3.2 First-Principles Calculation of Material Properties

Clarification of Microscopic Mechanisms of Semiconductor Epitaxial Growth and Device-Interface Formation by Large-Scale Quantum-Theory-Based Computations

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In the fiscal year of 2021, on the basis of the total-energy electronic-structure calculations and molecular dynamics simulations within the density-functional theory (DFT), we have studied the epitaxial growth of wide-gap power semiconductors, atomic and electronic structures of semiconductor-insulator interfaces. The main computational tools are our RSDFT (Real Space DFT) code and RS-CPMD (Car-Parrinello Molecular Dynamics) code as well as VASP code. Specifically, we have studied 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 danglingbond free interface of GaN and a gate insulator [3], and 4) the structural identification of the nano-meter-scale GaN growth surface using Bayesian optimization [4]. We have also developed 5) an order-N orbital-free DFT (OF-DFT) scheme by inventing kinetic-energy functional using the neural-network [5]. The below is the explanation of the issues 4) and 5) above.

Structural identification of GaN (0001) by Bayesian optimization

GaN, a premier material in optoelectronics is now emerging in power electronics due to its superior physical properties. However, to guarantee the expected high performance of the devices, it is necessary to forge high-quality epitaxial films of GaN. Despite many experimental efforts in this decade, the current quality of GaN crystalline films is unsatisfactory for replacing Si power devices in the market. To unveil the growth phenomena, atom-scale identification of the surfaces on which atomic reactions take place is an essential prerequisite.



Fig.1: Top view of the stable 6x6 surface structure discovered by the present Bayesian optimization (structure name #130 in Fig. 2). The black dashed line indicates a 6x6 area. Brown, blue and white atoms correspond to Ga, N and H, respectively.

We have identified the stable structure of nanometer-scale GaN (0001) surfaces with Gaand H-adsorbates, which are the fundamental basis for crystal growth modeling, by large-scale density-functional calculations combined with machine learning Bayesian optimization technique. We have been able to reach a single stable structure (Fig. 1) with satisfactorily low mixing enthalpy by 130 trials based on Bayesian optimization among 23C15=490,314 candidate structures (Fig. 2). We have found that the obtained structure lacks any postulated high symmetry previously introduced by human intuition, satisfies electron counting rule locally, and shows a complex adsorbate-rearrangement, leading to lower mixing enthalpy. The present scheme of Bayesian optimization combined with first-principle calculations paves a way toward identifying surface structures with a larger scale



Fig. 2: History of the exploration of the surface structure by Bayesian optimization. The objective is to minimize the mixing enthalpy. The black dashed line corresponds to the minimum value of the baseline models, and the red marker corresponds to the most stable structure #130 in the present exploration.

and more complex adsorbate-arrangements, and then determination of surface phase diagrams for design of further preferred growth conditions.

Order-N OFDFT scheme with machine learning

A scheme in DFT in which the kinetic energy functional is expressed by the sum of singleparticle orbitals squared is introduced by Kohn and Sham (KSDFT) and has been applied to a numerous number of applications with unprecedented success.

However, solving the Kohn-Sham equations for all the occupied orbitals in the system is a computational burden scaling with the system size N as $O(N^3)$. The scheme with lower-order scaling is highly demanded in materials science and also in advancing DFT. One of the solutions in a legitimate way is the orbital-free densityfunctional theory (OFDFT) in which the kinetic energy functional is expressed as a functional of the electron density $\rho(r)$ itself and an single Euler equation rather than Kohn-Sham equations is solved, being expected to be O(N) scheme.

We express the kinetic energy functional as

$$T[\rho] = \int \tau^{TF}(r) F(s^2, q; \mathbf{W}) dr ,$$

where τ^{TF} is the Thomas-Fermi kinetic energy density, the enhancement factor F is expressed as a gradient expansion with $s = |\nabla \rho| / [2(3\pi^2)^{1/3} \rho^{4/3}]$ and $q = \nabla^2 \rho / [4(3\pi^2)^{2/3} \rho^{5/3}]$. The enhancement factor is determined by the deep learning using the neural network where the set of weight parameters **W** is determined so as to minimize the cost function L expressed in terms of the kinetic energy functional derivative $\delta T/\delta \rho$:

$$L = \frac{1}{N_t} \sum_{n=1}^{N_t} \frac{1}{2} \left[\frac{\delta T}{\delta \rho}(r_n) - \frac{\delta T^{KS}}{\delta \rho}(r_n) \right]^2 ,$$

where the kinetic-energy functional derivative is computed at each real-space mesh points and compared with the corresponding values by the Kohn-Sham scheme. As a training data, we use the functional derivative in diamondstructured (ds) carbon at some mesh points.



Fig. 3: Computational time of KSDFT and OFDFT. Comparison of (a) t1 (subspace diagonalization), t2 (conjugate gradient minimization and gram-schmidt diagonalization), and t3 (SCF mixing), and (b) total time for the SCF iteration. The test system is 4H-SiC supercell with the number of atoms of 576 -4704. In both (a) and (b), data points obtained by KSDFT and OFDFT are plotted in red and blue colors, respectively.

The transferability of the kinetic-energy functional obtained by the deep learning with the training data of only diamond has been examined by the application to 23 test systems which include semiconductors, metals, ionic insulators and some of their polytypes: diamond, graphene, ds-Si, facecentered-cubic(fcc)-Si, beta-tin Si, zincblende (3C)-SiC, body-centered-cubic(bcc)-Li, fcc-Al, fcc-Cu, bcc-Na, and NaCl. The structural properties, i.e., lattice constants and bulk moduli of all those materials obtained by the present functional shows better agreement with the corresponding values by the Kohn Sham scheme.

The order N behavior of the computation time in the present OFDFT scheme is clearly shown in Fig. 3.

The group id codes for the achievements above are k0042 and m0037.

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First-principles prediction of stability and functionality of complex materials

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In recent years, considerable progress has been made in predicting material properties using the density functional theory (DFT) simulations and the DFT-based model simulations. In our group, we have developed a scheme to construct the exchange-correlation (xc) functional of the Kohn-Sham DFT by machine-learning the many-body wave function of small molecules [1,2]. In our prior study [1], small molecular systems were simply used as the learning set, but the success was limited to molecular systems only; problems remain in crystalline systems. To overcome this problem, physical conditions applicable to general materials were introduced into the learning process, and the resulting xc functional within the meta-GGA format was found to significantly improve the applicability [2]. The improved xc functional was implemented to an electronic structure calculation package VASP and is ready to distribute to supercomputer users. For further progress, we focused on techniques for the DFT for classical systems (classical DFT) and, in this case, low-density approximation of the nparticle density was found to be effective [3]. We consider that applying this method to electronic

systems will also be effective not only for electronic systems but also the hybrid solvation models that we have long been studying.

In view of ability of meta-GGA in describing the Mott insulators, this functional was used for our study on exotic materials such as the solid oxygens in the high-pressure phases and the Hgcuprate (HgBa₂Ca_{n-1}Cu_nO_{2n+2+x}) [4]. We found that the lattice parameters and the bandgaps become consistent with experiments with this functional, indicating that we are now at the start line of quantitative research.

One of the open problems of DFT-based simulation is to incorporate the nuclear quantum effect. Although the path integral molecular dynamics (PIMD) simulation is an established first-principles scheme, it becomes difficult to reduce the statistical fluctuation as the temperature is reduced and thus different scheme is needed. To overcome this problem for the hydrogen diffusion on metal surfaces, we have reformulated the quantum transition state theory that is based on a semi-classical approximation using an apparently full-quantum formulation. The fluctuation effect was found to be significantly reduced with the new method

[5].

We have also investigated the effect of nuclear quantum motion on the bandgap of insulators. This was done using the Allen-Heine-Cardona (AHC) theory and its extensions [6]. Herein the Debye-Waller terms of AHC was reformulated using the momentum operator, by which some of the electron-phonon coupling terms can be added to infinite order.

The description of electrochemical interfaces is a challenging problem of first-principles simulations, on which our group has long been studying. The difficulty of the simulation is due to existence the electric dipole layer (EDL) that can extend macroscopically. The thickness of EDL, however, is reduced to several nm when the ions are densely distributed as in strong acidic/alkaline solutions, but methods for the simulation has been developed only for the solution side. Therefore, EDL existing in the solid side of the interface remains to be a challenge; this is the case when semiconducting electrode is used. To simulate the ZrO_xN_{2-x} electrode, which is a candidate for Pt-free electrode of the next-generation fuel-cells, we have applied the first-principles Monte Carlo simulation with abICS [7] and then sped it up with the help of a machine-learned model potential. By the simulation, we could successfully obtain the distribution of oxygen vacancies and the nitrogen impurity atoms, and the result was used to describe the EDL. We further investigated efficiency of the oxygen

reduction reaction occurring thereon and considered the effect of liquid water as well. These results were shared with experimentalists and helped them in planning the electrode development.

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

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1 Introduction

Keeping in mind the importance and difficulty of atomistic simulations on structures and dynamics at surfaces, interfaces and defects toward development of novel information and energy devices, we have been investigating atomic structures and atom dynamics in various systems by first-principles calculations, in some cases combining them with multi-scale or machine-learning approaches. In the following, two of our recent results are described.

2 Band alignment of $LiTi_2O_4$ and $SrTiO_3$

Recently, it was found in thin-film solid-state Li batteries using LiTi_2O_4 thin films as positive electrodes, the spontaneous Li-ion migration between the solid electrolyte (Li₃PO₄) and LiTi_2O_4 occurs in the case of the conducting substrate, Nb-doped $\text{SrTiO}_3(001)$ [1]. That is, the LiTi_2O_4 turned to the $\text{Li}_2\text{Ti}_2\text{O}_4$ phase spontaneously.

To understand the above, we have investigated the band alignment of the $LiTi_2O_4/SrTiO_3$ superlattice model using the density functional theory (DFT) calculations. Here, we adopted the $SrTiO_3$ without Nd doping to examine the band alignment before the charge transfer. The calculated projected density of states (pDOS) reveals that the bottom of the conduction band is located above the Fermi level $E_{\rm F}$ in the central region of the SrTiO₃ layer. Since $E_{\rm F}$ of the Nb-doped SrTiO₃ is considered to be located near the bottom of the conduction band, this result suggests the electron transfer from the Nb-doped SrTiO₃ to LiTi₂O₄. From this result and the absence of a potential gradient in the metallic LiTi₂O₄ layer, we can say that the transferred electrons charge on the surface of LiTi₂O₄, which leads to a decrease in the electrochemical potential of Li ions at the LiTi₂O₄ surface. Consequently, the spontaneous migration of the Li ions occurs.

The present result suggests the possibility to control the spontaneous Li-ion migration between the solid electrolyte and LiTi_2O_4 by tuning the electrochemical potential difference via the substrate selection.

