we proposed a new method of refinement (improved metadynamics method: Refined MTD), and applied it to cyclization dehydration of 2,5-Hexanediol (HDO) [2].

Fig. 1 Reaction for 2,5-Hexanediol (HDO)

In the metadynamics method, by adding the bias potential according to the frequency of appearance on the free energy surface characterized by the reaction coordinates (CV), a chemical reaction that does not occur on the time scale of the usual molecular dynamics method is induced. From the deposited bias potential W(q), the free energy surface A(q) = -W(q) + const is obtained, and the minimum and saddle points of A(q) are obtained.

The activation barrier ΔA can be obtained

from the difference (the point where the reaction occurred). However, the height of the bias potential represented by the Gaussian function and the frequency of addition are finite, and an error of several k_BT occurs in the free energy surface. When comparing reactions with different environmental conditions such as pressure and temperature, or when there are competitive reactions, it is necessary to estimate the accurate free energy surface with an error of several k_BT or less. In this study, we used Refined MTD, which is a method to further refine the free energy surface obtained by MTD calculation. First, the W(q) deposited from the reactant to the product by metadynamics calculation is added to the potential of the system as a time-independent bias potential. Then, the canonical distribution $\rho_W(q)$ is generated by sufficiently sampling the system by molecular dynamics calculation biased by W(q). A(q) can be corrected using $\rho_W(q)$ as shown in the following equation [2].

$$\rho_{W}(q) \propto \int dr \, \mathrm{e}^{-\beta \, (\mathcal{V}(r) + W(q))} \, \delta(\mathcal{Q}(r) - q) \propto \mathrm{e}^{-\beta W(q)} \rho(q)$$
$$\therefore A(q) = -\beta^{-1} \ln \rho(q) \approx -W(q) - \beta^{-1} \ln \rho_{W}(q)$$

Sampling of the biased system must be performed sufficiently until the entire free energy surface in the CV space is sampled, and especially when the activation barrier is to be obtained, sampling not only near the minimum reaction energy point but also near the transition state is required.

Calculations were conducted using software PIMD [3] working with DFTB or VASP. The calculation system consists of 1 HDO molecule, 30 water molecules, and acidic molecules such as HCl added under the same thermodynamic conditions as in Experiment [1] (20 MPa, 523 K). CV is assumed for each product. The dihedral angle φ between the hydroxyl group and the main chain, the difference *d* in the O-C distances of leaving and bonding, and the proton coordination number *n* of the hydroxyl group were set according to the reaction path.

By using Refined MTD for the HDO system, the free energy surface of the system containing each acidic molecule was obtained. When the difference was taken before and after the correction for the minimum free energy surface of the system containing H₂CO₃, the maximum was 7.3 kcal/mol, and the average was 1.6 kcal/mol (RMSE). As a result of DFTB calculation using Refined MTD, it was confirmed that the free energy surface of the cyclization-dehydration reaction of HDO differs depending on the presence and type of acidic molecules (Fig. 3). For the higher acidic system such as a system containing H₂SO₄, metastable structure was found in the region where protons are added. In addition, the proton coordination number in the transition state was $n \approx 2.0$ in the system containing acidic molecules, whereas it was $n \approx 1.4$ in the pure water system, indicating that the reaction process differs depending on the acidity. The activation barrier ΔA (kcal/mol) were obtained as 50.6 (pure water), 39.6 (H₂CO₃), 35.4 (HCl), 26.3 (H₂SO₄).



Fig. 2 Free energy surfaces obtained for HDO dehydration reaction obtained by Refined MTD.(a) HCl aqueous solution, (b) pure water.

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Ultimate impedance of coherent heat conduction in van der Waals graphene-MoS₂ heterostructures

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Toward the ultimate goal of designing small thermal-conductivity materials at room temperature, herein we investigate the controllability of coherent phonon transport in van der Waals graphene-MoS₂ heterostructures with different stacking orders using nonequilibrium molecular dynamics simulations. Using Bayesian optimization-based materials informatics, the optimal stacking order of graphene and MoS₂ is efficiently identified from tens of thousands of candidates with varying degrees of phonon localization. The obtained thermal conductivity of the optimized heterostructure (0.026 W/m-K) is significantly lower than that of its building blocks, pristine MoS₂ and graphene.

There are growing efforts to control thermal transport via coherent phonons in the one-dimensional superlattice. However, in general, the difference in the intrinsic lattice structures of the constituent materials inevitably generate interface disorder during the fabrication process, greatly limiting direct experimental observation of the coherent phonon transport. The flexible integration and atomistic interlayer smoothness of van der Waals (vdW) heterostructure provide an ideal platform for the coherent phonon transport manipulation. Thus, in the current work, using the non-equilibrium molecular dynamics simulations, we investigate the coherent phonon transport in vdW graphene-MoS2 heterostructure with different stacking order.



Figure. Schematics of the machine-learning method to combine the molecular dynamics (MD) and Bayesian optimization.

The histogram of the phonon transmissions in different disordered structure exhibits a log-normal distribution, which reveals the localization of the coherent phonons. Furthermore, the optimal stacking order of the graphene and MoS2 is efficiently identified from tens of thousands of candidates by machine learning. The significantly suppressed of the phonon transmission in the low frequency (<5THz) phonons of the optimized structure lead to a significant reduction of the thermal conductance compared with the pristine graphite. Finally, the effects of the defect effect on the thermal conductivity of graphite and optimized structures are also discussed. Our work provides a deep insight into the coherent phonons transport behavior in the atomistically smooth vdW structure, which is beneficial for further development of phononics.

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Development and applications of first principles method for light-matter interactions beyond the dipole approximation

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Near field refers to a non-propagating light field. The interaction between the near-field and molecules can overcome the diffraction limit and can induce non-dipolar excitations, offering a unique platform for nanoscale spectroscopy and microscopy [1], as well as photochemistry [2]. Due to the localization of the near-field, theoretical framework beyond the dipole approximation is required. Thus, we have developed a first principles method based on the multipolar Hamiltonian, in which, the interaction is described by coupling the electric field and the molecular polarization field integrating over the space. The method has been used to study near-field electronic excitations [3] and vibrational excitations, i.e., the near-field IR combined with electrodynamics computations [4].

In this fiscal year, we have developed a method for near-field Raman [5]. The theoretical framework we established for near-field Raman is as follows. First, the multipolar Hamiltonian is implemented into a real-time timedependent density functional code, namely, Octopus 9.2 [6] and calculate the near-field excited electron dynamics to obtain the induced dipole moment of a molecule in the time domain, which is later Fourier transformed into the frequency domain. The induced dipole moments are calculated 6N times (N is the number of atom in a molecule) for distorted geometries where one of the x, y, and z coordinates of an atom is shifted slightly in either the positive and negative direction to obtain a derivative of the induced dipole moment with respect to the atomic Cartesian coordinate, which is then transformed into the normal coordinate derivative using the transformation matrix obtained by a normal mode analysis, performed separately. Finally, the Raman spectrum is obtained from the square of the absolute value of the normal coordinate derivatives.

As a demonstration, on- and off-resonance near-field Raman of benzene is studied. We showed that the obtained Raman spectra are well understood by considering both the spatial structure of the near field and the molecular vibration in the off-resonance condition. For the on-resonance condition, the Raman spectra are governed by the transition moment, in addition to the selection rule of offresonance Raman. Interestingly, on-resonance Raman can be activated even when the near field forbids the $\pi - \pi^*$ transition at equilibrium geometry due to vibronic couplings originating from structural distortions.

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Theoretical analysis of influences of phonons on magnetism

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It is extremely challenging to describe magnetism at finite temperatures by firstprinciples electron theory. There are at least two main contributions to excitation: magnons and phonons. Even though there are attempts to include finite tempearture effects through exchange-coupling constants J_{ij} in the Heisenberg model by first-principles calculations, dependences of phonons on magnetic states has been neglected. Such an approach is also computationally challenging, because first-principles phonon calculations and Monte Carlo simulations are required for precise evaluations in addition to the standard total-energy minimization.

In this project, we propose a new firstprinciples scheme to evaluate the Curie temperature taking the magnetism-dependent phonons and their feedback effect to magnetism into account, and apply the scheme to bcc Fe [1] and some B2 and L1₀ compounds [2]as examples. In our framework, we minimize the total free energy in the explicit consideration of temperature effects, because the magnetic and vibrational free energies correlate with each other. Both the influences of magnetism on phonons and the feedback effect from phonons to magnetism are taken into account using phonon calculations by ALAM-The feedback effect reduced the ODE [3]. Curie temperature of bcc Fe significantly as shown in Fig. 1, where the magnetic energy is calculated by the ALPS code [4] with J_{ij} obtained by Akai-KKR [5].

In addition, first-principles computations are performed for magnetic materials including permanent magnets [6] and multiferroic materials [7]. We also improved formulations to calculate J_{ij} in OpenMX [8] by introducing the orthogonalization of localized basis sets.



Figure 1: The equilibrium magnetic energy (solid lines) and the magnetic specific heat (dashed lines) of bcc Fe as a function of temperature obtained by the minimization of the total free energy and by the minimization of the magnetic free energy [1].

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Microscopic simulation for ultrafast electronic and atomic response driven by strong and short laser pulses

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The development of coherent light sources allows us to realize various nonequilibrium material dynamics. Such processes are initiated by electron excitation then undergoing atomic motion via the electron-phonon interaction. A theoretical description of the nonequilibrium dynamics for the whole system composed of electrons and the nucleus is one of the most challenging systems. We have investigated nonequilibrium systems along with two directions, a) electron-phonon interaction computation to understand the frequencydomain angle-resolved photoemission spectroscopy (FDARPES) under collaboration with experimentalists [1], and b) development of a theoretical framework of semiclassical modeling of the optical response for simple metals [2].

In Ta2NiSe5 (TNS), it is reported that the coexistence of insulator and semimetallic electronic structures in time-resolved angleresolved photoemission spectroscopy (TrARPES) [3] and Coherent phonon generation in time-resolved reflectivity measurement [4]. The semimetallic phase of TNS is realized above 328 K accompanied by structural phase transition. Our coauthors conduct experiments to discover TrARPES with fine enough temporal resolution to disentangle different frequencies of coherent phonon modes. By taking the Fourier transform of the TrARPES, we obtain FDARPES in which ARPES with a phonon electronic frequency shows structure modulation by the corresponding phonon. The metallic semiconducting and electronic structures coincide with 2 and 3 THz coherent phonons. To assign phonon modes to the frequencies, we perform density-functional perturbation theory (DFPT) calculation of the FDARPES. We reveal 2 THz phonon modes are a motion connecting the two, semiconducting and semimetallic, structures.

A mean-field type quantum theory hardly captures the colliding process leading to relaxation or equilibrium among the electron subsystem. A numerically efficient scheme to

describe electron scattering is a semiclassical equation of motion that the collision integral added to the Vlasov equation. The Vlasov equation can be constructed from a quantum mechanical equation of motion, such as timedependent density-functional theory (TDDFT), by the Wigner transformation [5]. The Vlasov equation is solved by the pseudo-particle method that the distribution function is described by a sum of classical particles having finite spatial and momentum width [5]. We develop a theoretical framework for a spatially periodic system based on the Vlasov equation with the pseudo-particle method and density-dependent functional taken from TDDFT, called Vlasov-LDA hereafter. A striking advantage of Vlasov-LDA is the much lighter computational cost compared to typical time-dependent quantum mechanical simulations. We apply Vlasov-LDA to crystalline Al and compare its results with TDDFT. Optical conductivity from Vlasov-LDA perfectly coincides with TDDFT, while computational is typically 50 times lighter than

TDDFT cost. We also perform systematic benchmarking for nonlinear optical responses compared with TDDFT. We are preparing the manuscript for this work.

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Ab initio Molecular Dynamics Study on Static Structure of Glass Materials

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We have studied condensed matter systems, which are crystal, liquid, and amorphous systems. In this project, we aimed to clarify the static structure of glass V_2O_5 under pressure using our original QXMD code, which is applicable to perform *ab initio* molecular dynamics (AIMD) and empirical molecular dynamics (MD) simulations [1].

In order to investigate the static and dynamic properties of disordered materials, we employed one of the machine learning method, the artificial neural network (ANN) technic [2]. This method enables us to perform MD simulations of the large scaled system with reasonably low calculation cost. However, the best method to construct the interatomic potential of high transferability for any calculation conditions is not established. That is, our priority mission is the establishment of construction of the ANN potential applicable for the wide range conditions based on the result of AIMD simulations. For this purpose, we try to construct new ANN potentials for different targets, liquid and crystal Na, and aand β -phases of Ag₂Se crystals. These targets

are suitable for such test because Na has only one valence electron and Ag₂Se has many electrons. The calculation cost of the former is low, therefore, it is easy to compare the result by ANN-MD with that by AIMD. While, the cost of the latter is high, hence, the efficacy of acceleration using ANN potential is checked.

In this study, it was found that an optimizing equation including the force and virial terms, which were often ignored, was needed for the phase transition [3,4].

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Ab initio calculation for thermodynamic phase diagram

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For the purpose of *ab initio* quantitative evaluation of thermodynamic physical properties of materials, thermodynamic phase diagrams based on first-principles calculations are calculated. Focusing on metal hydrides, which are important as hydrogen storage alloys, we will evaluate their phase diagram and pressurecomposition-temperature curves. The free energy model under the regular solid solution approximation is determined from the firstprinciples calculation, and the phase diagram of this model is obtained with the CALPHAD method.

As the benchmark, the phase diagram of the metal hydride Ti-H sysmtem is calculated. The calculation flow is as follows: The starting point is the Gibbs free energy cal-The free energy consists of three culation. terms, the enthalpy term, the phonon term, and the solid-solution entropy term, all of which are evaluated by first-principles calculation. The enthalpy term is evaluated from the density-functional calculation for pure Ti and TiH systems (using xTAPP [1] and VASP [2]). The phonon term is also evaluated from the first-principles phonon calculation for Ti and TiH (using PHONOPY [3]). The solid-solution entropy term is evaluated using cluster-expansion and cluster-variational methods [4]. For these calculations, a large amount of structural data created by inserting hydrogen or voids into the tetrahedralinterstitial site is generated, where we consider a metal having a face-centered cubic (fcc)

structure and the resulting structural data series is written as fcc-tetrahedron series. This structural series is generated using the software ATAT [5]. In this fcc-tetrahedron series, the total number of generated structural samples was 132. In addition to the fcc-tetrahedron series, fcc-octahedron series, body-centered-cubic (bcc)-tetrahedron series, bcc-octahedron series, hexagonal close-packed (hcp)-tetrahedral series, hcp-octahedron series, etc. are generated. First-principles calculations are performed for each structural series to obtain structural and energy data.