3 Neural network potential for multiple charge states of defects

In semiconductors and insulators, defects and impurities sometimes take various charge states depending on $E_{\rm F}$. To examine the point defect behavior in such multiple charge states, we have proposed a new scheme of neural network potential (NNP) [2]. In our scheme, only minimal modifications to the conventional scheme [3] is needed: One system charge ($Q_{\rm sys}$) node is added in the input layer. Here, $Q_{\rm sys}$ is defined as a constant value times a charge state of the considered supercell divided by its volume.

We have applied this scheme to wurzite-GaN with a nitrogen vacancy [2]. For the charge states of the vacancy, 0, 1+, 2+, and 3+ have been considered. By performing molecular dynamics simulations using the Stillinger-Weber potential, we have generated 4,550 pristine GaN structures and 4,550 structures with a N vacancy in total. Then the DFT data have been obtained for these sturctures. Total number of the DFT data is 22,750, because calculations have been performed for 0, 1+, 2+ and 3+ charge states in the cases of the structures with a N vacancy.

The NNP constructed using our scheme and the aforementioned data predict the total energies and atomic forces accurately for all the charge states: The root-mean-square-errors of the total energies and atomic forces were, respectively, 1.45 meV/atom and 63.8 meV/Å for the training dataset and 1.44 meV/atom and 64.6 meV/Å for the test dataset. Moreover, it has reproduced the phonon band structures and themodynamic properties of the defective systems fairly well.

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Quantum Simulations on Dynamical Heterogeneous Catalysts

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In 2021-2022, we carried out theoretical investigation of chemical processes at surfaces and interfaces, adsorption and reaction of polymeric formic acid on Cu(111), NO adsorption and dissociation on Cu(100), oxygen vacancy migration in SrFeO_{3- δ} and Sr₃Fe₂O_{7- δ}, dry reforming of methane on Co catalysts, and adsorption of CO₂ on terrace, stepped and defect sites on Pt surfaces.

In this report, we report the dry reforming of methane on Co catalysts, [1]. The emissions of greenhouse gases (CH_4 and CO_2) are rising exponentially due to human activities and increased energy demand, contributing to global warming and climate changes. To make use of CH_4 and CO_2 into renewable energy, catalytic dry reforming of methane (DRM) is an efficient pathway to convert them into syngas (CO and H_2). Currently, active transition metals known to be capable of catalyzing DRM are mainly group VIII elements such as Ru, Rh, Ni, Co and Pt. Among them, supported Ni could be the most studied catalyst due to its relatively high activity and low cost. However, the efficiency of Ni is widely known to be easily suppressed by carbon deposition.

On the other hand, Co is particularly interesting due to its excellent catalytic activity and considerably low carbon deposition. Experimentally, Co is more carbon resistant than Ni. Co could enhance the adsorption of CO_2 , which helps to inhibit the deposition of carbon and enhance carbon removal.

To gain insight into the occurrence of carbon deposition vs removal during DRM, we calculated the CO^{*} formation reaction through the surface reaction of C^* and O^* , and the CC* formation reaction through the C-C coupling. The present direct quantitative comparison between the activation energies of the involved reactions would clarify the competition between carbon deposition vs removal over different Co surfaces. In addition, we further compared our results with those of Ni to reveal the cause of the lower carbon deposition on Co than on Ni. The quantitative comparison of CO_2 activation, C-C coupling, and CO^* formation over Co and Ni could reveal the theoretical underlying mechanism of lower carbon deposition on Co than Ni.

The overall energy diagram illustrating the minimum energy pathway for reactions between CO_2 and C^* on all the investigated Co surfaces, which includes CO_2 activation (green region), O^* and C^* diffusion (blue region), and the competition between CO^{*} formation and C-C coupling (red region), is summarized in Figure 1. We consider the reaction of CO_2 with two predeposited C^{*}. As observed in Figure 1, the rate-determining step for the reaction between CO_2 and C^* on all the investigated Co surfaces is located in the red region, indicated by the energy needed for CO^{*} or CC^{*} dimer formation. Two conclusions can be drawn from evaluating the competition between CO^{*} and CC^{*} dimer formation on each surface. First, carbon graphitization is dominant on (111) and possibly on (110) because the CC^{*} dimer final state is of lower or equal energy r elative to its respective initial state, indicating that the CC^{*} dimer is stable and does not dissociate into atomic C*. In addition, CC^{*} dimer formation on these surfaces has a lower activation energy than CO^{*} formation. Even though the CO* final state is more stable than the CC^{*} dimer, the stability of the CC^{*} dimer compared to its initial state might give rise to nonreversible carbon graphitization, which could eventually cover the active surfaces. Thus, on (111) and (110), CC^{*} dimer formation has a higher degree of preference than CO^{*} formation. By combining this result with the fact that (111) is the most exposed surface of a Co nanoparticle, as indicated by the Wulff constructions, we hereby deduce that the origin of carbon deposition that leads to catalyst poisoning during DRM is caused by the high degree of preference for C-C coupling than CO^{*} formation, especially on (111). Second, on (100), (211), and (221), CC* dimer formation is not favorable because the CC^{*} dimer final state has a higher energy level than its respective initial state, indicating that the CC^{*} dimer is easily dissociated into two atomic C^*s . In addition, the CO^* final state is more stable than the CC^{*} dimer. The combination of the above mentioned points implies a higher degree of preference for CO^{*} formation on (100), (211) and (221), even though the energy needed for CC^{*} formation might be lower than that of CO^{*} formation. On the other hand, other surface reactions, such as CO_2 activation and surface diffusion of O^* and C* have lower activation energies than those of CO* and CC* dimer formation on each respective surface (Figure 1). The low energy needed for CO_2 activation implies that surface O^*s are sufficiently supplied for CO^{*} formation. In addition, the kinetic rate constants for CO* formation, CC* formation, and CC* dissociation over all the investigated surfaces were calculated and discussed in Section 12, S.I.. The result corresponds well with the findings where C-C coupling has the highest degree of preference on (111), followed by (110), however, is not favorable on (100), (211), and (221).



Figure 1: Energy diagram showing the minimum energy pathways of reactions between CO_2 and two C^{*} on FCC Co (111), (110), (100), (211), and (221).

The present study provides a comprehensive clarification on the mechanism of DRM, specifically on the surface reaction of CO_2 and C^* on the major flat and step FCC Co surfaces, namely, (111), (110), (100), (211), and (221). and/or promoted Co nanoparticles for DRM to restrict C-C coupling.

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Understanding superionic conductivity in disordered systems using machine learning potential molecular dynamics and Monte Carlo sampling

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The competition between order and disorder in materials leads to a wide variety of materials functionalities such as electronic, ionic, and thermal conductivity/insulation and catalytic activity. However, because of the huge number of degrees of freedom in disordered systems, successes in theory-driven design of such functionalities have been rather limited. In this research project, we tackled this problem through a combination of first-principles calculation and machine learning.

For disordered crystalline systems, we employed our abICS (ab Initio Configuration Sampling) framework for deriving an on-lattice neural network model from first-principles calculations [1] and used that to perform replica-exchange Monte Carlo sampling. One system that we have been examining is heavily Sc-doped BaZrO₃, which is known as a promising perovskite proton conductor for solid oxide fuel cells [2]. The oxygen vacancy is known to be the active site for the hydration reaction, which is the key reaction to introduce protons into the system. However, it is yet unclear which of the three types of vacancy environments, Sc-V₀-Sc, Sc-V₀-Zr, or Zr-V₀-Zr, are responsible for the hydration behavior. Using abICS, we have clarified that the former two are active sites for hydration, while the Zr-V₀-Zr site seldom exists under normal thermodynamic conditions and contributes little to the hydration reaction [3].

In the case of amorphous systems, we considered the use of the neural network potential (NNP) approach originally proposed by Behler and Parinello [4]. Although the neural network potential methodology seems to be a well-established approach at this point, we have found that it is quite a challenge to apply to many-component glass systems. This is because the NNP requires that the training set sufficiently covers the thermodynamically relevant configuration space, which will be huge for many-component glasses. We observe regularly that NNP molecular dynamics (MD) calculations 'fall apart' and exhibit completely unphysical structures after it wonders into regions of previously unlearned configuration space. To tackle this issue, we have been trying an active learning cycle approach where we take structures from the NNP-MD trajectory, perform DFT calculations on those structures, add them to the training set, and run the NNP-MD again with the new NNP. As shown in Fig. 1 for the AgI-As₂Se₃ superionic mixed glass system, increasing the number of cycles leads to improvement in the NNP predictions, although we have not been able to fully converge the low energy structures yet.

We have also been examining the feasibility of training on DFT data using high-cost functionals such as the HSE06 hybrid. Since it is not feasible to obtain a long enough MD trajectory to use as the training set with HSE06, we first performed first-principles MD using relatively low-cost GGA functional. the Afterwards, we took a subset of the structures (~1500 structures) and recalculated them using HSE06, which were then used as the training set in NNP training. This approach was applied to amorphous GeO₂, and we were able to obtain structure factors in excellent agreement with experiment (Fig. 2). This shows that NNP technology is promising for realizing long-time and large-scale MD simulations with the accuracy of high precision (and high cost) electronic structure methods.



Fig. 1: Improvement of NNP accuracy with active learning iterations for AgI-As₂Se₃



Fig. 2: Total structure factors from NNPs trained on various functionals and compared to experiment.

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Formation energy calcuation of defects in candidates of thermoelectric materials

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CAAL₂SI₂-TYPE ZINTL PHASE COMPOUNDS CAZN₂ X_2 (X = AS,P)

Thermoelectric performance of many kinds of $CaAl_2Si_2$ -type Zintl phase compounds has been theoretically estimated by first-principles band calculations[1]. This work suggests that $CaZn_2X_2$ (X = Sb, As, P) exhibits large ZT values in the electron-doped regime due to its high valley degeneracy of the electronic band structure. Indeed, this kind of 122 Zintl phase compounds have been synthesized and their electronic structure have also been investigated theoretically. However, these 122 Zintl phase compounds become *p*-type semiconductors because the cationsite vacancies are easily formed under usual synthesis conditions.

Given the above background, in 2021 fiscal year, we have explored the possibility of n-type (electron carrier) doping of $CaZn_2X_2$ (X = As, P) using first principles calcuation[2]. We have considered the possibility of *n*-type doping into $CaZn_2X_2$ for the following two situations: interstitial-site doping of the alkaline earth metals AE (= Mg, Ca, Sr, Ba) and group 3 elements G3 (= Sc, Y, La), and G3 substitutional doping for the Ca site. The former is analogous to Mg₃(Sb,Bi,Te)₂, in which excess Mg is introduced to the interstitial site of Mg3Sb2 so as to realize n-type doping [3]. On the other hand, the latter is another possible way to introduce electron carriers utilizing the difference in the valence number of the ion (Ca 2+ and G3 3+), and the relevant compounds with full rare earth substitution including La, CaAl₂Si₂-type arsenides $RE_{2/3}$ Zn₂As₂ (RE = La, Ce, Pr, Nd, Sm), do exist in reality.

In order to describe dopants and defects in a crystal under periodic boundary conditions, the supercell approach was adopted in our calculations. The atomic positions in the supercell were relaxed in the structural optimization after the lattice constants and atomic positions of the primitive cell are optimized. To consider the possibility of chemical doping, its defect formation energy of charged states was calculated using the supercells. To numerically evaluate the defect formation energy of chemical doping in $CaZn_2X_2$ (X = As, P), we have performed first-principles calculations within the generalized gradient approximation using VASP. We perform DFT calculations with the Perdew-

Burke-Ernzerhof (PBE) exchange-correlation functional and the projector augmented wave method.

We find that the interstitial-site doping of AE = Ca, Mg or G3 = Sc, Y, and G3 = La, Y substitutional doping for the Ca site is favorable both for CaZn₂X₂ (X = As, P) in terms of energy stability. In particular, the formation energy of the La substitutional doping is the lowest among the considered cases both for CaZn₂X₂ (X = As, P) and is negative, so that La is expected to be substituted for the Ca site and provide electron carriers spontaneously (Fig.1). We also find that the formation energy for CaZn₂As₂ is smaller than that for CaZn₂P₂, so that *n*-type doping is considered to be relatively easier in CaZn₂As₂ than in CaZn₂P₂.

$LAOXS_2$ (X = SB, BI)

In $LnOX \ Ch_2$, electron carriers are usually introduced by fluorine substitutional doping for oxygen, or the valence fluctuation of cerium ions for Ln = Ce compounds. Since atoms in insulating layers work as a charge reservoir in both ways, the charge carrier can be introduced without a large change in the electronic state of the conducting layers, which is also advantageous for studying their transport properties. In fact, our previous theoretical study showed that the thermoelectric properties of $LnOX \ Ch_2$ can become very good, provided that electron doping by introducing defects makes the system metallic without largely changing the elec-



FIG. 1. The formation energy of the G3 substitution for the Ca site against the Fermi energy $\Delta E_F = E_F - E_V$ for CaZn₂As₂. The group 3 elements G3 (= Sc, Y, La) are chosen as dopant D. The dotted line denotes the position of the conduction band minimum[2].



FIG. 2. Defect formation energies of anion point defects for (a) LaOSbS₂ (X = Sb) and (b) LaOBiS₂ (X = Bi). The horizontal line (the Fermi level) is restricted to the energy range between the band edges. The values of the charge q of the defects are shown beside the line[6].

tronic structure[4]. However, it has recently been found that it is experimentally difficult to enhance the electrical conductivity in X = Sb compounds against their robust insulating nature[5].

In 2021 fiscal year, in order to shed light on the puzzling transport properties of the doped layered pnictogen dichalcogenides, we have systematically investigated the defect formation energy of several point defects in LaOXS₂ (X =Sb, Bi) using first-principles calculation[6]. We used the PBE parametrization of the generalized gradient approximation and the projector augmented wave method as implemented in VASP.

We have found that anion replacements S_O (re-

placement of O by S) and O_S are not stable while V_O (O vacancy) and V_S can take place, where the formation energy of V_O is higher in X = Sb than in X = Bi (Fig.2). A characteristic feature is that $V_{S_{eq}}$ (S_{eq} is the in-plane S) becomes much more stable in X = Sb than in X = Bi, due to the formation of an Sb_2 dimer and the occupation of the impurity energy levels. The formation energies of cation defects, X_S , and S_X are found to be positive. We have also found that Fluorine likely replaces oxygen for both X = Sb and Bi. The defect formation energy of F_O is negative for both compounds, while that for X = Sb is much higher than X = Bi. Our study has clarified the stability of several point defects and suggested that the in-plane structural instability is enhanced in X =Sb. We expect that, although further study is necessary, the knowledge obtained in the study should be helpful for understanding/controlling the transport properties of $LaOXS_2$ and related compounds by impurity doping.

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Studies on superconductivity in nickelates from a multiorbital viewpoint

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DESIGNING NICKELATE SUPERCONDUCTORS WITH $d^{8+\delta}$ ELECTRON CONFIGUATION

In 2020 fiscal year (the last fiscal year), we theoretically designed unconventional nickelate superconductors with d^8 electron configuration[1]. We considered d^8 nickelates with K₂NiF₄ structure, where the apical oxygens are replaced by halogens or hydrogens. One of the best candidates was electron-doped Ca₂NiO₂Cl₂. The key point was that the large crystal field splitting of the orbital energy levels, induced by replacing the apical oxygens by halogens or hydrogens, is approximately equivalent to large interlayer hopping in a bilayer system. Applying the fluctuation exchange approximation to the five orbital model of these materials, we showed that the maximum superconducting transition temperature of some of them may be even higher than that of the high- T_c cuprates.

A major drawback of our proposal was that Ca₂NiO₂Cl₂ has never been synthesized previously, and it may indeed be difficult to synthesize. On the other hand, a similar material $Sr_2NiO_2Cl_2$ has been synthesized experimentally[2], but its lattice constant is too large compared to Ca₂NiO₂Cl₂, resulting in a smaller crystal field splitting, and hence the predicted superconducting T_c , if any, is low. In fact, a high spin state is suggested in $Sr_2NiO_2Cl_2$, which is unfavorable for our mechanism to work, Given this background, in 2021 fiscal year, we studied the hydrostatic pressure effect on $Sr_2NiO_2Cl_2$ in an attempt to mimic the situation of $Ca_2NiO_2Cl_2$. The structural parameters under pressure has been determined using VASP. We have obtained five orbital models through Wannierization, and studied the model using the fluctuation exchange approximation. This is still an ongoing research, and we

plan to publish the results as soon as possible.

EFFECT OF RESIDUAL HYDROGEN IN THE INFINITE LAYER NICKELATE SUPERCONDUCTORS

Our theory on designing $d^{8+\delta}$ nickelate superconductors may also be related to another newly discovered superconductor (Nd,Sr)NiO₂[3]. In this superconductor, the nickel electron configuration is expected to be close to d^9 , but this might be affected, e.g., by the reduction process during the synthesis of the material. Since the band structure of (Nd,Sr)NiO₂ itself, due to the absence of apical oxygens, resembles that of the proposed mixed anion-nickelates, (unintentional) reduction of the electron number in (Nd,Sr)NiO₂ may also result in a similar $s\pm$ -wave superconductivity.

In 2021 fiscal year, we have studied the effect of residual hydrogen using the adopting the supercell approach, which contains multiple Ni atoms in a unit cell due to the presence of eccess hyrdogens added at the apical site periodically. The structural parameters were determined using VASP. We have so far constructed 10 and 20 orbital models of these systems through Wannierization. We plan to analyze the possibility of superconductivity in these multiorbital models.

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First principles studies of impurity-dislocation complexes in GaN

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Line defects and points defects have intensively studied so far [1, 2]. However, complexes composed of line defects and point defects have not been considered yet. In this project, we have studied dislocation-impuritycomplexes in GaN by the first principles calculations.



Fig.1: Atomistic Structures of a calculation model of the complex composed of GaN screw dislocation and Mg and H impurities.

Calculations were performed by VASP package. We prepared 800 atom unit cells which contain a screw dislocation and Mg and H impurities as shown in Fig.1.

It is well-known in bulk GaN that Mg and H impurities tend to form complexes of the Mg-N-H local structure. However, calculated results indicate that Mg-H complexes do not form near the screw dislocation, although screw dislocations attract both Mg and H atoms.

Figure 2 shows the atomistic structures of the



Fig.2: Atomistic structures of a complex composed of a GaN screw dislocation and Mg and H impurities.

complex composed of a GaN screw dislocation and Mg and H impurities. As shown in this figure, the local Mg-N-H structure which is observed in bulk GaN is broken by the effect of the screw dislocation. This indicate that properties of point defects are totally changed by the effect of line defects in the dislocationimpurity complexes.

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First Pricnciples Study of N Vacancies in Si₃N₄ for Flash Memory Application

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Defects in Si3N4 are now used for the application of 3D NAND flash memories. Among Defects in Si₃N₄, N vacancies are considered as the physical origins of charge traps used in memory functions [1, 2]. Recently, the charge transfer between charge traps in Si₃N₄ has become serious problem in the miniaturized 3D NAND flash memories. However, the physical mechanisms of this charge transfer is not clarified. In this study, we investigated the charge transfer mechanism by the first principles calculations.

First, we calculated the formation energies of a N vacancy (V_N). The results are shown in Fig. 1. As shown in Fig. 1, stable charged states are -1, 0 and +1 in the Si₃N₄ Fermi



Fig.1: Formation energies of various charged state of the N vacancy as a function of system Fermi energy. -1, 0 and +1 charged states are stable.



Fig. 2: Formation energies of various charged state of the N vacancy as a function of system Fermi energy. -2, 0 and +2 charged states are stable.

energy. Next, we calculated the formation energies of a V_N -H complex as shown in Fig. 2. As shown in Fig. 2, stable charged states are -2, 0, and 2 in the Si₃N₄ Fermi energy. This indicate that H diffusion from one V_N to another V_N causes charge transfer when V_N traps electrons.

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Development of quantum algorithm for imaginary-time evolution

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Recently, the development of materials computation methods using quantum computers has attracted a great deal of attention. In particular, we have paid attention to the imaginary-time evolution method, which has been known for a long time in materials computation, and have worked on the development of algorithms for its execution on a quantum computer. As a result, we have succeeded in developing an algorithm for quantum imaginary-time evolution methods [1].

On a quantum computer, only unitary transformations and observations must be used to achieve the desired computation. The imaginary-time evolution operator is a nonunitary transformation, and its realization on a quantum computer is non-trivial. One approach developed in this study is to realize the approximated imaginary-time evolution operator on a quantum computer by finding a unitary operator that best approximates the quantum state after the operation of the imaginary-time evolution operator. This method uses a classical computer in finding the unitary operator, and its unique feature is that it is a

hybrid classical-quantum algorithm.

We have developed a so-called "nonlocal" approximation as a method for finding approximate unitary operators, and have developed the method to realize quantum imaginary-time evolution with a quantum circuit shallower than the conventional methods of imaginary-time evolution. We constructed an actual quantum circuit and applied it to the MAXCUT problem. For the calculations, we verified the effectiveness of the algorithm with a quantum circuit simulator. The results showed that the quantum imaginary-time algorithm does work, and at least 94% of accuracy is achieved for unweighted 3-regular MAXCUT problems with ten vertices. At the same time, we have found that there is an accuracy limit due to the introduction of an approximate unitary operator, and the algorithm does not completely match the exact solution.

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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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It is important for the investigation of the dynamic properties of covalent liquids and glasses under pressure to consider the stability of materials states under various conditions from the viewpoint of free energy. For this purpose, the thermodynamic integration (TI) method based on the first-principles molecular dynamics (FPMD) simulations is useful and effective. However, the system size and simulation time are limited due to the high calculation cost of FPMD. To solve this cost problem, we have used machine-learning interatomic potential based on artificial neural networks (ANN) trained from the results of FPMD simulations.