Next, we determine parameters of the effective model based on the regular solution approximation by fitting to the above obtained first-principles calculation data. In the first step, we use the cluster expansion method for the *ab initio* data to obtain expansion coefficients of cluster model, and then, to evaluate temperature dependence of the cluster model, cluster-variational method is performed for the cluster-expansion function of each structural series, which give the first-principles free energy surface. Finally, for the resulting free energy surface, the parameters of the regular solution model are obtained by fitting:

$$\mathcal{F}(x,T) = xG_{\mathrm{TiH}}(T) + (1-x)G_{\mathrm{Ti}}(T) + RT[x\ln x + (1-x)\ln(1-x)] + x(1-x)[(1-x) - x]^{0}(L_{0} + L'_{0}T) + x(1-x)[(1-x) - x]^{1}(L_{1} + L'_{1}T) + x(1-x)[(1-x) - x]^{2}(L_{2} + L'_{2}T),$$
(1)

where $G_{\text{TiH}}(T)$ and $G_{\text{Ti}}(T)$ are the free energies of TiH and Ti, respectively, and x or 1-xis fraction of vacancy or hydrogen in Ti. The free energy is modeled with the following function as

$$G_{\alpha}(T) = a_{\alpha} + b_{\alpha}T + c_{\alpha}T\ln T + d_{\alpha}T^{2} + e_{\alpha}T^{-1}, \quad (2)$$

where the subscript α specifies TiH or Ti, and $a_{\alpha}, b_{\alpha}, c_{\alpha}, d_{\alpha}, e_{\alpha}$ in Eq. (2) are determined by fitting to the *ab initio* phonon free energy data. The third term in Eq. (1) is the mixing entropy term in the binary alloy system. The remaining terms in Eq. (1) are the interaction term and $L_0, L'_0, L_1, L'_1, L_2$, and L'_2 parameters are determined by fitting to the *ab initio* cluster variational data. Table 1 lists our determined parameters in Eqs. (1) and (2).

Table 1: Determined parameters in Eqs. (1) and (2).

	bcc-tetra		fcc-tetra		hep	hcp-tetra	
	Ti	TiH_6	Ti	TiH_2	Ti_2	$\mathrm{Ti}_{2}\mathrm{H}_{4}$	
a	6413.24	60753.56	1978.90	-27924.55	-1944.38	-15163.09	
b	71.017	7.801	93.111	-23.512	87.479	-18.794	
c	-14.262	-1.308	-18.495	4.362	-16.921	3.644	
d	-0.005	-0.009	-0.007	-0.024	-0.009	-0.024	
e	0.001	0.000	0.001	0.000	0.001	0.000	
L_0	-105733.39		13618.96		43	4345.96	
L_0	-2.3605		-0.267		-1.7241		
L_1	-24563.95		-9933.31		-11022.69		
L_1	, -1.0794		0.1296		-1.5862		
L_2	-99788.53		-5491.55		-12354.91		
L_2	0.0787		-0.4376		2.	2.8456	

From the free energy curve of the regular solution model [Eq. (1)] obtained above, a phase diagram based on the CALPHAD method was calculated by using the software PANDAT [6]. Figure 1 (a) shows our calculated phase diagram of Ti-H sysmtem. The panel (b) also shows experimental phase diagram [7]. From the comparison between the two, we found that our result reasonably reproduces the experimental result. A Python Script was developed to generate PANDAT inputs from the results of the present regular solution models. We found that (i) the entropy term can be sensitive to the exchange-correlation functional used in the density-functional calculation, (ii) the phonon anharmonicity can affect the quantitative accuracy of the phase diagram boundary, and (iii) the quantitative accuracy of the interaction term depends highly on details of the cluster expansion (the cluster shape and expansion order, etc.) for the structure and energy data.



Figure 1: Thermodynamic phase diagram of TiH: (a) simulation and (b) experiment [7].

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Oxygen vacancy formation in metal-doped CeO₂ nanocrystals

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We studied Cr-doped cubic $\{100\}$ -faceted CeO₂ nanocrystals (NCs) with an average size of 7.8 nm fabricated by a supercritical water reaction. A considerably large amount of Ce³⁺ ions was detected in the Cr-doped CeO₂ NCs by scanning transmission electron microscopy combined with electron energy loss spectroscopy (EELS). The Cr dopants substituted the Ce sites in the amount of approximately 3 mol%. We experimentally observed that the oxygen-storage capacity (OSC) was substantially improved by a low amount of Cr doping, which can be attributed to the low oxygen vacancy formation energy and high mobility of oxygen atoms by doping Cr in CeO₂.

Plane-wave basis density functional theory (DFT) simulations were performed by using the VASP code to understand the effects of the Cr dopant on oxygen vacancy (Vo) formation. A Ce atom was substituted by one Cr atom in the 96-atom $2 \times 2 \times 2$ supercell of CeO_2 ($Ce_{32}O_{64}$) with a Monkhorst–Pack kpoint mesh of $4 \times 4 \times 4$, which is equivalent to the loading amount of Cr at 3 mol%. The incorporation of Cr in 3+ charge state can be compensated by the formation of an extra Vo (per two Cr^{3+} ions) or a Vo and a Ce^{3+} ion while the oxidation of Cr-doped CeO_2 NCs should create Cr^{4+} ions. Two Ce^{3+} ions were located in the next nearest neighbor positions with respect to the Vo, consistent with previous studies of CeO_2 with DFT+U. The Bader charge of the Ce^{3+} and Ce^{4+} ions was set +2.11|e| and +2.44|e|, respectively. The Vo formation energy (E(Vo)) in the Cr-doped CeO_2 was calculated as 0.99 eV, which was substantially decreased from 2.00 eV in the non-doped case. The high OSC performance can be attributed to the contribution of the valence change of Cr to E(Vo), and the structural effect of Cr doping on E(Vo). Only 3 mol% doping improved the OSC, suggesting that Cr doping affects the structure of CeO₂ significantly. The results of layer-by-layer EELS analysis indicated a significant increase in the amount of Ce³⁺ by Cr doping particularly in the internal atomic layers, which is more than the mere compensation of Cr³⁺ with Vos. The low E(Vo) of Cr-doped CeO₂ NCs can lead to a significant increase of Ce³⁺ ions even with a low amount of Cr doping, as observed in the experiments.

In summary, DFT calculations demonstrated that the Cr dopant reduces the E(Vo), resulting in the increase of the mobility of oxygen atoms in the nano-sized CeO₂. The high concentration of Vos as well as the high oxygen diffusivity improve the OSC performance of Cr-doped CeO₂ NCs, compared with the nondoped CeO₂ NCs. These effects provides a fundamental understanding of the role of dopants in formation and distribution of Vos in the metal-doped CeO₂ NCs [1].

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Oxygen vacancy formation in metal-doped CeO₂ nanocrystals

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van der Waals density functional study of Cu phthalocyanine adsorbed on the Au(110) surface

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The lowest molecular orbital (LUMO) plays an essential role in the electronic transport across a metal-organic interface. Since surface adsorption distorts the molecular structure, influencing the properties of LUMO, it is of particular importance to understand the interface structure microscopically. Here we investigate the geometric and electronic structures at a metal-organic interface of Cu phthalocyanine (CuPc) on the Au(110) surface [1]. The (1!2)missing-row reconstructed surface of Au(110) is modeled by removing Au atomic rows from a periodically repeated 6!4 unit cell of the Au(110) slab composed of six atomic layers. A CuPc molecule is adsorbed on a missing row, in which *n* Au atoms with n = 0, 2, 4, and 6 are added below CuPc to reproduce the finding of



Fig. 1: Schematic views of CuPc on the m row reconstructed Au(110) surface with The blue (red) balloons show the isosurfa absolute square of $e_{g(1)} [e_{g(2)}]$. STM measurements [1]. The van der Waals (vdW) interaction between CuPc and Au(110) is taken account of by the vdW-DF method [2].

Our calculated results indicate that CuPc prefers to adsorb on the center of the Au adatoms with an in-plane rotation as shown in Fig. 1, irrespective of the number of adatoms. The projected density of states (PDOS) onto the doubly degenerate LUMO, labeled as $e_{g(1)}$ and $e_{g(2)}$, of CuPc is plotted as a function of energy



. 2: Density of states projected onto the $e_{g(1)}$ ₂₎] orbitals of CuPc.

in Fig. 2, where the center of the peaks for the LUMO-derived states is lowered roughly monotonically as n is increased, in good agreement with the results of STS measurements. The lowering of the peaks is qualitatively consistent with lowering of the effective potential of the bare surfaces as a function of n. The splitting of the peaks suggests that the hybridization between CuPc LUMO and surface

states is enhanced for large n. Our results reveal that the LUMO of CuPc is sensitive to the detailed structures of the reconstructed Au(110) surfaces.

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First-principles study of molecule/metal interfaces Ikutaro Hamada

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Carbon-based nanomaterials, such as graphene and nanographene have attracted enormous attention, owing to their fascinating electronic, optical, and magnetic properties. For precise fabrication of nanographene, on-surface synthesis has been developed, in which precursor molecules are thermally induced to react on a surface, and the technique has been proven to be powerful to fabricate graphene based nanostructures. In this work, we propose an alternative method, in which a tip of scanning tunneling microscopy/non-contact-atomic-force microscopy is utilized as a manipulable metal catalyst, which activates cyclodehydrogenation of hydrocarbons [1].

we used diazuleno[1,2-*c*:2',1'g]phenanthrene (DAPh), as well as 10,10'dibromo-9,9'-bianthracene (DBBA) adsorbed on a Cu(100) surface, to demonstrate the tipinduced cyclodehydrogenation reaction. To investigate the mechanism of the tip-induced reaction, we performed atomistic simulations based on density functional theory (DFT) with the van der Waals (vdW) density functional (vdW-DF) [2] as implemented in our in-house DFT code STATE [3-6], to describe the interaction between organic molecule and metal accurately.

Experimentally, the DAPh molecule is thermally reacted into a cyclodehydrogenated diazulenopyrene (DAPy), but the reaction intermediate has not been determined. We performed extensive DFT calculations and successfully identified the intermediate as hydro-diazulenopyrenyl (hDAPyr). By using a Cu-terminal tip, induced the we cyclodehydrogenation of hDAPyr to form DAPyr. To understand the reaction mechanism, we used a 10-atom pyramidal model Cu tip over hDAPyr and could reproduce the tip-induced cyclodehydrogenation reaction. Furthermore, we clarified the detailed potential energy surface and by the electronic structure analysis, we revealed the electronic origin of the tip-induced catalytic dehydrogenation reaction.

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Theoretical study of oxygen-redox chemistry in spinel oxides

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Oxygen-redox chemistry has recently paved a path to develop large-capacity cathode materials for rechargeable batteries. Despite vast efforts on exploring oxygen-redox cathodes, few studies have been reported for the oxygen-redox reaction in spinel oxides. In this work, we theoretically uncover the oxygenredox behavior in the stable spinel framework using the density functional theory calculations.

We performed all calculations using Vienna Ab-initio Simulation Package. The projectoraugmented wave method with a plane-wave basis set was used. We applied the U values of 4.84 eV and 3.90 eV for Mn in the spinel and layered structures, respectively. The HSE06 hybrid functional was employed for calculating electronic structures. The crystal orbital overlap population was computed with the Lobster program and molecular orbitals were built with maximally localized Wannier functions using Wannier90 code.

The presence of ionic Mg²⁺ in spinel LiMg_{0.5}Mn_{1.5}O₄ brings labile O 2p states for oxygen-redox activity. However, in contrast with the dominant Mn-O interactions that could stabilize oxidized oxide ions in a typical lithium-rich layered oxide Li₂MnO₃, the spinel structure is dominated by O-O interactions near the Fermi level, which are less able to stabilize holes. Consequently, the spinel oxide is predicted to undergo structural degradation more easily during the oxygen-redox reactions.

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Fig. 1 (a) Spinel LiMg_{0.5}Mn_{1.5}O₄. Electronic structures of (b) spinel and (c) layered oxides.

Order-disorder transition in ultrahigh-pressure phase of the Na-Mg-F system

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MgSiO₃ bridgmanite with the orthorhombic perovskite structure is a major constituent of the lower mantle of the Earth. It takes the postperovskite (PPV) structure near the core-mantle boundary pressure (~125 GPa). The PPV phase is the final form of MgSiO₃ in the Earth. However, at much higher pressures in "super-Earths" which are exoplanets expected to be terrestrial with masses much larger than the Earth, MgSiO₃ PPV should undergo "post-PPV" transitions. So far, first principles studies have predicted the three-stage dissociation of MgSiO₃ PPV: MgSiO₃ PPV \rightarrow I-42d-type Mg2SiO₄ + P2₁/c-type MgSi₂O₅ \rightarrow Mg₂SiO₄ + Fe₂P-type SiO₂ \rightarrow CsCl-type MgO + SiO₂ [1-3].

NaMg₂F₅ is a low-pressure analog of MgSi₂O₅. Theoretically NaMgF₃ PPV was predicted to dissociate into NaF and NaMg₂F₅ [4] and this prediction has been confirmed by a recent experiment [5]. There are two kinds of the Mg sites. One of them is very similar to the Na site; both Na and Mg atoms are surrounded by 9 F atoms which form tricapped triangular prisms. This similarity leads us to an idea of orderdisorder transition at high temperature over the cation sublattice of Na and Mg atoms. A similar order-disorder transition has been predicted in I-42d-type Mg₂GeO₄ [6], a low-pressure analog of Mg₂SiO₄.

In this study, we investigated the orderdisorder transition in NaMg₂F₅ by first principles [7]. To deal with the order-disorder transition, we prepared as many configurations as possible in a supercell of 64 atoms and calculated a partition function. Then, the orderdisorder transition temperature (T_c) can be obtained by locating the peak temperature of heat capacity calculated from the partition function. Our calculations showed that Tc is 1500~2000 K over 20~100 GPa. The orderdisorder transition was not taken into account in the experiment [5]. We expect the disordered phase may show a better explanation of the XRD pattern in the experiment.

Since $NaMg_2F_5$ is the low-pressure analog of $MgSi_2O_5$, the order-disorder transition predicted in this study is expected to occur also in $MgSi_2O_5$ and will play an important role in modeling interiors of super-Earths.

The first principles calculations in this study were performed using the Quantum-Espresso package on the supercomputer (system B) at the Institute for Solid State Physics.

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First principles study of effect of Al impurity on the post-postperovskite transitions

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MgSiO₃ bridgmanite with the orthorhombic perovskite structure is a major constituent of the lower mantle of the Earth. It takes the postperovskite (PPV) structure near the core-mantle boundary pressure (~125 GPa). The PPV phase is the final form of MgSiO₃ in the Earth. However, at much higher pressures in "super-Earths" which are exoplanets expected to be terrestrial with masses much larger than the Earth, MgSiO₃ PPV should undergo "post-PPV" transitions. So far, first principles studies have predicted the three-stage dissociation of MgSiO₃ PPV: MgSiO₃ PPV \rightarrow I-42d-type Mg₂SiO₄ + P2₁/c-type MgSi₂O₅ \rightarrow Mg₂SiO₄ + Fe₂P-type SiO₂ \rightarrow CsCl-type MgO + SiO₂ [1-3].

In real super-Earths, impurities may play an important role in the above post-PPV transitions. In this study, we investigated the effect of Al atoms, one of major candidates of impurities, on the post-PPV transitions. To do it, we prepared supercells of $(Mg_{1-x}Al_x)(Si_{1-x}Al_x)O_3$, $(Mg_{2-x}Al_x)(Si_{1-x}Al_x)O_4$, and $(Mg_{1-x}Al_x)(Si_{2-x}Al_x)O_5$, for x=0.25, 0.125, and 0.0625. We found that Al atoms prefer to exist in Mg_2SiO_4 after the fist post-PPV dissociation. The presence of Al atoms decreases the transition pressure of the first dissociation. Considering effects of configuration entropy at high temperature, Al atoms start to exist also in MgSi₂O₅.

Recently, we predicted a new temperatureinduced order-disorder transition in I-42d-type Mg₂GeO₄, a low-pressure analog of Mg₂SiO₄ [4]. The knowledge obtained in this study will be utilized for the study in the post-PPV transition at high temperature, which is expected to occur in super-Earths.

The first principles calculations in this study were performed using the Quantum-Espresso package on the supercomputer (system B) at the Institute for Solid State Physics.

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First-principles molecular dynamics study of water/TiO₂ interfaces using hybrid functionals

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Density functional theory-based molecular dynamics simulations are increasingly being used for simulating aqueous interfaces. Nonetheless, the choice of the appropriate density functional, critically affecting the outcome of the simulation, has remained arbitrary. Here, we assess the performance of various exchange-correlation (XC) functionals, based on the metrics relevant to sum-frequency generation spectroscopy. The structure and dynamics of water at the water-air interface are governed by heterogeneous intermolecular interactions, therefore providing a critical benchmark for XC functionals. We find that the revPBE and revPBE0 with the dispersion correction show excellent performance. The poor performance of the empirically optimized density-functional (M06-L) manifests the importance of satisfying exact functional condition. Understanding the performance of different XC functionals can aid resolving the controversial interpretation of the interfacial water structure and direct the design of novel, improved XC functionals better suited to describe the heterogeneous interactions in condensed phases. [1]

We employed the CP2K code [2], which is based on the mixed Gaussian and plane wave basis sets. The simulation of the water/TiO2 interface is on-going.



Fig. 1: The ability of different functionals to accurately predict water properties is directly compared. The smaller (larger) score κ corresponds to better (worse) predictive power of the functional [1].

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Ab Initio Band Structure Calculation of InAsSb Using VASP Based on Hybrid Density Functional Theory

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The terahertz band (0.1 to 10 THz) is the main radio resource for future high-speed largecapacity communications and sensing systems. Sb-based high electron mobility transistors (HEMTs) are one of the most promising devices that can operate in the terahertz band. In our previous works, we developed InSb [1, 2] and GaInSb [3] channel HEMTs. In order to achieve higher speed operation of HEMTs, it is desirable that the electron effective mass in the channel semiconductor is lighter and the electron concentration in the channel layer is higher. InAsSb is a semiconductor that satisfies the above conditions [4].

In 2019, we carried out ab initio band structure calculations of unstrained and compressively strained InSb using Vienna Ab initio Simulation Package (VASP) based on the method in the local density approximation to obtain band parameters [5]. We used the hybrid coefficient of the density functional [6]. The hybrid functional used in [6] was a modification of PBE0 (Perdew-Burke-Ernzerhof 0). The functional is constructed by the mixing of a fraction α of the Fock exchange with a fraction $1 - \alpha$ of the PBE exchange. The exchange-correlation energy E_{xc} can be expressed by the following equation:



Fig. 1: InAs content x dependence of bandgap energy E_q .

$$E_{xc} = \alpha E_x + (1 - \alpha) E_x^{PBE} + E_c^{PBE} \quad (1)$$

where E_x is the Fock exchange, E_x^{PBE} is the PBE exchange, and E_c^{PBE} is the PBE correlation [6]. We obtained the bandgap energy E_g closest to the literature value by using $\alpha = 0.21$ for InSb. In this work, we applied this method to InAsSb to explore the potential of InAsSb channel HEMTs.

First, we applied this method to InAs. We obtained the E_g closest to the literature one by using $\alpha = 0.24$. We carried out the band structure calculations of InAs_xSb_{1-x} at x = 0.25, 0.50, and 0.75. For the α values of InAsSb, we used linearly interpolated values. Figure 1 shows the InAs content x dependence of bandgap energy E_g . The x-dependence of E_g is not linear and shows a downwardly convex dependency. We obtained the electron effective masses m^* 's in the Γ valley of InAsSb from the calculated band structures. Figure 2 shows the InAs content x dependence of electron effective mass the tructure of the tr

mass in the Γ valley m^* . The x-dependence of m^* shows a tendency similar to that of E_g . The m^* values of InAs_xSb_{1-x} at x = 0.25 and 0.50 are lighter than that of InSb. It is well known that the m^* in InSb is the lightest among group III-V compound semiconductors. According to the calculations in this study, the m^* in InAsSb is lighter than that in InSb depending on the InAs content. Therefore, InAsSb channel HEMTs have a potential to be the fastest of all HEMTs using group III-V compound semiconductors.

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Fig. 2: InAs content x dependence of electron effective mass in Γ valley m^* . m_0 is electron rest mass.

DFT calculation of atomic displacement captured by energy dissipation channel of noncontact atomic force microscope

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In the last two decades the conservative and non-conservative (dissipative) force interactions between a tip and a sample in proximity have been intensively examined by non-contact atomic force microscopy (nc-AFM). In particular, the channel of nc-AFM to measure the energy dissipation through the nonconservative force interactions has been regarded to have great potential to explore nanomechanical phenomena; the dissipation channel gives the change in the amount of mechanical energy to maintain the constant oscillation amplitude of an AFM cantilever. We had experimentally found that, when the nc-AFM image showed the high resolution for the individual adatoms on a Si(111)-(7 \times 7) surface, the simultaneously obtained energy dissipation signal increased in close proximity over the hollow sites surrounded by a Si adatom and a Si rest atom with a dangling bond per each [1]. Based on the experimental results, the dynamic atomic processes responsible for the dissipation had been discussed in regard to breaking of the backbonds of the Si adatom and subsequent bond formation in an alternative atomic configuration of the Si surface atoms, including the Si atom at the apex of AFM tip. In this study, to elucidate the phenomena, the surface diffusion potentials of a Si adatom were calculated using real-space density functional theory (RSDFT) [2] when the Si tip was brought closer to the Si(111)-(7×7) surface. RSDFT is a first-principles program developed by Oshiyama and Iwata, which uses a real-space difference method and a pseudopotential method.

First, we optimized the structures of a Si(111)- (7×7) reconstructed surface consisting of 298 Si atoms and 49 H atoms and a [001] oriented Si tip by RSDFT. Then, while the tip was placed over the hollow site and brought closer from 5.0 Å to 3.0 Å, the surface diffusion potentials for a corner Si adatom were calculated from the original position of the Si adaom to the neighboring hollow site. It is known that the hollow site is a meta stable site for the adatom, and there is a diffusion barrier between the original adatom site and the hollow site. Our calculations indicated that the diffusion barrier



Fig. 1 Calculated structures of Si(111)-(7×7) reconstructed surface and [001] oriented Si tip. (a–e) For the Si on the adatom site, denoted by the red circles. (f–j) For the Si on the hollow site. The number shown with the unit of Å shows the vertical separation between the tip atom and the Si atom on the site.

height was lowered as the tip was approached. However, we did not obtain the evidence for promotion of the adatom diffusion from the adatom site to the hollow site only by bringing the tip closer. Next, we calculated the structure changes and the forces for two cases: the Si atom on the original adatom site or on the hollow site with the tip approaching over the hollow site, as shown in Fig. 1. Even for the Si atom on the most stable adatom site, when the tip approaches the hollow site, the Si atom was lifted up (Fig. 1(ae)). But the Si atom did not move to the hollow site even when the tip was closer from a height of 3.0 Å (Fig. 1(e)). For the Si atom on the hollow site, it was found that the strong force acted between the tip Si atom and the Si atom on the hollow site (Fig. 1(f-j)), as a result of bonding formation between them. The paper of this study is under preparation.

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Construction of magnetic materials database by KKR Green's function method

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We have developed an automatic exhaustive calculation tool which is based on the Korriga-Kohn-Rostoker coherent potential approximation (KKR-CPA) method. Our tool can explore the huge materials space consisting of disordered systems and construct largescale materials databases. In this year, we implemented a new feature in our tool, where electronic structures, magnetic properties, and transport properties at finite temperature can be calculated [1].

In order to calculate electronic structures at finite temperature, we incorporate the effects of local phonon excitations and spin-wave (magnon) excitations in the framework of the KKR-CPA method. In the KKR Green's function method, the single-site *t*-matrix is the sum of the coefficients of partial wave expansion at each atomic position and contains information of the single-site scattering effect. We can thus replace the multiple scattering effect by an effective medium potential using CPA. We treat local phonon excitation and magnon excitation as the configuration average with respect to the local phonon displacements and local moment disorder (LMD) states, respectively.

For CPA calculation of the local phonon excitation, the probabilities of the atomic displacements must be known. Here, we employ an alloy-analogy model. The single-site t-matrix changes responding to the atomic displacements and has to be determined selfconsistently. In this case, it is convenient to expand each single-site t-matrix centered on the displaced position for self-consistent calculation. However, later, we must re-expand the displaced single-site t-matrix to partial waves centered on the undisplaced atomic position, and transform the scattering matrix for the displaced potential into that defined with respect to the regular lattice position. This is possible because the effect of atomic displacement on the electronic structure is local. Accordingly, the backscattering term of the Green's function referring to the regular lattice is also obtained. In the present calculations, we take six directions (i.e., $\{0,0,1\}$ cubic directions) into consideration for the local phonon displacements of each atom.

To handle the magnon excitation, we use the LMD model. When the temperature increases, the spin tilts slightly away from the direction of the magnetization, and its effect propagates to surrounding spins, namely, spin-wave excitation. We consider the configuration average of the linear combination of the spin flips at every site. This model is called the LMD state. We estimate it from the decrease in the spontaneous magnetization observed in the experimental data. For Co₂MnSi, for simplicity, we assume that the decrease in the magnetization originates solely from the spin-flip in the Mn atoms, and construct the LMD model as $\text{Co}_2\text{Mn}_{1-x/2}^{\uparrow}\text{Mn}_{x/2}^{\downarrow}\text{Si}$, where Mn^{\uparrow} and Mn^{\downarrow} denote the up and down magnetic moments, respectively. For instance, the magnetization ratio between 0 K and 300 K is 0.983. We thus assume that 0.85% of the spins are reverse while the others are unchanged at 300 K $(Co_2Mn_{0.9915}^{\uparrow}Mn_{0.0085}^{\downarrow}Si \text{ random alloys}).$

Moreover, we calculate the conductivity using the Kubo-Greenwood formula including vertex correction, in which the vertex functions are expressed using the ladder-like approximation. The conductivity tensor is defined as follows:

$$\sigma_{\mu\nu} = \frac{1}{4} \lim_{\eta \to 0} [\tilde{\sigma}_{\mu\nu}(\varepsilon + i\eta, \varepsilon + i\eta) \\ + \tilde{\sigma}_{\mu\nu}(\varepsilon - i\eta, \varepsilon - i\eta) \\ - \tilde{\sigma}_{\mu\nu}(\varepsilon + i\eta, \varepsilon - i\eta) \\ - \tilde{\sigma}_{\mu\nu}(\varepsilon - i\eta, \varepsilon + i\eta)].$$
(1)

Here, ε is energy and $i\eta$ is an infinitesimal imaginary part. Note that $\sigma_{\mu\nu}$ depends on ε . Moreover, $\tilde{\sigma}$ is calculated by

$$\tilde{\sigma}_{\mu\nu}(z_1, z_2) = -\frac{\hbar}{\pi N\Omega} \text{Tr} \langle j_{\mu} G(z_1) j_{\nu} G(z_2) \rangle_{\text{CPA}},$$
(2)

where N is the number of unit cells, Ω is the unit cell volume, and $j_{\mu(\nu)}$ is the current operator. The bracket indicates the configuration average for the disordered systems by CPA.

Figure 1 shows the the temperaturedependent electrical resistivity of Co₂MnSi using the Kubo-Greenwood formula. The resistivity of Co₂MnSi derived from a local phonon is proportional to the temperature except in the low-temperature region. The resistivity originating from the magnon scattering reflects the experimentally observed magnetization curve. We determined that either local phonon displacement or LMD alone was insufficient to reproduce the experimental data. This is expected because at low temperatures, scattering due to lattice vibration and spin fluctuation is suppressed, and impurity scattering becomes dominant. It is known that there are considerable native defects in Heusler alloys, such as vacancies, interstitials, and antisite defects. For Co₂MnSi, previous works suggest the presence of antisite disorders between Co and Mn. Scattering effects from these antisite defects may be the main source of the



Figure 1: Temperature dependent electrical resistivity estimated by the Kubo-Greenwood formula.

finite resistivity at low temperature. Therefore, we attempted to calculate the resistivities considering the Mn-Co antisite disorders. Antisite effects can be easily added to the calculation in the framework of CPA. If we assume that 1.0% of the Mn-Co antisite disorders (i.e., $(Co_{0.995}, Mn_{0.005})_2(Mn_{0.990}, Co_{0.010})Si)$ is introduced, the calculated residual resistivity is 6.47 $\mu\Omega$ cm. This value is consistent with the experimental results at extremely low temperature. The pink stars in Fig. 1 represent the calculated temperature-dependent resistivity of Co₂MnSi when the Mn-Co disorders are included in addition to local phonon and magnon disorders. The result is in reasonable agreement with the experimental results. Therefore, it can be concluded that to accurately calculate the finite-temperature transport properties of Co₂MnSi, three disorders (local phonon, magnon, and Mn-Co antisite disorders) should be considered in the comprehensive procedure on the basis of CPA.

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Hybrid Ab-Initio/Machine-Learning Optimization of Nano Interfaces and Molecular Structures

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Designing and developing functional materials/molecules often require vast searching of target properties from extra-large data set, which is far out of the capability of conventional computing algorithms. In recent years, the Deep-Learning (DL)-based molecular design methods have been extensively studied. Recently, we have reported [1] a machine learning method for predicting molecular properties by mapping a graph representation of a molecule to a latent variable space and by linking the variable to physical property of the molecule. Representing molecules in the latent space enables an efficient property search within existing data, because the DL model transforms the discrete representation of a molecular graph into a continuous variable space suitable for various numerical algorithms.

In the present study, we further improve the output rate of valid SMILES of decoder by introducing a discriminator attached to the VAE Adopting a molecular-mechanics stream. method to calculate 3D structure from SMILES, we can optimize physical properties of the molecule by other simulation methods such as density-functional-theory calculations even when there is not enough data set. The range of physical property space covered by the SMILES representation is thereby expanded and the datadriven optimization using Kernel Ridge Regression method can be performed within the search space. We have demonstrated the effectiveness of this method for optimizing a molecular HOMO-LUMO gap as an example.

Another effort is taken to perform efficient search for insertion/reaction path of an molecules on the surface of a functional materials. We computationally investigate an insertion process of water into the methylammonium lead halide perovskite (MAPbI₃). The rapid decomposition of MAPbI₃

reaction with water has been recognized to be a major obstacle to its solar-cell applications. To overcome this drawback process, it is important to identify the initial stage of water insertion into the MAPbI₃. The first-principles calculation based on the density-functional theory is performed to investigate the water insertion process on outer surface layer of MAPbI3 slab model. Using the Nudged Elastic Band method, we find that the initial insertion process follows the three steps: approaching, re-orienting and finally sinking into the perovskite layer. This process requires approximately 0.60 eV to overcome an energy barrier, which agrees with an in-situ X-ray diffraction (XRD) measurement of the reaction threshold of water molecules with the MAPbI₃ crystal at room temperature [2]. These computations have been done in part by using the Super-computing System at SCC-ISSP



Fig. 1 Insertion path of water molecules in the MAPbI₃ surfaces and barrier energy variation along the path.