In this study, we have calculated the melting temperature of diamond, one of the typical covalently bonded materials, using the TI method with the ANN potential as a function of pressure. Figure 1 shows the pressure dependence of calculated melting temperature. The results of this study are indicated by the red diamond symbols. The triangle up and down symbols indicate the results of the previous theoretical study, which carried out the direct simulation of solid/liquid coexistence by using a so-called two-phase simulation method based on FPMD [1]. Both results are in reasonable agreement with each other.

We have also obtained the melting temperature of binary alkali Na_xRb_{1-x} mixture [2] as a function of concentration x, and found that the melting temperature minimum occurs at x = 0.2, being in agreement with the experimental observation. These two findings for diamond and alkali mixture demonstrate the validity and usefulness of the current method.



Fig. 1: Pressure dependence of melting temperature of diamond.

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

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Silicon carbide (SiC) attracts attention because it is one of the most promising widebandgap semiconductors for developing nextgeneration switching devices operating in highpower and high-frequency applications. However, the potential of 4H-SiC has not been fully utilized owing to the low carrier mobility of 4H-SiC-based metal-oxide-semiconductor field-effect transistors, which is caused by defects at the $4H-SiC/SiO_2$ interface. To reduce the density of interface defects and increase the channel mobilities, post-oxidation annealing using N_2O , NO, or N_2 gas has been proposed. In this study, we propose the interface atomic structures in which N atoms are incorporated by replacing C atoms, and we investigate the total energies and electronic structures of the nitride layers by density functional theory (DFT) calculation. Universal atomicscale models describing 4H-SiC with a high-Natom-density layer in arbitrary crystal planes are proposed. To explore the most preferable crystal plane of 4H-SiC for N-atom incorporation, we study the stability and electronic states of the nitride layers on a 4H-SiC surface. We find that the nitride layers grow along the a face, which is consistent with the conclusion obtained using the bulk model[1]. Any defect states in the bandgap of 4H-SiC are not generated in our structure. The formation energy of the nitride layers at the topmost layer of the interface is smaller than that at the second layer, indicating that the N atoms accumulate

at the interface.

In our model, the surface of the 4H-SiC substrate is terminated with OH groups to imitate the SiO_2 layer and the other side of the substrate is terminated with H atoms. The rectangular supercells of 10.1 Å \times 10.7 Å \times 26.3 Å for the *a*-face model, $10.1 \text{ Å} \times 12.3 \text{ Å} \times 27.3$ Å for the *m*-face model, and 12.3 Å \times 10.7 $\text{\AA} \times 26.8 \text{\AA}$ for the Si(C)-face model were employed. The z-axis is taken to be the direction perpendicular to the surface. The numbers of atoms for the *a*-face, *m*-face, and Si(C)-face models are 176, 208, and 208. We considered the modification incorporating four Si vacancies ($V_{Si}s$) and 16 N atoms at C sites ($N_{C}s$). The cases in which V_{Si}s are arranged parallel to the surface were investigated to evaluate the anisotropy of the formation energy of the nitride layer. In our model, the areal N-atom density is on the order of 10^{14} cm⁻¹, which is consistent with the experimental results. Although there are two inequivalent lattice sites of 4H-SiC, i.e., h (hexagonal) and k (quasicubic) sites, our previous studies have shown that nitride layers tend to grow at the k site. Thus, we consider the cases in which $V_{Si}s$ are arranged at the k site. The interfaces with the nitride layer at the second layer are also investigated for all the faces. For the firstprinciples calculation, we used the RSPACE code[2, 3], which is based on the real-space finite-difference approach within the frameworks of DFT and is developed in this project.

We employed the local density approximation of the DFT to describe the exchange and correlation effects. Electron-ion interactions are approximated by the projector-augmented wave method. We adopt $6 \times 6 \times 1$ Monkhorst-pack k-point meshes including a Γ -point in the Brillouin zone. The real-space grid spacing is chosen to be ~ 0.21 Å. The structural optimization is performed until the residual forces are smaller than 0.001 Hartree/Bohr radius.

We assumed the interaction of the SiC substrate and the arriving NO molecule at the interface as

$$SiC^{(w/o \mod)} + 24NO$$

$$\rightarrow SiC^{(w/\mod)} + 4SiO_2 + 16CO + 4N_2,$$

with $\mathrm{SiC}^{(\mathrm{w/o\ mod})}$ (SiC^(w/mod)) being the interface without (with) the modification incorporating four V_{Si}s and 16 N_Cs. The formation energy of the above interaction for generating one V_{Si} is obtained as

$$E_{\rm form} = E_{\rm total}^{(\rm w/\ mod)} / 4 + E({\rm SiO}_2) + 4\mu_{\rm CO} + 2\mu_{\rm N} - E_{\rm total}^{(\rm w/o\ mod)} / 4 - 6\mu_{\rm NO}, \ (1)$$

where $E(\text{SiO}_2)$ is the total energy of a SiO₂ unit in a bulk of quartz SiO₂. $E_{\text{total}}^{(\text{w/o mod})}$ and $E_{\text{total}}^{(\text{w/mod})}$ represent the total energies of the interface without and with N-atom incorporation, respectively. In addition, μ_{NO} , μ_{CO} , and μ_{N} are the chemical potentials of a NO molecule, a CO molecule, and N atoms in a N₂ molecule, respectively. We set the temperature at 1000 K and the partial pressure of NO gas (p_{NO}) at 1 atm. The partial pressures of CO (p_{CO}) and N₂ (p_{N_2}) gases are set at 10^{-5} atm and 0.25×10^{-5} atm.

The formation energies of the nitride layers are shown in Table 1. We find that all the reactions are exothermic and the nitride layers growing along the a face are the most stable among those along the a, m, C, and Si faces. The formation energy of the nitride layer at the topmost layer is smaller than that at the second layer, resulting in the localization of the N atoms at the interface. Note that the NO

Table 1: Formation energy of nitride layers defined by Eq. (1).

I ()		
face	layer	$E_{form}~(eV)$
a	top	-7.43
a	2nd	-7.10
m	top	-7.13
m	2nd	-7.07
Si	top	-7.07
Si	2nd	-7.01
\mathbf{C}	top	-7.14
С	2nd	-7.01

annealing generates the nitride layers immediately below the SiO₂ layers without any transition layers. The difference in the formation energy between the nitride layers at the topmost and second layers is the largest for the a face. This result agrees well with the observation that the formation energy of the nitride layer along the a face is the smallest. The local densities of states of the interfaces reveal that there are no gap state at the interface. These results imply that NO annealing after the oxidation can contribute to the reduction in the density of interface defects by forming the nitride layer immediately below the SiO₂ layer of the interface.

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Analysis of Surface Reactions in Atomic Layer Etching Processes

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Thermal atomic layer etching (ALE) can be used for precise and damageless etching. For example, it can be used to fabricate magnetic tunnel junction (MTJ) stacks of magnetoresistive random-access memory (MRAM) devices [1]. The aim of isto understand the this studv mechanisms of thermal ALE of metal in general, whose cycle consists of an oxidation step and an exposure step to β–diketones, such as; hexafluoroacetylacetone (hfacH), (tfacH). trifluoroacetylacetone and acetylacetone (acacH) molecules. For instance, thermal ALE of Ni with hfacH starts with the deprotonation of hfacH molecules after the oxidation of the Ni By increasing the surface 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].

First, we examined the interaction of β -diketones with a metallic Ni surface, using STATE [6,7]. STATE is a simulation code based on density functional theory (DFT) with pseudo-potentials and a plane wave basis set. It has been found that the cleavage of a C-F or C-H bond of a β -diketone is more likely to take place than the deprotonation on a metal surface. The surface roughness can also help to form C-Ni bonds, which were also observed in experiments. The reaction mechanisms that we observed in these simulations have revealed the selflimiting nature of thermal ALE for metals with β -diketone gases in general, which is consistent with earlier experimental observations [5,8].

Second, we examined the interaction of β -diketones with oxidized metal surfaces, using TURBOMOLE program [9]. It has been found that, as β -diketones approach an oxidized metal surface, they deprotonate. In this way, volatile metal complexes and H₂O molecules can be formed when β -diketone molecules

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interact with an oxidized metal surface. The reaction energies of such interactions have been evaluated from the simulations and we found that etch oxidized metal has its own desorption energy or temperature to volatilize its metal complex. Therefore, the applied temperature can be used as a self-limiting condition if the target contains different materials. In addition, hfacH is found to get more stably bonded than acacH or tfacH with an oxidized metal surface because the negatively charged F atoms in CF₃ are repelled by O atoms of the surface, which forces a deprotonated hfac to adsorb on the surface nearly vertically. This does not happen to acacH, whose CH₃ groups tend to interact directly with the metal oxide. As a result, hfacH is considered more suited for ALD processes than other 8diketones.

In addition, we also examined the interaction of Y_2O_3 with incident F_+ and CF_{3^+} ions, using ion beam experiments with XPS and DFT simulations. It has been found that the penetration depth of F atoms in Y_2O_3 exposed to F^+ or CF_{3^+} ion injection depends essentially on the incident energy and hardly depends on the ion dose once a sufficient amount of fluorine is provided to the surface and saturate. We also obtained the atomic concentration depth profiles by XPS

measurement. The results indicate that carbon contained in the incident CF_{3}^{+} ions remove oxygen of Y_2O_3 more efficiently. Furthermore, high-energy incident CF_{3}^{+} ions promoted the formation of Y-F bonds near the surface region of Y_2O_3 films more efficiently than low-energy incident CF_{3}^{+} ions. Our simulation results are found to be consistent with these experimental observations.

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First-principles study on atomic and electronic structures of graphene/SiC interfaces

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Graphene is in the limelight as a post-silicon material in next-generation devices due to its unique electronic and mechanical properties and conductivity. In recent years, the epitaxial growth in the silicon carbide (SiC) pyrolysis method has attracted attention as one of useful methods for producing large-scale and high-quality graphene. However, in the pyrolysis method, the bottom graphene layer is covalently bonded to the Si atom of the SiC substrate. To separate the bottom layer from the substrate, atomic intercalation technique is employed. As the result, the bottom layer becomes an ideal single-layer graphene, and the Dirac cone appears in the electronic band structure. On the other hand, atomic vacancies are formed in the graphene during the epitaxial growth process. Since the intercalants can be bonded to the dangling bonds, which are affected on the energy band structure and the position of the Dirac point of graphene.

In this study, fluorine atoms are adopted as intercalants, and the effect of the bond between a fluorine atom and a dangling bond on the electronic state of graphene is investigated using the first-principles calculation code: RSPACE[1, 2]. We investigate the difference in the effects of the number of fluorine atoms adsorbed on the single vacancy in the graphene on the electronic state. It is found that, in the model where two fluorine atoms are bonded to the defect, the dangling-bond state is hybridized with the conduction band bottom of SiC substrate. Moreover, the conjugated π state of graphene is extended over the energy range in which the bandgap of SiC substrate is located (Fig. 1). On the other hand, in the system produced by hydrogen intercalation, the dangling bond state is in the middle of the band gap of the SiC substrate and extends to the inside of the substrate, which can cause a large leakage current.

This work has been performed on System B of the Supercomputer Center, the Institute for Solid State Physics, the University of Tokyo.



Figure 1: Local density of states of graphene with single vacancy on fluorine-intercalated SiC substrate. Two of dangling bonds are terminated by fluorine atoms.

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High-Throughput Polymer Electret Material Screening Based on Solid-State Quantum Chemical Calculation and Deep Learning

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Electret is a dielectric material with quasi-permanent charges and can trap charges stably for decades. Vibrational electret energy harvester (VEEH) can generate electricity efficiently from kinetic energy via the electrostatic induction. The VEEH with bipolar (both positively and negatively charged) electret leads to four times output power theoretically, thus specifying the importance of designing high-performance bipolar polymer electrets.

CYTOP (Cyclic Transparent Optical Polymer, AGC Chemicals) is one of the best polymer electret materials, with three commercialized types displayed in Fig. 1. Recently, we utilized quantum chemical analysis for evaluating the charge trap of CYTOP electrets [1]. It is found that although the repeat-unit-number of CTX-A is above 1000, the trapped charge is localized at the amide bond, which is formed by dehydration reaction between the carboxyl end group and the amine introduced. It is also shown that the computed electron affinities (EAs) and ionization potentials (IPs) by the density functional theory (DFT) with polarizable continuum model (PCM) correction agree well with the trends of the surface charge density and charge stability measured by the wet experiments.

Most recently, by employing the de novo molecule generation and the functional group enrichment analysis, we successfully proposed the electret CTX-A/APDEA with high bipolar charging performance via combining CTX-A with N-(3-aminopropyl) diethanolamine [2]. This result encouraged us to move further to search new amines in the open-source database PubChem, aimed at designing better bipolar polymer electret based on CYTOP CTX-A after the dehydration reaction.



Fig. 1. Chemical structure of CYTOP series.



Fig. 2. Prediction of PCM-DFT IPs for training and test sets using MEGNet.

Although solid-state quantum chemical calculation based on PCM-DFT can give quantitative EA and IP values, the average computation time is 41.4 CPU hours per monomer molecule and even as high as 2500 CPU hours per hexamer molecule. To reduce such heavy computational cost, we employ deep learning models to approximate the EAs and IPs efficiently.

To prepare the labeled data, 5522 amines were initially sampled from the PubChem. Thereafter, the virtual dehydration reaction was conducted and PCM-DFT computation was automatically made. Subsequently, a dataset mapping the PCM-DFT IPs and molecular structures was establised and splited into training-validation-test sets with the ration of 80%, 10%, and 10%, where the training set was used to teach the deep learning models and the performance of the models were tested on the test set. Fig. 2 illustrated the prediction results on the established dataset with one kind of deep learning models named MEGNet [3]. The mean absolute error (MAE) of IP is as small as 0.326 eV, with computational cost decreased significantly. Therefore, the present approach will be employed for screening bigger database for new highperformance bipolar polymer electrets.

The geometry of the molecule is relaxed under the open-shell condition and then the energy of both open-shell and closed-shell system are calculated and compared. All the quantum chemical calculations are made with the software GAUSSIAN [4] at the DFT level with the CAM-B3LYP functional and 6-31+G(d,p) basis set, while PCM is combined for solid-state analysis due to the solvation effect correction.

This work was partially supported by JST CREST Grant Number JPMJCR15Q3 and JPMJCR19Q1. The calculations are performed with SGI ICE XA ISSP system B and every calculation is done with 1 node (24 CPUs).

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First-principles calculations on muon in solids

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Hydrogen plays an important role in semiconductor materials; Well known examples are hydrogen passivation and carrier injection. The muon spin resonance is an effective tool to determine the dynamics of hydrogen in semiconductors since muonium consisting of a positive muon and an electron bears similarities to hydrogen. Observed hyperfine structures provide useful information on the atomic site of muonium, and thus that of hydrogen. In a previous study, we clarified that negative Fermi contact terms are caused by the electron correlation and observing the negative value suggests the formation of resonance bond of hydrogen [1].

One of the scientifically important new targets is hydrogen impurity in barium silicide (BaSi₂), which is a candidate for solar cell materials. It is known that hydrogen passivates the defect level of Si vacancy. This crystal includes Si tetrahedrons and electrons transfer from barium to silicon. We first confirm that this crystal has an indirect gap and the gap value calculated based on the hybrid density functional theory is 1.36 eV, which is close to the experimental value. On the other hand, the value calculated based on the GGA is small (0.71 eV). The Si monovacancy is found to form a triangle of the C_{2v} symmetry and to induce a midgap level having large amplitudes at the equivalent two atomic sites.

We find that the monohydrogenvacancy pair induces the gap level. On the other hand, we find that dihydrogen passivates the defect level. It is suggested from out calculation that trihydrogen-vacancy pair leads to n-type doping. We conclude that hydrogenation plays various roles in barium silicide, which depends on the concentration of hydrogen. The muon spin resonance measurement is expected to confirm the atomic geometry of the monohydrogenvacancy pair.

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GW + BSE calculation of RIXS spectra by the all-electron mixed basis program, TOMBO

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The initial state of X-ray emission spectroscopy (XES) and resonant inelastic X-ray emission spectroscopy (RIXS) is a highly excited eigenstate with a deep core hole after the X-ray photoelectron spectroscopy (XPS) and X-ray photoabsorption spectroscopy (XAS) processes, so that the XES and RIXS calculation offers a good example of extended quasiparticle theory (EQPT) [1] associated with many-body perturbation theory. Moreover, to overcome the basis set incompleteness problem, we adopt the allelectron mixed basis program, TOMBO, which uses both plane waves and numerical atomic orbitals as basis functions. We have successfully applied this approach in our previous XES [2] study. Here we applied the standard oneshot GW + Bethe--Salpeter equation (BSE) approach in MBPT to this problem on the basis of EQPT and analyze XES and RIXS energies for CH₄, NH₃, H₂O, and CH₃OH molecules.

Figure 1 shows the RIXS spectra of a CH₃OH molecule calculated by our method together with the experimental data [3]. Both results coincides very well without introducing any empirical fitting parameter.

Moreover, according to extended Kohn-Sham



Fig. 1: Calculated (above) and experimental [3] (below) RIXS spectra of a CH₃OH molecule.

theory [4], we gave a justification and comment of applying the method relying on time-dependent density functional theory as well as the one-shot GW + BSE approach to this problem.

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Theoretical study of electric double-layer structure of MXene electrode dependent on surface functional groups Atsuo YAMADA

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Aqueous electric double-layer capacitor (EDLC) is promising candidate for large-scale stationary storage due to non-flammability, low materials cost, and non-toxicity of aqueous electrolyte. Transition metal carbides/nitrides (MXenes) are appealing electrode materials for aqueous EDLCs owing to their high specific capacitance (> 300 F/g) in conventional aqueous electrolyte. Herein, we investigated the dependence of EDL capacitances on the surface functional groups of the MXene electrodes [1].

The ESM-RISM method was adopted to evaluate the capacitance of the MXene electrodes. The simulation cells are composed of MXene $Ti_3C_2T_2$ with different surface functional groups (T = F, Cl, Br, and I) and the 1 M KOTf/H₂O electrolyte. Here, MXene electrodes were treated quantum-mechanically using the density functional theory method, while electrolytes were described using the RISM method. All the ESM-RISM calculations were conducted with Quantum Espresso code.

The calculated EDL capacitance increased with the increase in the atomic number of halogen atoms (F < Cl < Br < I) (Fig.1a). The increased EDL capacitance is due to the biased distribution of excess electrons in the electrode toward the electrolyte, thus reducing the EDL thickness (Fig. 1b). The induction of electrode electrons into the EDL region is facilitated by the smaller negative charges of surface halogen atoms with lower electronegativity. Therefore, lowering the valence numbers of the MXene surface atoms should enhance the capacitance.

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Figure 1 (a) Calculated capacitances per unit surface area of MXene. (b) Spacial distributions of excess electrons of the electrode (red) and counter positive charges of the electrolyte (blue) at the electrode/electrolyte interface.

Elucidation of mechanism and theoretical prediction of super-functional materials using high-density hydrogen

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Hydrogen, a ubiquitous element, is present as an impurity in various materials and is known to significantly change materials' electrical and mechanical properties by assuming different charge states depending on the atoms' environment. In recent years, record-breaking superconductors and superionic conductors have been discovered in which protons and hydrides are major components. One of the most common problems in studying these materials is the difficulty in experimentally quantifying and observing the position of hydrogen, which has no inner-shell electrons.

Electronic structure calculations based on density-functional theory and first-principles molecular dynamics methods allow quantitatively predicting materials' structure and physical properties without empirical parameters. By these methods, the energy of the system and the forces acting on the atoms can be calculated using atomic configurations as input data. In principle, it is possible to predict how much and where hydrogen atoms are stable in a crystal and what physical properties they will

exhibit without experiments. In this project, we applied the methods to elucidate the mechanism of the photo-induced metallization of Yttrium oxyhydride recently discovered by a Tokyo Tech group experimentally [1].

In their experiment, light irradiation significantly reduced the electrical resistance of an insulator YO_xH_v epitaxial thin film, and the metallic state was maintained on a scale of several days. Conventional polycrystalline YO_xH_v on glass substrates exhibits a one-digit decrease in electrical resistance upon solar irradiation, while the epitaxial thin film has achieved a resistance reduction of more than three orders of magnitude. Furthermore, UV laser irradiation of the epitaxial thin film reduced the electrical resistance by more than seven orders of magnitude.

To explain these results, we constructed a structural model based on high-resolution measurements of the local structure and chemical composition, and calculated the electronic structure based on this model. As a result, we found that the hydrogen atoms change

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their position and the charge state, leading to the long-life metallization [1,2].

Another topic in this project is the study of ionic superconductor LiCB₉H₁₀. We first applied the data assimilation method for structure prediction [3] to find no significant difference between the high-T and low-T structures. From a first-principles molecular dynamics simulation, we found that the motion of Li ions strongly correlates with the rotation of the CB₉H₁₀⁻ complex. Finally, by constructing neuralnetwork interatomic potentials, we calculated the ion conductivity by a large-scale molecular dynamics simulation in good agreement with experiments. Through these simulations, we found that the ion conductivity of the high-T phase is enhanced one order of magnitude by the concerted motion of Li ions and another one order of magnitude by the rotation of the CB_9H_{10} complex [4].

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

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We investigated the catalyst adsorption and diffusion properties on light-element doped graphene supported on the magnetic substrates and hydrogen dissolution and diffusion properties in the amorphous ceramic materials, with the aid of the first-principles calculation based on the density functional theory (DFT) and machine learning potentials.