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Investigation on the electronic structure of photo-catalytic double-perovskite

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In recent experiments, a significant band gap widening was observed when Sb was substituted for Bi in the double-perovskite Ba_2PrBiO_6 . In this work, we study a series of double-perovskites, $Ba_2Bi^{III}Bi^VO_6$, Ba_2PrBiO_6 , and Ba_2PrSbO_6 using the firstprinciples density functional theory with the Heyd-Scuseria-Ernzerhof hybrid functional to investigate the substitution effect on the structural and electronic properties [1].

We use the density functional theory (DFT) as implemented in the Vienna ab-initio Simulation Package (VASP) and the projector augmented wave (PAW) potentials to study the structural and electronic properties of the double perovskite. We use the Heyd-Scuseria-Ernzerhof hybrid functional (HSE06) to account for the strong correlation effects of the system. We use an energy cutoff of 500 eV for plane wave basis set together with a $6 \times 6 \times 6$ **k**-point grid. The rather high energy cutoff and dense **k**-point grid are necessary to predict correctly the crystal structures in the HSE06 computations. Equilibrium crystal structures were achieved so that the maximum force component was smaller than 1 meV/Å³, and the maximum stress component smaller than 1 $meV/Å^3$.

In a monoclinic system, the shape of the Brillouin zone depends non-trivially on the lattice vectors. In fact, there are five possible shapes of Brillouin zones for the monoclinic crystal structure depending on the choice of lattice vectors. Where we choose the C2/m which corresponds to the $MCLC_1$ lattice. To generate the set of **k**-points along the edges of the Brillouin zone, we use the code **pymat-gen**. We show the obtained band structure in the Figure 1.



Figure 1: Band structure and density of states curve of $Ba_2Bi^{III}Bi^VO_6$. Fermi level is at 0 eV.

We find that the Bi^{III} 6s states at the top of valence band of $\text{Ba}_2\text{Bi}^{\text{III}}\text{Bi}^{\text{V}}\text{O}_6$ vanish on the Pr substitution for Bi at B' ^{III}-site. When Sb is substituted for Bi at B'' ^V-site, the Bi^V 6s states at the bottom of the conduction band vanish causing additional widening of the band gap.

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Studies on electronic structures and optical properties in ternary oxide crystals

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Lithium niobate ternary compound is known to exhibit several interesting properties such as superconducting behavior under delithiated phase. Deeper understandings for this compound are important from both technological and basic viewpoints [1]. In this research, we intend to compare calculation results on the complex dielectric function and experimental data.

We used the Quantum-ESPRESSO package to optimize the crystal structure and perform the band structure calculations. In this work, we used a set of the optimized norm-conserving pseudopotentials. The corresponding activity diagram is shown at the right hand side. We confirmed that evaluated bandgap energy (BGE in the figure) is similar to that evaluated by Ylvisaker *et al*[1].

We then moved into study on optical properties. For the optical spectra calculations such as dielectric functions, we used Respack ab-initio package [2]. Neglecting contributions from the optical anomalies, overall $\varepsilon_1(\omega)$ in the calculated spectrum is a monotonically decreasing function with upward convex in the 1.5-4-eV range (not shown in a figure). This feature is in good agreement with the experiment [3].



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Vacancy cluster stabilization by impurities and their migration property in tungsten

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Introduction

Tungsten (W) and its alloys are plausible candidates for plasma facing materials (PFMs) used in fusion reactors because of their excellent properties, e.g. high melting point, low hydrogen (H) solubility, and toughness for irradiation. However, a large amount of H and H isotopes are retained in vacancy (V) and vacancy type lattice defects in W specimen nucleated under the irradiation circumstance. In particular, tritium (T) retention in the PFMs is a serious problem for safety operation of fusion reactors. So, the control of the vacancy type lattice defects is important subject in the field of PFMs. Vacancy clusters and their interaction with impurities included in W are investigated by experimental and computational methods. According to first-principle calculations, divacancy (V_2) in W are unstable compared with isolated vacancies. However, the di-vacancy and growth of vacancy clusters in W materials were observed in positron annihilation lifetime spectroscopy. In the present work, we investigated the stabilization of di-vacancy by impurities contained in the W specimen.

Simulation method

The binding energies of impurities to vacancy and stabilization of di-vacancy by the impurities were calculated in terms of first-principle calculations based on density functional theory. We used the Vienna ab-initio simulation package (VASP). A large simulation cell, composed of 6x6x6 bcc lattice (432 atoms), were used in order to reduce the effects of periodic boundary condition imposed on the simulation cell. The cut-off energy of plane wave was 520eV.

The binding energy of impurity (X) to vacancy (V) was defined as

 $E_b(\mathbf{VX}) = E[\mathbf{V}] + E[\mathbf{X}] - \{E[\mathbf{VX}] + E_{ref}\},\$

where *E* is cohesive energy of the supercell containing V, X and vacancy-impurity complex XV, and E_{ref} indicates energy of perfect lattice. Similarly, the binding energy between VX and V, stabilization of di-vacancy by impurity, was defined as

 $E_b(V_2X) = E[VX] + E[V] - \{E[V_2X] + E_{ref}\}.$

Positive binding energy corresponds to attractive interaction. Besides, migration energies (E_m) of impurities and vacancy were estimated by nudged elastic band (NEB) method.

Results

We investigated interaction of vacancy with interstitial type impurities, i.e. hydrogen (H), carbon (C), nitrogen (N), and oxygen (O). As listed in Table I, the four impurities can be accommodated in a W vacancy, because the binding energies $E_b(XV)$ are positive. While, the interaction between two vacancies is repulsive, that is, $E_b(V_2)$ = -0.13eV. According to $E_b(V_2X)$, all impurities stabilize di-vacancy in W. However, the stabilization effect of H is quite small compared with those of other impurities.

Fig. 1 shows barrier height of the impurities and vacancy along the migration paths. The migration energies for H and O are quite small compared with those of C and N. The reason is that H and O are located at tetrahedral interstitial sites, while C and N are located at octahedral interstitial sites. Therefore, the migration paths between neighboring interstitial sites of H and O are shorter than those of C and N.

Table I: Binding energy of impurity to vacancy $E_b(VX)$, stabilization of di-vacancy by impurities $E_b(V_2X)$, and migration energy of impurities and vacancy E_m .

impurity	$E_b(VX)$	$E_b(V_2X)$	E_m
Н	1.22	0.17	0.20
С	1.97	1.09	1.48
Ν	2.43	1.14	0.76
0	3.04	1.39	0.18
Vacancy	-0.13		1.69

Discussion

Let's consider the stabilization of di-vacancy by the interstitial impurities. W specimen for the positron annihilation lifetime spectroscopy were prepared in water coolant circumstance, so impurities of low migration energy (H and O) were possible to migrate in the specimen and trapped in W vacancy to form vacancy-impurity complex VX. On the other hand, vacancy diffusion was observed at about 623K, which corresponds to migration energy for W vacancy (1.69 eV). The binging energies of H and O to vacancy were estimated to be 1.22 and 3.04 eV, respectively. Therefore, we infer that VO complex is stable at the vacancy diffusion temperature, while VH complex may be dissociated at the temperature. Therefore, O is still accommodated in W vacancy at the vacancy diffusion temperature. O is the most plausible candidate for di-vacancy stabilization among the interstitial impurities contained in W specimen.



Fig. 1: Barrier height of each impurity and vacancy along migration path.

Optical gaps of metastable Ga₂O₃ and GaN with impurity doping effect

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Electronic state of Mg-doped GaN was calculated using VASP package based on local density approximation. In contrast to the most stable phase of a well-studied wurtzite GaN, thin films of haekelite phase (4|8-GaN) are suggested to show stable p-type semiconductor even with the dope.

At the same time, we calculated spindependent electronic structure of twodimensional spin network of organic molecule array, made of metal-organic-framework (MOF) Cl[5,10,15,20-tetra(4from carboxyphenyl)-porphyrin] TCPP with Mn(II) and Fe(III) at the center hole. Spin-resolved density of states for several spin-polymorph are obtained, as in Fig.1, and photo-absorption spectra were calculated. These results suggests that several spin states would coexist because the eigenenergies were mutually very close, and that ferrimeagnetic phase could be discernible when the system is cooled. The optical results are consistent with our experimental findings by means of magnetic circular dichroism (MCD) of optical transmission spectroscopy. The observed MCD signals originate from the



Fig 1. Calculated electronic states of an isolated molecule (top), and MOF structures of Fe-TCPP for ferro-magnetic and antiferromagnetic structures, and the latter converges at ferrimagnetic states.

photo-transition in the intramolecular spin states, and some signals do from Cu-ions that link the molecules in MOF formation.

Optical gaps of metastable Ga₂O₃ structures modulated by impurity dope

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Ga₂O₃ has good electrical conductivity, and its wide bandgap of 4.8 eV offers great potential for various applications. The most of researches of this oxide material are limited within the most stable β phase. We previously reported optical spectra [1] of κ - and ε -Ga₂O₃, which is widened by Co-doping. The change in the electronic states due to this Co impurity was calculated (Fig.1) to clarify the experimental photo-absorption.

The photo-absorption in Ga₂O₃:Co is difficult to be simply associated to the bandgap of oxide material. But the adjustable shift of the cutoff in the photo-absorption is accounted by the theoretical calculation in this study. The change of the experimental workfunction due to the Co doping was also explained with a band diagram of ε -phase in Fig. 2. In this phase *n*-type pinning occurs due to unintentional impurities such as Si and Ge, as is intrinsic especially ε -phase, and Ovacancy less contributes.

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Fig.1: The density of state of Ga₂O₃:Co.Blue thin curve is the density projected to Co impurity.



Fig.2: Calculated photoabsorption modulated by the Co-impurity dope. This accounts for the experimental optical spectra.

Effects of electron–phonon and electron–magnon scattering on finite temperature magnetic properties

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There are several kinds of excitations that have to be taken into account when discussing finite temperature magnetic properties of magnetic materials. Among them are phonons and magnons. Usually, single electron excitations at Fermi surfaces do not contribute significantly to the magnetic properties at the assumed temperature range of $0 \sim 1500$ K. We have studied the effects of phonons and magnons on finite temperature magnetism, targeting at permanent magnet materials.

The effects of phonons are taken into account through random displacements of atoms around their equilibrium positions. The average displacements are estimated from either the Debye model or first-principles phonon calculations: no notable differences between the two was found. The effects of magnongs, on the other hand, are calculated by randomly flipping the local magnetic moments with probability determined self-consistently at each temperature. All the calculations were performed in the framework of first-principles calculation using KKR-CPA [1].

In the case of bcc Fe, there is a significant effect of electron-phonon scattering on the Curie temperature $T_{\rm C}$, while that of magnons is not prominent. The effect of magnons, however,

Table 1: Calculated $T_{\rm C}$			
	phonons only	plus magnons	
0K	1062K	561K	
$500 \mathrm{K}$	1198K	548K	

becomes remarkable in the case of Nd₂Fe₁₄B permanent magnet materials. Some examples of calculated $T_{\rm C}$ are given in Table 1. The first column indicates the temperature in which the average displacement due to phonons is calculated. The experimental value of $T_{\rm C}$ is 585K.

Figure 1 shows the calculated magnetizations of Nd₂Fe₁₄B. Both the effects of phons and magnons are included. The theoretical curve shows a weak first-order transition at the magnetic transition temperature, which occurs as a result of electron-phonon coupling. The temperature is scaled so that $T_{\rm C}$ reproduces the experimental value of 585K although the scaling factor is close to 1. The calculated results are fairly consistent with experiments is concluded.



Figure 1: Calculated and experimental magnetizations vs. temperature of $Nd_2Fe_{14}B$

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Rare-earth permanent magnet materials of $SmFe_{12}$ family attract much attention because expected performance using NdFe₁₂ family as a main phase of permanent magnets has been recognized as hardly reached. Much work has been done to seek better intrinsic magnetic properties for $SmFe_{12}$ by adding some elements as ingredients. In this study, we have tried several $SmFe_{12}$ family cases, which are implied from experiments to be possible candidates for permanent magnet materials. Finite temperature properties, including the magnetizations, Curie temperatures, and magnetocrystalline anisotropy, were examined.

Figure 1 shows the calculated magnetizations as functions of temperature where the Curie temperatures are scaled so as to fit the experimental ones. More precisely, first the Curie temperatures, which are not necessarily known experimentally, are estimated by fitting the temperature dependence of magnetic moment by Kuz'min's empirical formula. On the other hand, the theoretical Curie temperatures are obtained by first-principles calculation using KKR–CPA[1]. Theoretical temperature dependence of magnetization is then obtained again using Kuz'min's formula. Finally, the temperatures are scaled using experimentally estimated Curie temperatures.

The crystalline magnetic anisotropy constant K_1 of $(\mathrm{Sm}_{1-x}\mathrm{Zr}_x)(\mathrm{Fe}_{1-y}\mathrm{Co}_y)_{11.5}\mathrm{Ti}_{0.5}$ is also calculated. Since the treatment for 4f states of Sm is still rather controversial, we neglect the contribution of 4f to magnetic anisotropy through hybridization, adopting an open core treatment. These results indicate that adding Co improves the magnetization although it degrades the magnetic anisotropy. Zr slightly contributes to improve the magnetization but not much to the anisotropy. Main contribution of Zr must be that to structural stabilization.



Figure 1: Temperature dependence of magnetization of various systems of SmFe₁₂ family.

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Theoretical Analysis of Photocatalytic Reaction Mechanism at Titanium Dioxide Interfaces

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We have studied the reaction mechanism of photocatalytic oxidation at anatase TiO₂ surfaces [1] using cp2k program package (MPI parallelization with multiple threads). We focused on the energetics and structure during the hole migration. This is a collaborative work with the experimentalist (Prof. Satoshi Yamauchi Ibaraki University), at who conducted the LPCVD experiment.

This experimental and theoretical study clarifies facet dependence the of the photocatalytic reaction at the anatase TiO₂ surface. The <112>-oriented anatase TiO₂ layer is deposited on the Ru(0001) substrate at 360°C by low-pressure chemical vapor deposition. The deposition rate is three times higher than that of the multi-orientation layer on the Pylex glass. The photocatalytic activity induced by ultraviolet (UV) irradiation around 365 nm in methylene blue solutions aqueous is significantly high. The density functional theory (DFT) calculations using the constrained DFT method [2] and the hybrid functionals show that the (112) surface stabilizes the adsorbed water molecule most strongly. The photogenerated hole is stably trapped not at the bare surface but at the hydroxylated surface, especially at the hydroxyl group of the hydroxylated (112) and (001) surfaces. The experimental and theoretical findings consistently elucidate the high photocatalytic activity at the anatase $TiO_2(112)$ surface.





Fig. 1: Molecular mechanism of hole migration.

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Ab Initio Calculation of High-Rate Deposition of Metal Films by LowPressure Chemical Vapor Deposition

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We have studied low-pressure chemical vapor deposition of Cu on Ru substrate using CuI [1] using cp2k program package (MPI parallelization with multiple threads). This year, we focused on the *ab initio* calculation of desorption of by-products. This is a collaborative work with the experimentalist [2] (Prof. Satoshi Yamauchi at Ibaraki University), who conducted the LPCVD experiment.

In this study, we elucidated the molecular mechanism of Cu deposition using copper(I) iodide (CuI) on Ru substrate by low-pressure chemical vapor deposition through electronic structure calculations. Figure 1 shows the molecular mechanism of Cu deposition by the LPCVD method. Using density functional theory (DFT) molecular dynamics (MD) simulations, we show that CuI molecules adsorb and decompose exothermically due to a strong adsorption of iodine atoms onto the Ru(001) surface. The rate-limiting step of the Cu deposition is found to be the desorption of iodine atoms or molecules from the Cu(111) surface by molecular dynamics simulations.