At first, we investigated the stabilities of Pt atoms on light-element doped graphene supported on the magnetic substrates. We considered Fe and Ni as the magnetic substrates. We performed the total energy and electronic structure calculations using The Vienna Ab initio simulation package (VASP). We revealed that the adsorption of Pt atoms on light-element doped graphene with flat becomes structures stronger through supporting on the magnetic substrates. However, in most cases of steric lightelement doped graphene, the magnetic substrates weaken the Pt adsorption on the light-element doped graphene. We also found that the magnetic substrates reduce the diffusion barriers of Pt atoms. Therefore, the magnetic substrates enhance the catalyst

diffusion and coarsening. In addition, we also revealed that the Cl⁻ ion adsorption enhances the anisotropic catalyst nanorod growth.[1]

We also investigated the hydrogen dissolution and diffusion properties in the amorphous ceramic materials. We considered the Al₂O₃ as the hydrogen permeation membrane. Since DFT calculations of amorphous materials require quite large computing costs, we constructed the machine learning potential reproduce to the interatomic potentials obtained with DFT calculations. We performed melt-quenching technique to obtain the amorphous structure. We performed 2000 DFT calculations with various hydrogen positions in amorphous Al₂O₃ to construct the database for machine learning. The obtained machine learning potentials reproduce the stable adsorption structures, however, cannot reproduce the diffusion barriers obtained with DFT calculations

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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 doped graphene supported on the magnetic substrates with the aid of the first-principles calculation based on the density functional theory (DFT). Besides, we performed electron energy loss spectroscopy (EELS) simulations of heteroatom-substituted brownmillerite-type oxides to characterize the EELS spectra obtained with transmission electron microscopy.

At first, we investigated the stabilities of Cu atoms on light-element doped graphene supported on the magnetic substrates. We considered Fe and Ni as the magnetic substrates. 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 adsorption of Cu atoms on light-element doped graphene becomes stronger with the magnetic substrates. However, in cases of some light-element dopants, the magnetic substrates weaken the Cu adsorption on the light-element doped graphene. This is because the active dangling bond forms strong chemical bonds with magnetic surfaces, hence, Cu atoms cannot form stable chemical bonds with the lightelement doped graphene. We also investigated the diffusion properties of Cu atoms on lightelement doped graphene supported on the magnetic substrates. We found that the magnetic substrates reduce the diffusion barriers of Cu atoms. In addition, we also revealed the effect of Cl⁻ ions on the catalyst nanorod growth.[1]

We performed EELS spectra of the partially substituted Ca₂AlMnO₅. We considered Sr dopants, which show promising oxygen absorption properties.[2] The obtained EELS spectra show good agreement with the experimental results.

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First-principles calculation of energy materials

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1. Topological thermoelectric materials

Thermoelectric conversion based on the anomalous Nernst effect has received a lot of attention as ANE achieves more efficient heat recovery and heat recovery from more heat sources than those based on the Seebeck effect. For the anomalous Nernst effect, the topological nature of the wave functions, and the Berry curvature, a fictitious magnetic field, is essential. We have studied the anomalous Nernst effect of iron-based ferromagnetic materials such as $\text{Fe}_3 X(X=\text{Al}, \text{Ga})[1]$ and $\text{FeCl}_2[2]$ by first-principles density functional calculations. To evaluate the anomalous Nernst coefficient, a detailed Fermi energy dependence of the anomalous Hall conductivity is required. We have implemented a finite difference algorithm in OpenMX[3] to calculate the Berry curvature of *metallic* system given by the averaged *local Berry phase* of the momentum space[4]. This implementations open up the possibility of efficient thermoelectric material design based on high-throughput screening.

$2. \ Photovoltaics$

Material property data was extracted from about 1500 papers on organic thin film non-fullerene solar cell materials, and highperformance material conditions were derived based on data statistical methods[5]. One of the conditions obtained was the empirically known "open-circuit voltage (Voc) of 0.8-0.9 V is appropriate", and the database we created rediscovered this rule of thumb. In addition, it was suggested that the sulfur atom content is an important factor for high performance photovoltaics materials.

We have performed first-principles calculations of the topological phase transition in strained inorganic halide perovskite CsPbI₃. For the experimental lattice constant, the bandgap decreases from 0.15 eV to 0 eV when a strain of c/a > 1 is applied. Increasing the strain will gradually open the bandgap. We calculated the topological Z_2 invariants that characterize the topological insulating phase. From the results, the bulk crystal CsPbI₃ showed a strain-induced topological phase transition, changing from a trivial insulator to a topological insulator phase. This topological phase transition of the strained inorganic halide perovskite has the potential to be applied to new energy devices.

3. Graphene and diamond

Applying the supercell scheme to the study of alloys and various perturbed system including impurities and vacancies raises band folding problems. The unfolding method is expected to obtain the meaningful energy-momentum relationships by avoiding it. The method proposed by Chi-Cheng Lee et al proved[6] very useful for calculating the electronic structure of a vacancies system with OpenMX code. We have calculated and observe the graphene flake size dependence of Dirac cone in the unfolding band structures.

Negatively charged diamond nitrogenvacancy centers are promising for many applications, such as high-resolution sensors for electric fields and quantum computer Qubits . Density functional calculations are often performed in supercell systems. However, as the number of supercells increases, the first Brillouin zone (FBZ) shrinks and the band becomes more complex. An unfolding band method calculation was performed to study the electronic properties of the nitrogen vacancy center diamond using the OpenMX code. Our results show that the unfolded band of the bulk diamond supercell and the nitrogen vacancy center of the diamond have fewer lines than those of the traditional folded band. The shape of the unfolded energy band matches the primitive cell band. The dedailed electronic band structure of diamond with nitrogen vacancy center are analyzed.

The Al_2O_3 /diamond(111) interface containing three types of impurities was calculated. We predicted three different Al_2O_3 /diamond(111) interface structures and investigated their band edge changes. Band edges are evaluated by calculating the local electron density. Compared to diamond bulk, the band of Al_2O_3 bulk is generally shifted downward. The band offsets for dangling bonds, C-H bonds, the ideal O-terminal interface are estimated. Our research helps to assess the impact of interface structure on device performance and provide a reference for improving experimental methods.

4. Crystal structure prediction for spintronics materials

Bismuth tellurium iodide (BiTeI) has attracted great interest as a potential material for spintronics device. We have performed crystal structure prediction for BiTeI crystals by genetic algorithms and density functional calculations. We found 4 BiTeI crystal structures with high stability , including one structure that has been observed in experiments and 3 brand new structures, and then performed detailed first-principles analysis of the elctronic structures to predict their physical properties. We calculated the Z_2 topological invariant and spin-textures of the new structures. Among the 3 new structures, we found that two structures with centro symmetry were strong topological insulators, and one structure without centrosymmetry had wide band gap and strong Rashba splitting.

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Development of crystal structure prediction methods using machine learning

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We search for solid electrolyte materials that can be synthesized in the systems of Li-Mg-SiO₄ using crystal structure prediction (CSP) by CrySPY [1]. We investigate whether it is possible to synthesize structures with high ionic conductivity by changing the ratio of Li to Mg from Li₂MgSiO₄. We performed CSP simulations with random search. In the CSP simulations, first-principles calculations were carried out using the VASP code [2], and a gradient approximation generalized was employed for exchange-correlation functional. The compositions calculated in this study were Li₂MgSiO₄, Li1.5Mg1.25SiO4, and Li_{2.5}Mg_{0.75}SiO₄. The number of searching trials for each composition was 200, which were conducted using the ISSP supercomputer. Our calculated formation energies showed that Li₂MgSiO₄ can be synthesized, however, Li1.5Mg1.25SiO4 and Li2.5Mg0.75SiO4 are unlikely to be synthesized, leading to phase separation. These results are consistent with our experiments. Therefore, it is difficult to synthesize solid electrolytes in the system of Li-Mg-SiO₄ except for Li₂MgSiO₄.

We have also studied on algorithm development for CSP. Look Ahead based on Quadratic Approximation (LAQA), which is one of the selection-type algorithms we previously developed [3], can control the optimization priority of the candidates. We have proposed an improved score of LAQA, where the stress term is added to overcome the drawbacks of the previous score. CSP simulations by this improved algorithm are performed to investigate the searching efficiency for typical materials such as Si (16 atoms), Al₂O₃ (10 atoms), NaCl (16 atoms), and SrCO₃ (20 atoms). We used the CrySPY code for the CSP simulations. For the system of SrCO₃, we employed the VASP code to evaluate the energy and to carry out the local structure optimization using the ISSP supercomputer. For the other systems, the QUANTUM ESPRESSO was also used. The total-energy calculations were performed using the density functional theory with the projectoraugmented wave method. The generalized gradient approximation was used for exchangecorrelation functional. Figure 1 illustrates the
number of total optimization steps required to find the most stable structure, obtained by the CSP simulations using random search (RS), Greedy, and LAQA. The searching efficiencies of LAQA with the weight parameter of stress w_S of 10 (red bars in Fig. 1) are not always the best, however, it demonstrates high searching efficiency on various data sets. In other words, the introduction of the stress term makes LAQA more robust and versatile [4].

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Fig. 1: Number of total optimization steps required to find the most stable structure.

Development of Exciton Maps for Identifying Active/Inactive Thermally Activated Delayed Fluorescence Molecules

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А high internal electroluminescence quantum efficiency in the third-generation organic light-emitting diodes is based on the mechanism of thermally activated delayed fluorescence (TADF), in which triplet spin excitons are converted to singlet spin excitons via reverse intersystem crossing (RISC). The existing energy barrier between a singlet spin exciton and a triplet spin exciton, commonly named as singlet-triplet splitting (Δ^{ST}), should be almost zero for TADF to occur. In recent experimental studies, however. certain carbazole benzonitrile (CzBN) derivatives, in which the carbazole moiety acts as an electron donor and the benzonitrile moiety acts as an electron acceptor, can be TADF active and inactive: nevertheless, their Δ^{ST} are typically about 0.2 eV. However, we must reconsider the mechanism of TADF to completely understand it. We have studied the mechanism of TADF using the first-principles GW+Bethe-Salpeter method and exciton analysis method with exciton wave functions [2]. Before discussing the optical properties of CzBN, we compared the simulated photoabsorption spectra with the available experimental spectra and confirmed

that our method successfully reproduced the spectra. By sandwiching an arbitrary operator with the exciton wave functions, we estimated the expected values such as the exciton size, electron-hole separation distance, electron (or hole) delocalization, and exciton binding energy based on two-particle picture and proposed an exciton map [2]. We revealed that the TADF active/inactive molecules could be classified well in the exciton map by choosing the exciton binding energy as the vertical axis and the ratio of electron and hole delocalization as the horizontal axis. Indeed, we concluded that there are two kinds of TADF active molecules existed based on the following: first, the ratio of electron and hole delocalization was proportional to the exciton binding energy, and second, the hole state spatially localized more than the electron.

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Maximization of interface magnetoelectric coupling with Bayesian optimization

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To reduce energy consumption in magnetic devices, the control of magnetism by the electric current through the magnetic field should be replaced with that by the electric field. Interface multiferroicity is promising, because the magnetoelectric (ME) coupling is much larger than that of single phase multiferroics [1]. In addition to choosing optimal materials for ferromagnetic and ferroelectric phases, the interface modification is also a choice to enhance the ME coupling.

In this project, we performed large-scale first-principles calculations of multiferroic interfaces [2, 3, 4]. We explored better insertion of transition-metal atomic layers into Fe₃Si/BaTiO₃(001) interfaces using the Bayesian optimization. As is shown in Fig. 1(a), the Bayesian optimization improved the interface ME coupling by 55% that is obviously much better than the random search.

As a by-product of the Bayesian optimization, we successfully provided an explanation of the mechanism for the multiferroicity enhancement [2]. Figure 1(b) shows the dependence of the change in the interface magnetic moment on the exchange-correlation functional and the electron localization controlled by the Hubbard U parameter. The large ME coupling due to the change in the magnetic moment in V comes from the nearly half occupied 3d bands causing peaks in the density of states close to the Fermi level [2]. In contrast, the following three cases exhibit tiny ME coupling. Insufficient occupancy causes stronger ionicity reducing interaction with Ti. Excess occupancy makes the hybridized states too deep. In addition, 4d electrons are too itinerant to have sufficient hybridization with Ti.

In addition, the enhancement of the ME coupling due to the change in the magnetic anisotropy has also been studied. Changes in the magnetic anisotropy of a whole ferromagnet by the exchange coupling [5] are further enhanced by the strain effect at the interface [3].



Figure 1: (a) The Bayesian optimization of Fe₃Si/BaTiO₃ interfaces with inserted atomic layers. (b) The change in the interface magnetic moments.

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First-Principles Design of Spin-Polarized Bandstructure at MoTe₂/Bi₂Se₃ Interface

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We are studying magnetism and topological properties in various materials by means of the first-principles density functional theory (DFT) calculations aiming at the spintronics application.

Since last year, we have investigated the magnetic stability in 2D magnetic material VI₃ making a comparison with CrI₃ using the VASP code at the ISSP *ohtaka* supercomputer. In VI₃, it turned out that under the trigonal 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. This finding may pave a way to the spintronics application with 2D materials [1].

Next, we explored a heterostructure that consists of transition-metal dichalcogenide and 3D topological-insulator to investigate the hybrid spin state in which the out-of-layer spin polarization and the helical spin polarization may merge. We show that $MoTe_2$ and Bi_2Se_3 lattices match well and in-plane strain provides a handle to manipulate the spin-polarized band alignment near the Fermi energy. This interface shows the various spin degree of freedom, and it may be useful as an advanced spin generator [2].

In this year, we also studied the cathode properties of sodium transition-metal oxides (such as Na_2NiTiO_4) by means of DFT calculations and the machine-learning approach to reduce reliance on Li-ion batteries and aim at the sustainable development goals. We found a strong relation between the cation ionic radii and the structural stability. This finding may lead to the future industrial application to the sodiumion rechargeable battery [3].

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First-principles lattice-dynamics calculations for negative-thermal-expansion materials

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Negative-thermal-expansion (NTE) materials have attracted considerable attention because they contribute to sustaining largely expanding materials and also because of their fascinating and counter-intuitive thermal properties. The well-known and representative NTE materials are Si [1], ReO₃ [2], ScF₃ [3] ZrW₂O₈ [4] and KZr₂P₃O₁₂ [5]. Since the reports of negative thermal expansion in various materials in the past few decades, it has been widely known that the mechanism for NTE is the transverse acoustic phonon modes, which have negative Grüneisen parameters. However, the detailed mechanisms for the NTE properties are uncovered ever since now. Here, we report our progress for elucidating the microscopic origin of NTE in Si, ReO₃, and KZr₂P₃O₁₂.

Our first-principles calculations were performed by using the projector augmentedwave method [6] as implemented in VASP [7]. The phonon band structures were derived from the calculated force constants using PHONOPY [8].

As shown in Fig. 1, we present the



Fig 1. Calculated phonon bands for (a) Si, (b) ReO₃, and (c) KZr₂P₃O₁₂ and Grüneisen parameters for (d) Si, (e) ReO₃, and (f) KZr₂P₃O₁₂. The red and blue respectively indicate the degrees of positive and negative values of Grüneisen parameters.

calculation results of phonon band with Grüneisen parameters for Si, ReO₃, and KZr₂P₃O₁₂. From Figs. 1(a, b, d, e), one can see that the zone-boundary phonon modes in Si and ReO₃ generate negative Grüneisen parameters, triggering the NTE. In Si, the most important phonons for realizing NTE are the atomic vibration eigenvectors which transform as irreducible representations X_4 and L_3^- . On the other hand, in ReO₃, the most important phonons for the NTE are the eigenvectors transforming as irreducible representations M_2^+ and R_5^- . The phonon modes of M_2^+ and R_5^- correspond to the ReO₆ octahedral rotations. Note that these zoneboundary phonon modes of Si and ReO3 are lowenergy transverse acoustic phonon modes. It is also noteworthy that transverse acoustic phonon modes do have crystal momentums, which clearly indicate that they must be Brillouinzone-boundary phonon modes. Very intriguingly, however, as shown in Figs. 1(c, f), a Brillouinzone-boundary mode transforming as irreducible representation Γ_2^+ in KZr₂P₃O₁₂ contributes to NTE the most. These results suggest that not all negative Grüneisen parameters are from transverse acoustic phonons.

Further, to confirm the validity of our calculation results for KZr₂P₃O₁₂, we also prepared the polycrystal of KZr₂P₃O₁₂ and examined the thermal expansion coefficient by conducting X-ray diffraction in relevant temperatures. As shown in Fig. 2, our calculations are qualitatively consistent with the experimental results.



Fig 2. Theoretical and experimental thermal expansion coefficients for KZr₂P₃O₁₂. The blue and red colors respectively indicate the results from calculations and experiments. The red broken line is derived by least-square method.

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

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We have studied several systems in highperformance spintronics and magnetic materials on electronic structure and magnetoelectric effect. In these investigations, we took some attempts for improving physical accuracy or finding new candidates in the materials of spintronics application. Here, we report the developments of (A) investigation on magnetic anisotropy energy (MAE) in antiferromagnet (AFM) L1₀-MnX (X=Ir, Pt), (B) optimization in a computational code for quasi-particle selfconsistent GW (QSGW) method, and (C) investigation on electronic structure in magnetic shape memory alloy (MSMA) Ni₂MnGa.

(A) MAE in AFM MnX (X=Ir, Pt)

We investigated the control of magnetic properties by structural strain using the firstprinciples calculations based on spin-density functional theory (SDFT) in L1₀-type Mn alloy; MnIr and MnPt. Contributions to the MAE were calculated from both the magnetocrystalline anisotropy energy (MCAE) arising from the spin-orbit coupling and the shape magnetic anisotropy energy (SMAE) arising from the magnetic dipole interaction energy. The MCAE was evaluated using the total energy (TE) and grand-canonical force theorem (GCFT) [1,2]. Our self-consistent calculations revealed that the intra-c-plane AFM configuration was stabilized as the ground state for both of the materials. The MCAE is obtained to be negative, indicating a favor of in-plane anisotropy. The absolute value of MCAE tends to decrease as the ratio of lattice constants c/a increases. The SMAE is always positive, reflecting the AFM configuration. In MnPt, we obtained an anisotropy transition in the investigated range of strain, namely, the whole MAE became positive (perpendicular to c-plane) at larger c/a, from the in-plane anisotropy. Through this investigation, the approach GCFT was confirmed to be an efficient approach to analysis of MAE.

(B) QSGW method

It is well known that the DFT suffers from many deficiencies such as small band gap, electron over binding property, etc.. To improve these deficiencies, extension methods of DFT such as DFT+U have been developed. However, they often have a semiempirical character, and are not universal and parameter-free. In the other



Fig. 1: Speedup factor in the new code.

hand, QSGW is a universal approach to the reliable prediction of electronic structure [3]. The idea of QSGW is an optimization of the onebody Hamiltonian by performing a selfconsistent calculation in the many-body approach with GW approximation, where the self-consistency is constructed to minimize the perturbation. QSGW has already had success in the estimation of band gaps and other properties for a wide range of materials. The requirement to be paid is computational cost. QSGW needs roughly 100-1000 times more expensive in computational time than DFT. We parallelized the part of calculation for the polarization function (PF) in GW approach, which is one of the most expensive (time-consuming) parts in QSGW. As a result, the computational time of PF was reduced from 11 hours to 1 hour in the application to 4O structure (16 atoms in the unit cell) of Ni₂MnGa. The parallelization efficiency, as shown in Fig. 1, was almost ideal when the number of processor elements (PEs) was small, but decreased as the number of PEs increases; with an efficiency of 60% at 30 PEs. This

decrease in parallelization efficiency was found to be due to the communication time among PEs. (C) Electronic structure in Ni₂MnGa

Recent results on Ni₂MnGa show that the modulated martensite phase is more energetically stable than the non-modulated (NM) phase, supporting an importance of electron-correlation effect [4]. The GGA+Ureveals that the stability of the austenite and martensite phases is dependent on U. We investigated the electronic structure of MSMA Ni₂MnGa using QSGW [4,5]. The Ni eg orbitals in the cubic (austenite) phase, which lead to martensite phase transition by band Jahn-Teller effect, were found to locate on the Fermi level.

The NM and 4O structures of Ni₂MnGa were calculated with QSGW. The peak of density of states near the Fermi level for the minority-spin channel was located above the Fermi level in NM and below the Fermi level in 4O. This difference might be related to the presence of nanotwin double layer in modulated martensite phases.

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Prediction of new crystal structures based on the densest ternary sphere packings

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Densest unary sphere packing was proven to be the FCC structure in the 2000s, but the densest binary and ternary sphere packings have not yet been identified analytically. To discover the unknown putative densest packings, we have created an algorithm to explore them, and we successfully found the 12 putative densest binary sphere packings (PDBSPs) with confirming the known PDBSPs with a small correction of the phase diagram [1].

On top of the success of the discovery, we planned to explore the putative densest ternary sphere packings (PDTSPs). If we only search the periodic packings of n different sizes of spheres, the packing fraction at a given composition ratio is maximized by filling the space with not more than n kinds of packing structures. Since no seminal study seems to construct the phase diagram, we made the ternary phase diagrams to identify the PDTSPs that are denser than any other combination of packing structures. The example of the ternary phase diagram is shown in Fig. 1.