Based on this study, we are now extending

our calculations to analyze the dynamical properties by the constrained DFT[3] and the dynamical reaction path analysis.[4]



Fig. 1: Molecular mechanism of LPCVD of Cu.

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Dynamical stability of two-dimensional simple metals and ordered alloys

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The family of two-dimensional (2D) materials has been expanded significantly in recent years. However, the dynamical stability as well as the synthesizability of 2D metals have not been explored in detail irrespective of the presence of the interrelationship between the energetic stability in the 2D and threedimensional (3D) structures. In this study, we have performed high-throughput density functional theory (DFT) and density functional perturbation theory (DFPT) calculations to construct the metastability database for simple metals and ordered alloys. The database currently includes (I) the phonon dispersions of 46 simple metals from Li to Pb in the three 2D structures, including the planar hexagonal, the buckled honeycomb (BHC), and the buckled square (BSQ) lattices [1]; (II) the phonon dispersions of 2D Po, named poloniumene, in the planar square structure [2]; and (III) the formation energies of 1081 binary compounds in the 2D structures (BHC and BSQ as shown in Fig. 1) and the 3D structures $(B2, L1_0, and$ B_h corresponding to bcc, fcc, and hcp in simple metals, respectively) and the phonon dispersions of more than 50 ordered alloys in the BHC structure [3].

In Ref. [1], we have demonstrated that the trend in the dynamical stability of 2D metals is correlated with that of 3D metals. This provides design principles of ordered alloys: 2D metals are building blocks for constructing 3D alloys, where the similarity regarding the dynamical stability of different 2D metals is important for creating dynamically stable alloys.

In Ref. [2], we have shown that the 2D polonium has the planar square lattice structure as its ground state and demonstrated that the



Figure 1: Schematic illustration of binary ordered alloys in the BHC and BSQ structures. After Ref. [3].

spin-orbit coupling (beyond the scalar relativistic approximation) suppresses the Peierls instability and is necessary to obtain no imaginary phonon frequencies over the Brillouin zone.

In Ref. [3], by analyzing of the formation energy and the dynamical stability of binary alloys, we have demonstrated that (i) a negative formation energy is neither a sufficient nor necessary condition for producing the dynamical stability of 2D ordered alloys; and (ii) if an ordered alloy in the B_h structure is synthesizable, that in the BHC structure is dynamically stable. In addition, the stability of ordered Au-Cu alloys has been studied in Ref. [4].

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Boltzmann equation solver for nonequilibrium electrons and phonons in solids (BENEP). II. Application to experiments

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Understanding the ultrafast electron dynamics of laser-excited solids, where the electron-electron (e-e) and electron-phonon (eph) scatterings occur simultaneously within a picosecond time scale, is important to analyze the pump-probe experimental data. The author has developed the Boltzmann equation solver for nonequilibrium electrons and phonons which enables us to study the ultrafast electron and phonon dynamics [1]. We have applied our code to the calculation of the femtosecond infrared photoluminescence (PL) of silver (see Fig. 1). The preliminary results have been reported in Activity Report 2019.



Figure 1: Flow chart describing the timeevolution calculation of the distribution functions in metals. After Ref. [2].

Figure 2 shows an application to the timeevolution of PL spectra and the transient PL at 0.9 eV in silver. The agreement between the theory and experiments is good, indicating that the effect of electron nonequilibrium is important in the PL dynamics. The disagreement may be attributed to the nanoscale roughness at metal surfaces and the e-e umklapp scattering on the ultrafast electron dynamics [2].

The author thank Prof. Tohru Suemoto for useful discussions.



Figure 2: (a) The evolution of PL in silver: The experimental PL (circle) and the calculated PL (solid). (b) Comparison of the transient PL at 0.9 eV. After Ref. [2].

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Noisy simulations of first-principles calculations using quantum classical hybrid algorithms

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In recent years, quantum computers with dozens of qubits have been built; we now expect to see quantum devices with hundreds of qubits in the near future. Such quantum computers are often called noisy-intermediate scale quantum devices (NISQs) since they do not have quantum error correction functionality. Nonetheless, in 2019, Google showed that a NISQ with as few as 53 qubits could already outperform supercomputers when limited to a specific task. Many research projects have been currently underway to exploit the computational potential of NISQs.

One promising algorithm for NISQs is the quantum-classical hybrid algorithm, which can operate even in the short coherence time of a NISQ. Among them, the variational quantum eigensolver (VQE) can be applied to firstprinciples calculations of materials or molecules. An advantage of the VQE is that it can parametrize some wave functions ansatzes such as unitary coupled clusters (UCC)in polynomial time, while the UCC is exponentially computationally expensive on classical computers. However, if a NISQ is used for the VQE, the computational results are unavoidably

affected by noises.

In this work, we have investigated the influence of this noise on the VQE by using a quantum circuit simulator. There are many types of noises in quantum computers, such as readout error and amplitude damping. Since it is difficult to model all kinds of errors, we have only dealt with depolarizing noise, which is a typical error model for quantum computers, in this study. This noise can be described as Pauli operators probabilistically acting on each gate of quantum circuit. In the presence of а depolarizing noise, we can effectively say that the noise probabilistically changes the quantum circuit at each sampling. It means that the numerical simulations with depolarizing noise using classical computers, are required to simulate various quantum circuits: the simulation with depolarizing noise is much more expensive than the simulation without it. Besides, because such a simulation is a sampling problem, the individual circuits changed by the noise are independent. Hence, the VQE with depolarizing noise can be highly parallelizable.

This year, we have realized the simulation with depolarizing noise up to 1 million samples by using the MPI parallelization and the supercomputer of the ISSP. In addition, by using a many-body expansion, we have studied the effect of depolarizing errors on up-to a 100qubits problem. We have chosen the most basic molecule, the hydrogen molecule, as the benchmark system. In our program, the PySCF quantum chemistry program library [1] is used to prepare the second quantized electronic Hamiltonian; Qulacs is employed as a quantum circuit simulator [2]. The obtained numerical results illustrate that it is impractical to achieve chemical accuracy with the error rates of today's quantum computers. This implies that an efficient way to suppress the effect of depolarizing noise is vital for the practical application of first-principles calculations using NISQs.

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First principles calculations of crystals with quantum classical hybrid algorithms

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First-principles calculations of solids or solid surfaces are routinely performed in materials science. They have become an indispensable tool in the fields of condensed matter physics and inorganic chemistry. The workhorse of these ab initio calculations is currently density functional theory (DFT). An approach beyond DFT is the introduction of quantum chemical methods such as the coupled-cluster theory (CC).

The problem of CC is that it works well only for weakly correlated systems. It is known to break down in systems with strong electron correlation. This issue comes from the fact that CC is not variational. Although there is a variational CC method, such a method is exponentially expensive in terms of computational costs. However, in 2014, it was shown that a kind of variational CC, the unitary CC (UCC), can be solved in polynomial time using a quantum computer.

This method is called the variational quantum eigensolver (VQE). In the VQE, the wavefunction ansatz is represented by a quantum circuit. Then, a classical computer updates the VQE's wavefunction parameters as quantum circuit parameters.

This year, we have extended the VQE to solid-state systems [1]. Specifically, we prepare a second quantized Hamiltonian in the crystal orbital representation, and make a one-to-one correspondence between crystal orbitals and qubits. The UCC ansatz in the crystal orbital representations has also been converted into the qubit representation. These mapping allows us to describe the electronic structure of a crystalline system on a quantum computer.

We have applied the developed VQE-UCC to one-dimensional hydrogen chains and calculate their potential energy surface, confirming that the VQE-UCC works in the regime where the electron correlation becomes strong so that the conventional CC does not work. We have also developed an algorithm to calculate the quasiparticle band structure from the VQE wave function based on the extended Koopman's theorem [1].

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First-principles Calculation of Electric Field Effects in Spin-to-charge Conversion Materials

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We have studied materials possessing the Rashba effect that induces spin splitting, which is applicable to spin-to-charge conversion [1]. The Rashba effect originates from spin-orbit interaction and spatial inversion symmetry breaking, and is controlled by electric fields. Based on the modern theory of electric polarization, one can apply uniform electric fields even for bulk insulators in calculations with density functional theory (DFT) codes with the periodic boundary condition [2]. We have developed a linear-combinationof-pseudo-atomic-orbital (LCPAO) version of such a function making **k**-dependent potentials and implemented it to the OpenMX code. This year, we tried to focus on electric field effects in such Rashba systems with Berry phases by using the OpenMX code. Under an electric field, cations or anions are expected to shift their positions slightly, but shifts of ions' positions induce such a large electric polarization that Rashba spin splitting occurs. During structural relaxation, such ions move by following forces on themselves, but the forces are often smaller than a usual criterion of calculated forces (e.g. 10^{-4} Ha/Bohr) when we consider the realistic strength of electric fields. However, for nonorthogonal cells such as hexagonal cells, in the case of generalized gradient approximation (GGA), the "egg box effect" appeared as a difficulty because OpenMX uses PAOs expanded in the real space grid to compute physical quantities, but description of PAOs depends on the origin of the grid, that is, introducing the grid causes numerical errors. To overcome the difficulty, we added functions of calculations of a total energy and forces with several grid origins. Once calculations of electronic systems converge, one can get density matrices (DMs) and taking another real space grid with a different origin, one can evaluate an energy and forces again with the frozen DMs. In the way, we succeeded in evaluating forces under electric fields with a moderate number of grids (i.e. cutoff energy). We also added a function to change the order of the Lagrange interpolation to estimate density gradients, and it improved evaluation of forces. These two functions enabled us to predict not only relaxed structures under electric fields but also static dielectric constants and Born effective charges in any cell shape. Indeed, we confirmed that our calculated values of dielectric constants and Born effective charges for typical insulators are consistent with the prior theoretical and experimental studies. Since we encountered the problems of the "egg box effect", we have not done calculations of applications, but we have suggested a simple model of surface alloys, such as Bi/Ag surface alloys inducing giant spin splitting, based on DFT calculations [3]. This year, we also succeeded in reducing half of computational time for Berry phases averagely through tuning, and running our implemented code with up to 32^3 k-points for zinc blende primitive cells through efficient transfer of arrays of k-dependent potentials in the message passing interface (MPI).

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First-principles study of atomic and electronic structures of intermetallic compound catalysts

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This fiscal year, we carried out the following studies using the VASP code with the PAW method and the PBE exchange-correlation functional.

Quasicrystals (QCs) are long-range ordered materials with no translational symmetry. Partly because the atomic structure of most QCs have not been solved completely, DFT studies have usually been carried out using the surface of a crystalline phase having a close composition and common structural building unit to the quasicrystalline phase. Recently, however, single-element quasiperiodic ultrathin films have been obtained using the Ag-In-Yb QC as a template. The Ag-In-Yb QC belongs to the only QC family whose atomic structure has been solved unambiguously. Thus, DFT studies using the actual quasiperiodic surface atomic arrangement are required to elucidate the atomic structure of the ultra-thin films. Although a straightforward way to approximate the QC surface is to use an atomic cluster extracted from the structural data of the QC, the cluster size dependence of the adsorption energy for the aperiodic surfaces has not been well studied. Therefore, this time we studied the convergence behavior of the adsorption energy of a single Bi atom concerning the cluster size [1]. Two types of clusters, the cylindrical and hemispherical clusters, are tested. Unnaturally rippled potential energy surfaces were obtained for clusters with smaller radius regardless of the cluster thickness. It was revealed that the ripples are disappeared when clusters with a sufficient

cluster radius of 1.4 nm or larger are used. This trend is also confirmed in their root mean square errors. Consequently, it was concluded that both cluster models tested with a specific size are expected to give relative adsorption energy within an error of 0.15 eV. It was also pointed out that the cylindrical cluster model is relatively economical in terms of the calculation cost than the hemispherical cluster model.

We also investigated the surface atomic structure of the antiferromagnetic 1/1 Au-Al Tb approximant crystal using DFT calculation[2]. Experimentally observed stable surface atomic structure showing a linear row structure of Au/Al atoms, which is an example of a surface reconstruction in this family of QC-related systems, was found stable by the calculation.

We studied the influence of the adsorbed oxygen atoms on the surface atomic structure and electronic structure of PdZn(111) surface using DFT calculation[3].

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Study on Removal Mechanism of Single Crystalline Si Planarized by Catalyst-Referred Etching in Pure Water

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There is a growing demand on ultraprecision optical components for scientific and industrial applications, especially in extreme ultraviolet (EUV) and X-ray regimes. Using the short-wavelength light, scientific imaging of cutting-edge materials/biological samples and nanoscale lithography have become possible thanks to the ultra-precision optical components. Low thermal expansion materials such as glass and Si are still the main materials used for fabricating these optical components. Compared to glass, Si possesses more attractive properties, such higher cleanliness, as machinability, and workability. Accordingly, ultra-precision surface machining for Si surfaces has been achieved significant advances in accuracy and smoothness. A highly ordered surface with a root mean square roughness at the level of several tens of picometer is greatly desired for the highest reflectivity and the lowest unwanted scattering [1].

In this study, we apply catalyst-referred etching (CARE), an abrasive-free polishing method, to planarization of a crystalline Si surface, using Pt as the catalyst and pure water as the etching solution [2]. An atomically smooth surface with sub-Angstrom root-meansquare roughness is achieved on the Si substrate.

Our recent studies indicated that the removal mechanism of SiC and SiO₂ etching via CARE is hydrolysis reaction, in which the catalyst assists dissociation water and stabilization of hypervalent state, increasing rate of the reaction [3]. Thus, the purpose of the proposed research is to clarify the removal mechanism of Si etching via CARE using firstprinciples calculation. Additionally, in Si polishing, the effect of self-oxidation by oxygen and water is still not well understood due to the instability of Si under ambient condition. Thus, the oxidation effects of oxygen and water are also taken into account.

The mechanistic removal pathway of CARE for Si(111) has been clarified and shown in Fig. 1. In the pathway with the Pt catalyst, at first, a water molecule is dissociatively adsorbed on Pt. In the next step, the adsorbed OH is transferred to the targeted Si, forming the five-fold coordinated state in the metastable state (MS). At this state, the Si-Si back-bond is elongated and weekend. Finally, the Si–Si back-bond is broken by a proton transfer at the final state (FS). The activation barrier is reduced from 1.0 eV (without the Pt) to 0.6 eV (with the Pt). We expected that similar results would be observed on a Si(100).



Fig. 1: A mechanistic reaction pathway of the Pt-catalyzed water etching of the Si(111) surface in comparison with the pathway without the Pt catalyst.

We consider oxidation effects by an oxygen molecule at terrace and step-edge sites on a Si(111) surface, as illustrated in Fig. 2.



Fig. 2: Illustration of oxidation effects by an oxygen at terrace and step-edge sites on a Si(111) surface (top-view).

The activation barriers of the oxidation by an oxygen molecule are 0.46 and 0.15 eV, respectively (Fig. 3). The obtained results indicated that the oxidation might occur readily in the air at a step-edge site. However, the oxidation by oxygen at a terrace site might be difficult. The obtained results are quite consistent with the previous study [4]. The obtained results could also explained why the wettability of Si(111) surface could be lasted for several hour in the ambient conditions in the previous experimental study [5].



Fig. 3: Atomic configurations and energy diagrams of oxidation by an oxygen molecule at a step-edge and a terrace site.

The study has clarified the mechanistic removal pathway of CARE for Si in pure water and oxidation effect of a Si(111) surface by oxygen or water. Oxygen plays an main role in the oxidation of a Si(111) surface. Moreover, combined oxidation effects of oxygen and water might be an important factor to be considered in the future.

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Doping and molecular adsorption of graphene

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Graphene is one of candidate device materials for molecular sensors using field-effect transistors due to their high charge mobility and chemical reactivity to adsorbates. Recently, we have reported the adsorption properties of environmentally polluting and/or toxic molecules (NO and NO₂ molecules) onto boron and nitrogen-doped graphenes, and only NO and NO₂ molecules in air are strongly adsorbed on the B-doped graphenes.

We here report the adsorption property of a toxic CO molecule on the boron-doped graphene and (8,0) CNT to reveal the curvature effects of the graphene using a firstprinciples density-functional calculation [1, 2, 3].

Table 1 shows the adsorption energies and the binding distances between the B atom and the adsorbed molecule for the CO molecule on the B-doped monolayer and bilayer graphenes, and B-doped (8,0) CNT. The CO molecule is found to be adsorbed not strongly but weakly with short distance and small adsorption energy on the B-doped monolayer graphene. In the case of the B-doped bilayer graphene, the adsorption energy and the binding distance for the adsorption of the CO molecule show similar

Table 1: Adsorption energy E_a (eV) and binding distance d (Å) between adsorbed molecule and B atom for CO molecules adsorbed on Bdoped monolayer and bilayer graphenes, and B-doped (8,0) CNT.

	E_a	d
Monolayer	-0.12	2.89
Bilayer	-0.12	2.89
CNT	-0.62	1.53

to those of the B-doped monolayer graphene, respectively.

We also study the adsorption energy and the binding distance of the CO molecule on the B-doped (8,0) carbon nanotube (CNT). Unlike monolayer and bilayer graphenes, the CO molecule is found to strongly bind on the Bdoped (8,0) CNT with the large adsorption energy and the short binding distance. Thus, the adsorption properties of the CO molecule on the B-doped (8,0) CNT is found to be enhanced, compared with those on the B-doped monolayer and the B-doped bilayer graphenes due to the curvature effects.

In summary, we have studied the adsorption properties of the toxic CO molecule on the B-doped monolayer and bilayer graphenes, and B-doped (8,0) CNT, using first-principles density-functional calculations. The B-doped monolayer as well as bilayer graphenes does not strongly but weakly bind with the CO molecule, while the B-doped (8,0) CNT can strongly bind with the CO molecule. The Bdoped (8,0) CNT may be useful for sensor applications to detect CO molecules.

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Stability and electronic structures of MoS₂ nanowires

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Nanotubes of layered materials started with the discovery of variety of helicities in carbon nanotubes. Since then, various layered materials are found to form nanotube structures. These structures show important functions such as catalytic activities, lithium ion storage, transistor action and chemical sensing. Recently, we discovered that FeO nanoparticles work as catalyst to make MoS₂ nanowires[1]. We found that the cross section of the MoS₂ nanowires show rectangular shapes. In order to investigate the mechanism of the formation and possible new functions of these nanotubes, we used VASP to calculate the stability of MoS₂ nanotubes with cylindrical and square shaped cross sections with armchair and zigzag helicities[2]. The calculation result shows that this structure has lower strain energy in the lowdiameter region (~30 Å) than the conventional cylindrical nanotubes (Fig.1). The electronic structure and the surface energy per length of the square nanotubes showed unique properties because of five coordinated Mo atoms at the corner. Catalytic activities and unique sensing functions are expected.



Fig. 1: Strain energy of MoS₂ nanotubes with square or cylindrical cross sections.



Fig. 2: 2D deformation charge density map of square-shaped nanotube.

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First-principles derivation of a many-body effective model based on PMT basis

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To establish a construction method to obtain a model which captures the lowenergy part of electronic structures obtained in first-principles calculation is an urgent problem. The model is often used to calculate physical quantities such \mathbf{as} self-energy, conductivity, and transition temperatures of magnetism or superconductivity. The Maximally localized Wannier function (MLWF [1]) is often used to derive a tight-binding model reproducing the first-principles band structure very well. However, MLWF has a problem that it requires several optimization parameters. This requirement inhibits the automation of model construction. If the automation is achieved, we can search the materials having desirable from properties material databases. In addition, MLWF has a difficulty in the model construction for slabs and surfaces.

To overcome the problems of MLWF, we propose a construction method as Muffin-tin based Localized Orbital (MLO) based on the PMT basis function

[2]. The PMT basis function is a hybrid basis between the plain wave basis and the muffin-tin basis. In the new model construction method. effects only described in the plane waves basis set are taken into account in the model Hamiltonian expressed on the muffin-tin orbital basis. Namely, we obtain a projection operator from full-space (PMT space) to the (reduced) model space, which is spanned by muffin-tin orbital. In the operator, we introduced weight function so as to reproduce the band structure of low energy region. Note that the new method does not require any handful parameters, so this can be used in the automation of model constructions.

We have applied MLO to Si crystal. The figure 1 shows the comparison of the energy eigenvalues between the firstprinciples calculation and MLO. We can see MLO nicely reproduce the firstprinciples eigenvalues. Even in other semiconductors such as GaAs and GaN, the eigenvalues are well reproduced.

In summary, MLO basis function can

accurately reproduce the eigenvalues calculated in the first-principles calculations. In the next step, we apply MLO to more difficult systems such as interfaces or slabs.



Figure 1: Result of MLO in a simple Si crystal. Solid line shows the eigenvalues obtained in first-principles calculations and circles shows the MLO results. The triangles show the result considering only the MTO basis.

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First-Principles Analysis of Melt Structure and Property in Na Flux GaN Growth

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To produce high-quality III-V nitride semiconductor devices at low cost, large bulk GaN crystals for freestanding substrate are demanded. The Na-flux method is one of the most promising crystal growth technique for bulk GaN. It is known that C additives improve the growth rate and suppresses the generation of polycrystals [1]. Using firstprinciples calculations, we previously found that formation and dissociation of the C–N bond in the Na–Ga melt strongly affects the mechanism for enhanced GaN growth [2].

At first, graphite was used as a C source. After that Murakami et al. used methane (CH_4) gases and found they were more effective than graphite [3]. In this study, we investigated activation free energies for C–C and C–H bond dissociation in Na–Ga melts using first-principles calculations and clarified the reason why CH₄ gases are more effective than graphite.

We used the first-principles molecular dynamics (MD) simulation program STATE-Senri (Simulation Tool for Atom TEchnology), which is based on density functional theory with norm-conserving/ultrasoft pseudopotentials and plane-wave basis sets [4]. We used the generalized gradient approximation of Perdew et al. for the exchange-correlation function [5]. The cutoff energies for the wave functions and charge densities were 25 and 225 Ry, respectively. The number of k-points for Brillouin zone sampling was $1 \times 1 \times 1$.

We modeled Na–Ga (Na:Ga \approx 4:1) melt

models composed of about 54 atoms. A set of C and C or C and H atoms was included in the models. Periodic boundary conditions were used in all directions. We performed constrained MD simulations for 10 ps at 1073 K and at constant volume. The C–C and C–H interatomic distances were constrained to the range of 1.0–3.5 Å. By using data from the latter half of the 10 ps period, free energy profiles were calculated with the blue-moon ensemble method [6, 7].

Figures 1 show plots of the free energy profiles for C–C and C–H bond in Na–Ga melt. The horizontal axis is the constrained interatomic distance. The interatomic distance at which the free energies reach a local minimum indicates a stable bond length. The dissociation activation energies were determined from



Figure 1: Free energy profiles for the C–H bond in the Na and Na–Ga melts.

the energy difference between a local maximum and a local minimum. From the result, we found that the activation free energies for C–C and C–H bond dissociation are 2.71 and 1.34 eV, respectively [8]. Because the dissociation energy of the C–H bond is lower than that for the C–C bond, CH₄ gas decomposes more easily than graphite; that is, CH₄ gas is more effective as a C additive than graphite.

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Analysis on atomic and magnetic structure in magnetic molecular complex, crystal and interface and investigation of external electromagnetic field effect

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We have investigated the electronic and magnetic structure of ferrimagnetic spinel of NiCo₂O₄ by using the beyond generalized gradient approximation (GGA) approach such as GGA+U or quasi-particle self-consistent GW (QSGW). The NiCo₂O₄ spinel has drawn a lot of attention for its material application due to its low cost with excellent electronic conductivity, redox reaction, and high electrochemical activity. However, some of the latest reports of its first-principles calculation result have some discrepancies with the experimental one. One of the reasons may come from the poor electron correlation description of GGA calculation. For this study, the first-principles calculation package ecali [1], which adopts the mixed-based set between local orbital and plane waves, is used. We mainly focused on the inverse spinel structure containing 14 atoms, namely, eight oxygen and six cation atoms, in the primitive cell.

The results show that both GGA and QSGW gave the ferrimagnetic magnetic structure with a half-metallic electronic configuration[2].

However, some differences should be pointed out, e.g., the size of the energy gap on the majority spin. Remarkably, QSGW predicts the unoccupied energy of Ni e_g orbitals to be more than 1 eV higher than those calculated by GGA. It may affect the estimation of electric and optical properties such as reflectance or transmittance.

We also extended the QSGW calculation by combining it with the effective screened medium method [3]. It allows us to estimate the finite electric field effect of slab systems on GW level without relying on perturbation theory. We have succeeded in evaluating the dielectric constant in high accuracy [4].

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Molecular dynamics study on non-equilibrium processes of silica and silicates using first-principles calculation and machine leaning

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In this project, we studied (1) pressureinduced amorphization behavior of fayalite and (2) shock-compression behavior of quartz based on molecular dynamics simulations.

First-principles molecular dynamics simulation of pressure-induced amorphization of fayalite

Fayalite (Fe₂SiO₄), an end-member of the olivine. undergoes crystal-to-amorphous transformation at high-pressure and roomtemperature conditions [1]. It was reported that this pressure-induced amorphized fayalite exhibits different features from olivine glasses synthesized by heat-and-quench processes [2]. However there are no theoretical investigations about the pressure-induced amorphization and phenomenon the pressure-induced amorphized phase yet.

In this study, we perform first-principles molecular dynamics study of fayalite to investigate energetic and structural properties of the pressure-induced amorphized fayalite. The volume-and-energy relations, partial pair distribution functions, and coordination number changes of crystalline and amorphous phases of fayalite during compression and decompression processes were obtained. We elucidated that the high-fold coordinated Si atoms exist in the amorphous phase even after decompression to an ambient conditions. Additionally, it was found that the Si atoms play a role of networkformer in the amorphous phase at high-pressure, but change into network-modifier at an ambient conditions. Furthermore, it is expected that the medium- or long-range order of Fe atoms are partially remained in the amorphous phase, resulting in the appearance of its unique magnetic ordering structure.

Molecular dynamics simulation of shock-compression behavior of quartz using ANN potential

Artificial neural network (ANN) potential, which is an interatomic potential constructed by machine-leaning, attracts attention as а promising method to achieve extra-large-scale molecular dynamics (MD) simulation with first-principles accuracy [3,4]. Application of ANN-MD far-from-equilibrium this to phenomena, such as fracture and pressureinduced transformation, is important to understand structural properties of materials under extreme conditions. For this purpose, we have tried to perform ANN-MD simulation of shock-induced structural transformation of silica.

To compute shock-compression behaviors within the framework of MD method, the multiscale-shock technique [5] was employed in our simulations. Potential energy of shockcompressed a-quartz obtained by firstprinciples MD (FPMD) method is used as a reference data for training of ANN-potential. As a result of ANN-MD simulation for elastic shock-wave region, elastic-deformation behaviors of α -quartz was successfully reproduced with high-accuracy [6]. On the other hand, for plastic shock-wave region, the ANN-potential has completely failed on prediction of both structure and energy, because of that irregular structure appears and rapid movement of atoms occurs during the elasticto-plastic transition process.

In order to improve the predicting ability of ANN-potential, we introduce a more accurate training method that uses not only potential energy but also atomic force and pressure as reference data [7]. Using this improved ANNpotential, it was succeeded that reproducing the elastic-to-plastic transition behavior and plastic deformation of α -quartz with an accuracy close to FPMD simulation. Thus, the ANN-potential trained with energy, force, and pressure is a potentially powerful tool to investigate wide range of far-from-equilibrium phenomena and will also provide useful information for solid earth physics field in future.

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Search and realization of novel electronic properties of solid surfaces and interfaces and of small particles

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We mention two subjects which we addressed this year.

The Ni(110)–(2x1)O surface is known to have a missing-row reconstruction structure, as is shown in Fig. 1 [1]. Oxygen (O) atoms are adsorbed at bridge sites to form Ni–O–Ni atomic chains in the y, namely, [001] direction. The O–derived bands exist near the upper and lower edges of the substrate Ni bands. The bands around the lower edge have already been studied well by means of firstprinciples calculations using small-scaled slabs and some experimental studies.

This year, using a large-scaled slab composed of 21 Ni atomic layers and adsorbed O atoms at both surfaces, we investigated the upper O-derived bands, and identify them with surface states when separated up from the upper edge of the substrate bands.

We employed the program package 'Vienna Ab initio Simulation Package' (VASP) [2,3] on systems B and C.



Fig. 1 Missing- row reconstruction structure at the Ni(110)-(2x1)O surface $\overline{1}$ 10]

Graphene is a very popular single-layer structure of carbon (C) atoms arranged in a hexagonal lattice. The band structure of this material is characterized by a so-called Dirac cone, and predicts an extremely high electron mobility. When this material takes a form of nanoribbons, the band structure due to π orbitals around the Fermi level depends on edge shapes.

Nanoribbons with zigzag edges have localized edge states, while those with armchair edges possess no edge states.

We consider the electronic structure of graphene systems of finite area. By means of the tight-binding method, we examined if edge-localized states can be formed in finite graphene systems, and how the electronic structure of these systems depends on system shapes or areas.

(1) Identification of surface states at the Ni(110)-(2x1) O surface [4]

Assuming a slab of 21 Ni-atom layers with O atoms adsorbed at each surface and using the generalized gradient approximation, we obtained the optimized ground state structure. Figure 2 (a) shows the band dispersion on the $\overline{\Gamma} - \overline{Y}$ line for majority spin. As is displayed by an arrow, there exist a pair of nearly degenerate bands that lie above the densely distributed substrate bands due to Ni *d* orbitals. Figure 2 (b) exhibits electron-density isosurfaces of the higher energy one of the above paired states at the



Fig. 2 (a) Band dispersion on the $\overline{\Gamma} - \overline{Y}$ line for majority spin and (b) electron density isosurfaces of the state on the midpoint of the $\overline{\Gamma} - \overline{Y}$ line, as is arrowed in (a).

middle point of the $\overline{\Gamma} - \overline{Y}$ line. Isosurfaces of the lower one are almost the same. This isosurface map clearly indicates that this state is localized near the surface, and that the p_x orbital of an O atom, which extends in the x, namely, $[\overline{1}10]$ direction, plays a major role, and it bonds to d_{xy} orbitals of a surface Ni atom. We can recognize this tailed localization at the surface only in such a large-scaled slab as ours. However. we still have to verify that these surface states really exist even in a semi-infinite substrate. We consider that bulk which can be obtained in the limit of increasing the slab thickness, and evaluate the upper edges of those bands which correspond to the substrate bands of the slab. We find that these upper bulk-band edges are below the paired nearly degenerate bands. Through this analysis, we concluded that the surface states are really present in the semi-infinite substrate.

We made the same analysis of the O-derived bands around the upper edge of the substrate bands on the $\overline{\Gamma} - \overline{X}$ line as well. We identified the surface states in which the p_y orbital of an O atom bonds to the d_{yz} orbitals of a surface Ni atom.

(2) π -band structure of finite graphene systems [5]

We examined the electronic structure of finite graphene systems for various shapes and areas. Each eigenstate is expressed in a form of a linear combination of p_z orbitals of C atoms extending in a plane-normal direction, and each component of its eigenvector represents the p_z orbital coefficient of the corresponding C atom.

As an example of the results, figure 3 displays the p_z -orbital coefficients in color scale of (a) the lowest-energy state (n=1), (b) the highest-occupied state (n=23) and (c) the highest energy state (N=46) for a parallelogram graphene with 46 C atoms. This parallelogram is quite special in having only zigzag edges.

As is shown in Fig. 3 (a), the p_z orbital coefficients in the lowest-energy state are coherent in sign. On the other hand, figure 3 (c) indicates that, in the highest-energy state, the coefficient alternates in sign along each hexagonal atom ring. In either of

these states (a) and (c), the coefficient amplitude tends to decrease as we move from the center to the edge. These features are common to various shapes of finite graphene.

Figure 3 (b) shows that the highest occupied state has edge localization. Red and blue circles indicate atoms with large positive and low negative coefficients, respectively. These coefficients with large amplitudes alternate in sign along the edge line. The electron density distribution is localized around the acute-angle vertices, namely, at those edges farther away from the center. Generally, edge localization occurs at zigzag edges in specific states at or just near the Fermi level.



Fig. 3 p_z -orbital coefficients in color scale for a parallelogram graphene. (a) Lowest- energy state, (b) Highest-occupied state, (c) Highest-energy state.

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Theoretical Study on Electronic Properties in New Nanoscale Surfaces and Interfaces

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In 2020 we theoretically studied onedimensional Rashba systems. Perfect spinpolarization and spin-orientation reversal of photoelectrons have been observed in spinand angle-resolved photoelectron spectroscopy (SARPES) of strong spin-orbit systems [1, 2]. These phenomena have theoretically been explained in terms of mirror symmetry of the systems [2, 3]. A problem, however, is that the states having mirror symmetry are restricted to lines in two-dimensional Brillouin zones. Only a small amount of photoelectrons are fully spin polarized. To improve the efficiency of spin polarization we considered a one-dimensional Rashba system and theoretically investigated it.

Mirror-symmetrical two states with respect to each other in a two-dimensional Brillouin zone form a mirror-symmetrical state by making the system finite along the direction perpendicular to a mirror symmetrical line. All states become mirror symmetrical in onedimensional systems and all photoelectrons excited with linearly polarized light are spinpolarized. However, the wave functions are either symmetrical or anti-symmetrical, and the spin orientation of photoelectrons is determined by the symmetry of wave functions. The spinor in strong spin-orbit systems contain both type of wave functions and the magnitude of these components vary.

To investigate the spin polarization in onedimensional Rashba systems we used a simple Rashba Hamiltonian and numerically solved it. We used both plane-wave expansion and finite difference methods, and verified that the difference between results by these methods is small. Figure 1 shows an example of calculated results. The electron spin is positively and negatively polarized for $k_x < 0$ and $k_x > 0$, respectively, where k_x is the wave number along the one-dimensional direction. The polarization decreases with decreasing $|k_x|$. However, spin polarization is not necessarily low even near $k_x \sim 0$. This is due to the properties of the Rashba Hamiltonian for the states with energy E < 0.



Figure 1: Spin expectation values calculated as a function of k_x for a fixed energy E < 0. Red and green circles show symmetrical and antisymmetrical components of wave functions. Expectation values are weighted with the norm of each component.

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Study on structural elementary excitations at semiconductor surfaces and interfaces

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Our project has been focused on physical properties of structural elementary excitations of semiconductor surfaces and interfaces. We have performed one topic in this year. It is the physical properties of oxygen vacancies (V_O) in SiO₂ at interface with Si. [1] The calculations were performed based on the first-principles calculation. Program package PHASE/0 was employed.

Because of recent progress of integrated three-dimensional metal-oxidecircuits. semiconductor field-effect transistors (MOS-FETs) have been attracting attention. The vertical body-channel-MOSFET has a gate insulating thermally oxide Si film around a Si pillar with a diameter of several tens of nm, but it is considered that a large stress distributes in the oxide film. When a Si nanowire with a width of 50 nm and a thickness of 30 nm is processed by dry oxidation at 1000°C for 80 min, it is known that a compressive strain of about 3% is accumulated near the interface and a tensile strain of about 3% is accumulated near the outer surface.

The strain induced in the oxide film must have an unconventional effect on the film reliability such as dielectric breakdown. It is known that the dielectric breakdown of the oxide film is triggered by V_O -related defects in the film. The V_O -related defects trap holes, and transform into 3-coordinated Si's with +1 charge. These 3-coordinated Si's diffuse and aggregate under a gate-channel electric field of MOSFET operation to create a one-dimensional conductive chain from the Si interface to the gate interface in the oxide film. Then, a gate leak current flows through this chain, and leads to the dielectric breakdown. Since the oxide film of the three-dimensional MOSFETs is subjected by the strain, it is considered that these processes are also affected by the strain.

We focused on the fundamental properties of V_{O} in the oxide film, and investigated the effect of strain on them using the first-principles calculation. We found that the stability of V_{O} increases under compression. We also found that the height of the diffusion barrier increases under compression. In addition, we found that the diffusion barrier height is determined by the Si-Si bond length of the V_{Ω} . Considering the gate oxide film in the vertical body-channel-MOSFET, the V_{O} density increases because the interfacial oxide film is subjected to compressive strain. This suggests that interfacial traps are more likely to occur and performance may be slightly degraded. On the other hand, tensile strain is applied to the surface oxide film to reduce the density of V_{Ω} , but diffusion of V_O is promoted. This means that the reliability of the oxide film is affected by the stain because V_O can diffuse from the interface of the oxide film to the surface.

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Prediction of properties of organic ferroelectrics and piezoelectrics by first-principles calculation

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Organic small-molecular crystals show a variety of crystal structures and electronic properties. Among them, there is a class of compounds called "hydrogen-bonded systems", in which proton transfer causes π -bond dipole switching. Some of them show ferroelectricity or antiferroelectricity [1]. First-principles calculations together with the Berry phase theory successfullty predict spontaneous polarization values of such ferroelectrics [2, 3, 4, 5, 6]. Antiferroelectrics consist of polar subunits. By applying a strong electric field, some of them can be converted into ferroelectric phases. Evaluating polarization of the subunit, the total polarization can be predicted in such induced ferroelectric phases [7, 8].

In 2020, we have applied this approach in predicting electric-field-induced polarization of bis-(1H-benzimidazol-2-yl)-methane (BI2C), in which non-polar and/or polar subunits exist depending on temperture, and the obtained polarization values are in good agreemet with experimetally obtained results [9]. In addition, similarly to our previous work on antiferroelectric squaric acid [10], calculations with a computationally-applied electric field are ongoing for several hydorogen-bonded ferroelectrics and anitiferroelectics.

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Search of accessible surfaces for catalyst informatics Yoyo HINUMA

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High catalytic reactivity in oxides is expected in high index surfaces and at surface defects, such as corners and step edges, since there are cations and anions with more unfavorable coordination environments including low coordination number. Theoretical studies are leading experimental investigations on irregular sites because of the difficulty of the latter.

To increase the volume and variety of the data without compromising veracity, surfaces that are appropriately reconstructed need to be added. From another viewpoint, terminations that are likely to be experimentally accessible need to be distinguished from those that are not because only surfaces that can be experimentally synthesized, preferably with less effort, can be used industrially and therefore contribute to improvement of our society.

This study considered 67 terminations (34 orientations) of β -Ga₂O₃. The automated nonstoichiometric and nonpolar slab-and-model generation algorithm already developed by Hinuma et al. [1,2] was expanded to allow automatic derivation of models where the

topmost and bottommost surfaces need to be reconstructed, which is the case in the normal spinel surfaces in this study [3]. Surfaces which do not have the lowest energy for a given orientation, including terminations found by genetic algorithm calculations (obtained using the USPEX code [4]), or its surface energy can be reduced by forming macroscopic facets [5], were removed.

The following orientations were found to be experimentally accessible in β -Ga₂O₃, in order of increasing surface energy: (100), (20-1), (310), (101), (11-2), (11-3), (11-1). This method can be used for other materials, and will be a powerful tool to find overlooked high-energy surfaces.

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Calculation of multication oxide surface properties for catalyst informatics

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Surface point defects of metal oxides, for instance O vacancies, have a dominant effect on heterogeneous catalysis. The Mars-Van Krevelen mechanism is one of the most frequently encountered catalytic process. In one example, O vacancies on a metal oxide catalyst surface act as reaction sites. The energy minimum required to remove O from a surface, which is denoted as the surface O vacancy formation energy (E_{Ovac}) , can be used to rationalize and predict catalytic performance in such a catalytic process. Calculation of E_{Ovac} requires a slab-and-vacuum model with sufficient spacing between O vacancies, hence some estimation of E_{Ovac} from less costly calculations, such as slab-and-vacuum model calculations with minimum cell size and even bulk calculations, will be effective in screening materials for a given purpose.

The E_{Ovac} of ZnM₂O₄, where M is one of Al, Ga, In, V, Cr, Mn, Fe, or Co, was calculated. These compounds take the normal spinel structure, and the (100), (110), and (111) surfaces were evaluated. The automated nonstoichiometric and nonpolar slab-and-model generation algorithm already developed by Hinuma et al. [1,2] was expanded to allow automatic derivation of models where the topmost and bottommost surfaces need to be reconstructed, which is the case in the normal spinel surfaces in this study [3]. A large variation of up to 3.6 eV in the smallest E_{Ovac} of surface observed for different а was orientations of same material. EOvac was typically higher in a more stable surface within the same compound, which is in line with chemical intuition. A good correlation between E_{Ovac} and E_{bulk} , band gap, and electron affinity was obtained between the same orientation for (100) and (110) surfaces, although the trend for the (111) surface was contradictory.

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First-principles study on complexes of impurity and dislocation in GaN p-n diodes

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The development of power semiconductor devices is one of the key issues for the realization of a sustainable society. GaN has properties suitable for power devices, such as a large band gap, and is expected to be a candidate for next-generation power semiconductor materials. On the other hand, the threading dislocations generated during the synthesis of GaN become a source of leakage current, which impairs the rectifying effect, an important characteristic of the device. It has been reported that the leakage current is related to the type of threading dislocation and the condensation of impurities around the dislocation, but the microscopic mechanism of leakage current generation has not been clarified.

Power semiconductor devices consist of a combination of p-type and n-type layers, with impurities such as Si and Mg doped to each layer. To understand the mechanism of leakage current generation, it is necessary to understand the electronic state in each layer. The electronic structure of the complex of Mg and screw dislocations doped to make the p-layer has been clarified by our previous studies using first-principles calculations and atom probe tomography. [1] The purpose of this study is to analyze the interaction between Si impurities doped to make the n-layer and dislocations, and to clarify the properties of the complex consisting of Si and dislocations.

The effective mass of electrons is smaller

than that of holes in GaN, and the effective Bohr radius, which indicates the width of the impurity states, is larger. Therefore, it is necessary to consider larger systems. For larger system size calculations, we use RSDFT[2, 3], a highly parallelized and efficient first-principles code. In this study, we consider a screw dislocation with the Burgers vector [0001]. The dislocations break the periodic structure and we use a supercell. In order to avoid these strains affecting each other at the periodic boundary, a vacuum layer is inserted in the lateral directions of c-axis.

We consider a 21 Å \times 27 Å \times 30 Å supercell, which includes about 800 atoms. An Si atom is substituted at a Ga site. In order to analyze the binding energy of Si, we performed calculations for several substitutional sites. We optimized the atomic positions and obtained the stable structures of the complex. We are analyzing the results for the binding energy of Si to the screw dislocation.

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Simulation of scanning tunneling microscopy images of graphene ribbons with edges

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We are aiming at elucidating local electronic structures of finite-size graphene sheets and their impact on scanning tunneling microscopy (STM) images. For this purpose, we have started first-principles calculations of singlelayer graphene ribbons possessing either zigzag or armchair edges by the use of a simulation package named STATE (Simulation Tool for Atom TEchnology). STATE is based on the density functional theory. The exchange and correlation potential is described by the generalized gradient approximation by Perdew-Burke-Ernzerhof (GGA-PBE). We also used both plane-wave basis а set and pseudopotentials. When running STATE, we first defined the atomic structure of a finite-size graphene. This model as well as other parameters were placed as an input file on a supercomputer. The self-consistent field method was employed, which is an iterative method that involves selecting a Hamiltonian, solving the Kohn-Sham equation to obtain a more accurate set of orbitals, constructing the potential for each wave function, and solving the Kohn-Sham equation again with these until the results converge. In order to draw a map of local density of states, an electron density was integrated over a specific energy window, or *a* eV, below HOMO (Highest Occupied Molecular Orbital). At each (*x*, *y*) coordinate, a *z*-height possessing the same electron density (6.72×10^{-4} /Å³) was investigated and its contour map was depicted. This approximates a simulated STM image at the sample bias of *a* V. We used the module (intel/18.0.5) for the compilers and mpt/2.16 for MPI library. The set of calculation was usually executed on F4cpu or F36cpu with suitable nodes in ISSP.

To check the performance of our calculation, we modeled a graphene nanoribbon with zigzag edges terminated by H atoms. Figure 1(a) shows a simulated STM image of a zigzagedged ribbon named C28 at the sample bias of -1.0 V. C28 indicates the ribbon width possessing 28 dimer lines across the width. In Fig. 1(b), a hexagonal carbon network is superimposed in the image in Fig. 1(a). Figure 1 shows that either a hexagonal or a triangular pattern is formed in the interior of the ribbon whereas isolated bright spots are formed at both edges of the ribbon. The latter is caused by the localized electronic states at a zigzag edge, which agrees with literature [1]. In the next fiscal year, we are going to characterize the distribution of local charge densities of the armchair-edged graphene ribbon and to unveil its relationship with an STM image around the Fermi level.

Regarding this project, we had three oral presentations at domestic meetings in 2020 [2-4].



Fig. 1 (a) Simulated STM image of zigzagedged graphene nanoribbon (C28). (b) A carbon network is superimposed in the image in (a).

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A theoretical study on the effect of impurity doping on the thermoelectric performance of environmental friendly silicide SrSi₂

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Thermoelectric semiconductors, especially those operating at low temperatures, are expected to be applied to power generation systems that utilize the vaporization of liquefied natural gas as cold heat energy sources, and to self-powered wireless sensors.

 α -SrSi₂ has been identified as a potential TE material, and its main attributes are its light weight, its non-toxicity, and the worldwide abundance of its constituent elements. α-SrSi₂ has relatively good power generation performance, with a dimensionless figure of merit ZT = -0.15 at 300 K [1] and p-type composition is conduction when the stoichiometric. For practical use, in order to further improve the p-type thermoelectric performance and achieve n-type conduction of α -SrSi₂ so as to configure pn devices, it would be necessary to quantitatively understand the electronic structure through experimental studies and theoretical calculations.

The electrical properties of polycrystalline α-SrSi₂ have been examined by M. Imai et al. [2], who revealed that α -SrSi₂ is a narrow-gap semiconductor with an energy gap of 35 meV and that its dominant carriers are holes. Their results, however, were not consistent with the electronic-structure results of previous calculations for which density-functional theory (DFT) with the conventional generalized gradient approximation was used. Most of the calculated bandgap values were about 0 eV or less, which is much smaller than the experimentally observed values. This difference makes it difficult to predict the thermoelectric properties from theoretical considerations.

This year, we carried out DFT calculations of the transport characteristics of α -SrSi₂ using the Heyd–Scuseria–Ernzerhof screened hybrid functional, and then compared the experimentally measured thermoelectric properties with the computational results.

The bandgap of the polycrystalline α -SrSi₂ grown by vertical Bridgman method estimated from the carrier density dependence on temperature was 13.1meV. When the mixing parameter of the Hartree-Fock contribution to the exact exchange was 18.7%, the bandgap was estimated to be 13.27 meV, which almost reproduces the experimental E_{g} value. Furthermore, Seebeck coefficients were calculated using the Boltzmann transport theory, and the results obtained using the chemical potential that matches the carrier concentration, which was determined experimentally, were in good agreement with the temperature dependence of the Seebeck coefficient obtained experimentally. It was concluded that first calculations using the hybrid principles functional successfully predict can the thermoelectric transport properties of narrowgap thermoelectric semiconductors.

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STM simulations for Si(111)7 \times 7 surfaces

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Using scanning tunneling microscopy (STM), author's group has been studied ironsilicides formation on Si(111) [1] prepared in ultra-high vacuum. In the initial stage of Si(111) 7×7 with isolated Fe atoms, we observed 5 different adsorption types in experimental STM images [2]. Using the super computing system in the institute for solid state physics, we carried out first principles calculations for several configurations of Fe atoms on Si(111)4 × 4 surface in the last year. The small-size 4×4 surface has an advantage of fast calculation compared to that in the 7×7 surface, maintaining the specific 7×7 surface property (dimer – adatom – stacking-fault structure): 4 Si adatoms on 2×2 T₄ sites, and 2 of 4 restatoms terminated with H atom, in a 4×4 unit cell.

On the basis of these results we extended the calculations to 7×7 surfaces in this year, firstly focusing a clean surface using the calculation package of Simulation Tool for



Fig. 1. Schematics of clean Si(111) 7×7 surface model in side (upper left) and top (upper right) views, and simulated STM images in filled states (left panel) and empty states (right panel) at different sample bias voltages (Vs). The red arrow represents side-viewing direction.

Atom TEchnology (STATE)-Senri [3]. The calculated clean 7×7 model consists of a Si adatom-layer, six Si-layers, and a bottom H-terminated layer, with 347 atoms. All atoms except the last Si layer and bottom H layer are fully relaxed at <0.05 eV/Å from atomic positions predicted in the 4 × 4 model, under 700 bands without spin polarization. STM images are simulated using a special STM displaying tool [4].

The obtained STM simulation images in Fig. 1 display 12 adatoms in a 7×7 unit cell at the all Vs, and successfully 6 restatoms at Vs = -1.0 V. We also recognize that corner adatoms (COA) are brighter (higher) than center adatoms (CEA), and atoms on a faulted half (FH) unit cell are brighter (higher) than those on an unfaulted half (UH) unit cell, in filled states. These features are consistent with the experimental results. The relaxed 7×7 clean surface structure can be applied for the starting

structure capturing an Fe atom, extension of the Fe adsorption configurations in the 4×4 models.

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First-principles Study of Defects of Magnesium Alloys

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Magnesium (Mg) has been of increasingly interest from the engineering viewpoint, because of its low density and relatively high specific strength.

In this study, we calculate generalized stacking fault energy (GSFE) surface, to evaluate activation of each slip system in Mg, using first-principles calculations. In GSFE calculations for pyramidal slips, it is important to take account of relaxation of atomic configuration perpendicular to the slip direction. For the first-pyramidal slip, out-plane atomic relaxations were observed during the slip process. The out-plane atomic relaxations reduce the GSFE and cause an energy minimum on the curve, corresponding to the stable stacking fault energy (SSFE). For the second-pyramidal slip, in-plane atomic relaxation perpendicular to the slip direction was associated with the stable stacking fault.

In order to investigate effects of alloying elements, we carried out the GSFE calculations with alloy models in which one solute atom was substituted at the slip plane. The unstable stacking fault energy (USFE) and SSFE for the first-pyramidal slip were more reduced by addition of the solute atom of the larger atomic radius. On the other hand, changes in USFE and SSFE for the second-pyramidal slip were not monotonic with respect to the atomic radius of the solute atom.

In Mg-Y alloy, enhanced activation of pyramidal slips improves ductility. It has been suggested that the activation of pyramidal slips was attributed to intrinsic I_1 stacking fault (SF) energy stabilized by Yttrium addition. We investigated defect nucleation in the vicinity of a pre-existing intrinsic I1 SF by molecular dynamics simulations. While formation of (11-21) twin was observed under shear stress on <c+a> (0001)along [11-20], partial dislocations were generated with SFs for higher resolved shear stress for pyramidal slips. The dissociation reactions of the dislocations at the side ends of the I₁ SF were energetically evaluated, and it was implied that nucleation of the <c+a> dislocations on the first-pyramidal planes is more favorable than on the secondpyramidal planes.

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Elucidation of the mechanism of self-ordering phenomena at the interface between organic and inorganic materials

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We have studied an interface system between an inorganic solid surface and organic molecules, PTCDAs on Ge(001) surface using the Density Functional Theory (DFT) calculations with the climbing image nudged elastic band method and kinetic Monte Carlo simulation. All MPI parallelized DFT calculations were performed using Vienna Ab initio Simulation Package (VASP) version 5.4.4 on the ISSP's new supercomputer system.

First, we elucidated the hopping mechanism of the isolated adsorbed PTCDA molecules on Ge(001) surface. [1] Subsequently, we simulated that a PTCDA molecule hops on the Ge(001) under the intermolecular interactions as shown in Fig. 1. It was found that lone adsorbed PTCDA molecules cannot hop on Ge(001). On the other hand, they can hop under the intermolecular 500K. interactions at Successively, we performed kinetic Monte Carlo simulations using the activation energies obtained by DFT calculations for the hopping of PTCDA molecules in various proximity adsorption configurations at medium coverage. As a result, the formation of one-dimensional molecular chains was confirmed.

Next, the flip-flop motion of the Ge(001)

surface dimer was investigated to explicitly account for Ge(001) surface dimer conditions. On the Ge(001) clean surface, the obtained activation barriers for dimer flipping under various dimer configurations are enough small to overcome at high temperature as well known in many previous experiments. The activation barrier of surface dimers between adsorbed molecules was larger than that of the clean surface, but sufficient to overcome it at 500K.



Fig. 1: The hopping of PTCDA on Ge(001) under the intermolecular interaction.

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Study on Machine Learning Model of Carrier Dynamics in Semiconductor Devices

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In a two-dimensional nanowire system with random impurity distribution, we developed a model to predict the electron transmission probability from the impurity distribution by combining the time evolution of the electron wave function and machine learning.

Electron conduction in nanoscale twodimensional wires with random impurity distribution is investigated. To prepare the dataset for machine learning, the timedevelopment of an electron wave-packet is calculated, and obtain the transmission probability. The time-dependent schrödinger equation is solved where the finite difference method is employed with the second-order split operator method [1,2]. Note that a supercomputer system was used for these time-consuming time evolution calculations. Then, a model that can predict the transmission probability of electron wave packets from the space distribution of impurities build by using the machine learning. Through this process, the ways to extract the features of the transmission on this system is investigated.

The impurity distribution can be reproduced when the central coordinates are available. Therefore, this can be used as a feature. However, this does not directly include the whole shape of the potential distribution. Therefore, the features of the system were extracted by analyzing the time variation of the electron density distribution using time evolution calculations. For example, the transmission probability with impurity in the nanowire is sensitive to the position shift of impurities for y-direction (see Fig.1). As the machine learning method, a Random Forest (RF) is employed for modeling. The mean absolute error is evaluated. As the result, the accuracy of the model is improved by performing machine learning based on the extracted features. The proposed method provides a new perspective for analyzing the motion of electrons in nanoscale semiconductors.



Fig.1 Transmission probabilities with the electron energy where the positions of impurities are shifted 3.3 nm to y-direction between the case (a) and (b).

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Temperature dependence of liquid ethanol based on semiclassical Kramers-Heisenberg formulation

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The hydrogen bonding in the condensed phase plays a important role in the understanding related liquid such as water and liquid alcohols. We have studied temperature dependence of liquid ethanol using X-ray emission spectroscopy (XES) theoretically and experimentally. The approach of combining theoretical and experimental methods is important for obtaining the hydrogen bonding information. The experimental XES ware carried out using the BL07SU HORNET station at SPring-8.

In theoretical method, combining molecular dynamics simulations (MD) and density functional theory (DFT) calculations performed. To construct structure of ethanol in liquid phase classical MD are adopted in the NVT ensemble at 240 K and 340K and 1 bar using GROMACS 5.1.4 with OPLS force field. To calculate the XES spectra, the DFT calculation performed using deMon2K program package. The detail of DFT calculation method are following the previous studied for methanol [1] and ethanol [2]. In short, the 17 ethanol cluster obtained from final snapshot of MD simulations are



extracted randomly. The number of snapshots are 100 for each temperature. XES spectra can be calculated by applying semi-classical Kramers-Heisenberg (SCKH) formulation to the electronic state of each snapshots. Fig A shows the XES spectra based on SCKH. The calculated spectra well correspond to the experimental spectra. Now, we analyze the MD snapshots and investigate the relationship between XES spectra and hydrogen bonding.

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Development of analysis method for molecular crystal surface using wave number space-resolved photoelectron spectroscopy

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By using wave number space photoelectron spectroscopy, it has become possible to obtain a photoelectron momentum maps (PMMS) of a molecular thin film in a short time. This allowed us to obtain tomography of the wavefunction. It is suggested that more information can be obtained by analyzing PMMS in detail. We have been analyzing the surface of molecular crystals with the aim of establishing a method for analyzing momentum maps based on the multiple scattering method. For the initial state, we refer to the electronic state of the adsorption system calculated by Vienna Ab initio Simulation Packge (VASP) [1,2]. So far, we have suggested that by PMMS, it may be possible to identify the adsorption position of molecules adsorbed on the substrate surface [3]. In 2020, we expanded the sample to a more complex system. We placed VASP on the

Supercomputer of Institute for Solid State Physics and performed two calculations.

1. Structural optimization and multiple scattering calculation of PTCDA / Ag (111).

The initial position of 3,4,9,10-Perylenetetracarboxylic dianhydride (PTCDA) was set to the Short-bridge site on Ag (111), and structural optimization was performed. Since PTCDA does not contain transition elements, the calculation cost is low. Periodic DFT calculations were carried out with VASP code using the projector augmented wave (PAW) method with a plane wave energy cutoff of 400 [eV] and the PBE exchange-correlation functional. The criterion convergence chosen for the SCF cycle was 10⁻⁸ eV, and optimization were considered converged once the forces on all atoms were lower than 10^{-8} [eV/Å] The slab was 12.1 x 12.1 [Å] large, and 10 [Å] thick (60 Ag atoms, 2PTCDA per unit cell) with a vacuum separation 20 [Å]. The three lowest layers were frozen during optimizations. The Brillouin zone was sampled with a 4x4x1 k-point grid. Electron occupancies were determined according to a Methfessel-Paxton scheme (order1) with an energy smearing of 0.2[eV].

As a result of structural optimization, PTCDA was curved in an arc with respect to the surface. PMMS calculations (using our computer) were performed using these coordinates. The PMMS has changed significantly compared to the results without the substrate. When I did the same calculation on multiple sites, I found that PMMS was different for each site. This indicates the possibility of obtaining information on the adsorption position from PMMS.

2. Structure optimization and multiple scattering calculation of CuPc and TiSe₂

In order to calculate the PMMS of Copper (II) phthalocyanine (CuPc) / TiSe₂, the structure of CuPc and TiSe₂ was optimized. First, we performed structural optimization of CuPc. CuPc has a large number of constituent atoms and contains transition elements with spin. The calculation cost is high and the calculation method is complicated. Highest Occupied Molecular Orbital (HOMO) -1 was not calculated in the correct position when Generalized Gradient Approximation (GGA) was used as a functional. It has been reported that HOMO -1 can be calculated correctly using the hybrid functional according to Heyd et al. (HSE), but the calculation cost is high [4]. We also tried this, but couldn't succeed.

Next, the structure of TiSe2 was optimized. TiSe2 takes the CDW layer at low temperature and undergoes a phase transition to the normal phase at around 200 K [5]. To obtain information about the relationship between σ and temperature during smearing, we calculated the temperature dependence of the charge density wave (CDW) structure and the normal phase. Structural optimization was performed for two layers of TiSe2. The calculation conditions are the same as those described above. The normal layer extended the (1x1) structure to (2x2). For the CDW layer, the coordinates were entered based on the paper [5].

Figure 1 shows the temperature dependence of energy. The horizontal axis is temperature, and the longitudinal axis is energy, white triangles are the CDW layer, and black squares are the normal phase. From this calculation, it was found that 200K at which the phase transition occurs is approximately $\sigma = 0.3$. This calculation provided us with a guideline to use σ = 0.1 for low temperature calculations and σ = 0.4 for room temperature calculations in future.



Figure 1. Energy dependence of sigma

Using these calculation results obtained, we plan to calculate the structural optimization and electronic state of the adsorption system in 2021.

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Analysis of local quantities of electron field in material surface

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The local physical quantities, which is defined in the framework of quantum field theory (energy-momentum tensor density, current density, chiral current density, and so on), are significant to understand physical or chemical properties of surface materials, since it is not easy to be explained by bulk feature in solids such as a band structure.

In the previous work, we developed a program code which enables us to calculate local physical quantities as a post-process calculation from OpenMX [1] (DFT calculation program code) in order to evaluate the local physical quantities in large periodic systems. To proceed the discussion on a relation between the chemical bonding and the local electronic stress, recent research revealed the importance of evaluation of local physical quantities in a certain energy range. Therefore, in this project, we developed a program code which enables us to calculate local physical quantities in a specified energy range or orbitals.

The physical and chemical nature around the interaction region between atoms in Ag(FCC) were investigated as a demonstration. In Fig. 1 (a), the positive stress (tensile stress) and the eigenvectors form the spindle structure [2], which visualize a covalent bonding state. On the other hands, in Fig. 1 (b), the negative stress (compress stress) and the eigenvectors form the anti-spindle structure [2], which visualize an anti-bonding state. Moreover, the distribution of the isotropic negative stress as shown in Fig. 1 (d) reveals the "liquid" character of bulk metallicity. These characterizations will help us to understand chemical bond formation between a material surface and a molecular cluster deeply.



Figure 1: (a) Density of state, (b)-(d) distributions of maximum eigenvalues and eigenvectors of the electronic stress tensor density of Ag(FCC).

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