As a result, we have discovered the 59 kinds of PDTSPs [2,3]. The newly found PDTSPs have unique structural properties, and some of them have high symmetry. The (4-3-1) has the P6/mmm symmetry, and if a line of small sphere in the (4-3-1) structure is replaced of one small sphere, we can get the crystal of $SmCo_5$. Note that we name a PDTSP consisting of l small, mmedium, and n large spheres per unit cell as (l*m-n*) structure, and the small, medium, and large spheres in figures are represented by pink, yellow, and purple balls, respectively. The (9-7-3), (10-6-3), and (13-3-1) structures can be derived from the Perovskite structure, and they have the $Pm\bar{3}m$ symmetry. Remarkably, an edge of unit cell of the (9-7-3) structure is constituted by a line of four medium spheres. The (13-2-1) has the $Fm\overline{3}m$ symmetry. Large spheres constitute the FCC structure without contact, and a tetrahedral site is occupied by one medium sphere. The medium and large spheres are surrounded small spheres constituting semi-



Fig.1: An example of ternary phase diagram

regular polyhedrons. This structure is predicted to become the PDTSP at the several radius ratios such as 0:44 : 0:64 : 1:00, at which small and medium spheres would be too large to be placed in the tetrahedral and octahedral sites if large spheres comprising the FCC structure with contacts. Finally, large spheres in the (16-2-2) structure are surrounded by the network structures of small and medium spheres.

The six exemplified PDTSPs might be used as the structural prototypes for crystals under pressure. For example, the (13-2-1) and (13-3-1) structures might be realized by metal hydrides with replacing small spheres of hydrogen atoms. We have been exploring the quartic metal hydrides that have the isotypic crystal structures to the (13-2-1) and (13-3-1) structures, but the calculations have not yet been finished.

The computational cost of the structural optimizations is low, so all the process can be finished in one processor, so the exploration of the structures was effectively parallelized.

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Low Thermal Conductance Generated by van Der Waals Interaction

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Clathrate compounds are promising for thermoelectric candidates materials in terms of the "electronphonon-glass" crystal concept. Clathrate compounds are composed of guest atoms encapsulated in cagelike structures. It is expected that electrons can transport in the framework with much less scattering rate than that for phonons because of guest atoms leading to significant phonon scattering. Particularly, in type-I clathrate compounds, guest atoms vibrate in a strong anharmonic potential because they are composed of a Weaire-Phelan structure, which divides a space with the maximum volume with the same crosssectional area (Fig. 1(a)). In this study, we have studies type-I $Ba_8Ga_{16}X_{30}$ (BGX, X = Si, Ge, Sn) to gain insights of the effect of phonon anharmonicity on heat transport.

Phonon properties were calculated with the self-consistent

phonon (SCP) theory [1] and unified theory [2]. The SCP theory is used to consider effects of forth-order anharmonic potential and to obtain temperature-dependent harmonic interatomic force constants (IFCs). Using the unified theory, one can consider the coherent contribution. that of interbranch tunneling, to heat transport as well as the population contribution, which is considered also in the context of Peierls Boltzmann transport theory. We have employed ALAMODE package [1] to perform the above approaches and VASP to calculate forces on atoms.

While phonon dispersion have imaginary (negative) frequencies when guest atoms have negative harmonic potential at low temperatures, negative frequencies became positive at finite temperatures, as shown in Fig. 1(b). For type-I BGSn, harmonic potential was positive above 100 K, and



Fig. 1 Phonon properties of type-I clathrate compounds. (a) Crystal structures of type-I clathrate. (b) Phonon dispersion of $Ba_8Ga_{16}Sn_{30}$ (BGSn) without considering renormalization (grey), at 300 K (blue), and at 600 K (red). (c) Temperature-dependent thermal conductivities of BGSn. Population (blue), coherent (orange), and electron (green and red) contributions were considered.

conductivities thermal could be calculated at this temperature range. The calculated thermal conductivities including all the contributions (population, coherent, and electron contributions) were in good agreement with experimental data, as shown in Fig. 1(c). To gain insights into the effect of phonon anharmonicity, have also we analyzed mode dependent phonon properties at high temperatures in details (> 100 K). While a unique

temperature-dependence of type-I clathrate at low temperatures (≈ 10 K) have been widely studies, we have revealed intriguing phonon properties at high temperatures in type-I clathrate [3].

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A Unified Understanding of Thermodynamic Properties in Icy Planets and Icy Moons

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The high-pressure properties of hydrogen sulfide have drawn considerable attention in terms of its superconductivity and metalization [1]. Astronomical observations have detected H_2S from the atmosphere of icy planets (ice giants) like Neptune and Uranus [2, 3], and also in plumes coming from the interior ocean of Enceladus, a Jupiter icy moon [4]. These findings provide insight for estimating the interior of icy bodies and their physical and chemical origins. Although H_2S would be one of the typical minor components of ice mantle in icy planets and satellites inside and outside our solar system [5], the phase diagrams and properties of H₂S and its mixture have not yet been revealed, especially at high P-T conditions.

Our project aims to elucidate possible mixing states and thermodynamic conditions in the icy bodies by *ab initio* calculations. We focus on the properties of H₂S as the first onset from the interest above and perform density functional molecular dynamics (DFT-MD) simulations for H₂S in the temperature range of 500 ~ 10,000 K and the density range of 1 ~ 5 g/cm³ using the QUANTUM ESPRESSO package. More than 10 ps for MD simulations are allowed after thermal relaxation with a 2 × 2 × 2 supercell containing 32 H₂S molecules, and the ion temperature is controlled in the *NVT* ensemble with an energy cutoff of 80 Ry.

Pressures in our calculations were up to \sim 250 GPa, corresponding to the values at the



Figure 1: Radial distribution function g_{HS} for Pmc2_1 structure.

deep mantle of ice giants [6]. Figure 1 presents the radial distribution function between H and S atoms for Pmc2₁ phase of H₂S. The fluid phase emerged at higher temperatures (e.g., $\sim 3,000$ K with $3 \sim 5$ g/cm³), and at lower densities like 1 g/cm³, the phase appeared at more higher temperatures. Moreover, diffusion coefficients in Figure 2 implicate the transition from the solid phase to the superionic and then to the fluid, like H₂O and NH₃ [6]. The difference in diffusion between hydrogen and sulfide becomes more prominent at higher



Figure 2: Diffusion coefficient of H and S for $Pmc2_1$ structure.

temperatures (all the conditions are not plotted in Figure 2). Thermodynamic quantities, e.g., free energy, are being evaluated, and an equation of state (EOS) including H_2S is being constructed, which are significant for understanding conditions realized in icy bodies.

The computation was partly carried out using the computer resource offered under the category of General Projects by the Research Institute for Information Technology, Kyushu University.

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First-principles transport calculations for single-molecular junctions

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Single-molecule devices attract attentions because of possible bottom-up construction, potential for device miniaturization, and utilization of unique electrical responses of organic materials. Since it is not possible to directly observe the bridging structure of the molecule between electrodes, the presence of the molecule should be confirmed through the conductance histogram. The conductance histogram is normally broad, ranging orders of conductance values, while conventional firstprinciples transport calculations are performed only for the most stable structure, which is assumed to be the peak top value of the conductance histogram. A combined molecular dynamics and transport calculation is required to reproduce the broad conductance histogram and discuss the structure-property relationship.

In this work, a reactive force field to simulate the break junction procedure has been developed. Three junction structures (on top, bridge, and hollow) were prepared and 200 break junctions for each structure were simulated using the molecular dynamics (MD) method. We further performed first-principles transport calculations using the SMEAGOL codes for the snapshots for the MD trajectory. We observed that the peak top value largely depends on the molecular junction structures.



Fig. 1: Snapshots of the molecular dynamics trajectory.



Fig. 2: Calculated conductance histograms for Au-BDT-Au molecular junctions.

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First-principles study of quantum transport in nanostructures

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An atomic-scale understanding of quantum transport properties in materials is an important issue in materials science and nanotechnology. The aim of this project is to reveal and predict quantum transport properties in materials from first-principles. We have developed the nonequilibrium Green's function (NEGF) method, and the O(N) time dependent wave-packet 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. [2] We have applied the method to analyses of thermoelectricity of Heusler compounds. The electronic structures and thermoelectric properties are analyzed, and high performance systems are designed.

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 recently expand the method to analyze thermoelectric properties, and demonstrated Seebeck coefficient and power factor calculations for a huge system of 100 million atoms.

Furthermore, we have analyzed the gate induced modulation effects of electronic states in monolayer organic field-effect transistor as shown in Fig. 1. [3] Organic field-effect transistors with ionic liquids have attracted much



Figure 1: Schematic pictures of the C_8 -DNBDT monolayer organic field-effect transistor.

attention, since the ionic liquids induce an intense electric field at a semiconductor interface, resulting in a high concentration of charge carriers. We elucidated that strong electric fields and highly doped charges induce significant modulation effects on the electronic band structure and the mobility.

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First-principles study on charging-induced structure phase transitions of thin film oxides

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HfO₂ has various crystal structures depending on the growth conditions. Although the orthorhombic (Ortho) HfO₂ is thermodynamically unstable, it can be grown on metal electrode substrates such as TiN and Pt and has giant ferroelectricity, thus being expected as a promising material for future memory devices. However, it has not been clarified why such unstable Ortho phase is realized in experiments. In this work, we study the stabilization mechanism of Ortho HfO₂ phase using the first- principles calculations.

Since the ferroelectric phase of representative BaTiO₃ is normally realized by the substrateinduced strain, we first consider the effect of strain. Fig.1 shows formation energies of stable monoclinic (Mono) and unstable Ortho phases in bulk and thin-film forms as a function of the cross-section area, i.e., biaxial strain. The energy increase in thin films occurs due to the surface energy loss. As seen in both figures, by applying tensile or compressive strain, the Mono phase increases the energy compared to the Ortho phase. This is because the Mono phase is stabilized by lowing its crystal symmetry and the deformation from such stable structure promotes large energy loss. However, the Ortho phase always has larger energy than the Mono one. Thus, the strain is not a single origin of the Ortho-phase formation.

Next, we consider the effect of oxygen vacancy (Vo), which is a representative defect and is often generated in oxides. Vo produces an electronoccupied state below the conduction bands, thus stabilized by the positive ionization. Fig.2 shows the energy difference between Ortho and Mono phases as a function of Vo ionization charge. From this figure, we know that the Ortho phase becomes



Fig.1. Calculated formation energies of Mono and Ortho HfO_2 in bulk (left) and thin-film (right) forms under (111) biaxial strain, relative to the most stable Monoclinic bulk phase, as a function of an area of formula unit.



Fig.2. Calculated difference in energy between Ortho and Mono phases in bulk forms, as a function of the ionization charge of oxygen vacancy (Vo). The zero energy corresponds to the Mono phase.

the most stable when the 4-5% Vo's exist and they are +2 charged. However, considering that the formation energy of Vo, is relatively large around 4-5eV, the assumed composition 4-5% is still large. Thus, the ionization of Vo is also not a single origin of the Ortho-phase formation.



Fig.3. Calculated difference in energy between Ortho and Mono phases in thin-film forms, with/without 1-4% strain and 3% charged oxygen vacancy (Vo). The cases of (a) (111) tensile strain and (b) (001) compressive strain are shown.

Then, we consider the case when both the strain and the Vo ionization coexist in HfO₂. Fig.3 shows the energy difference between Ortho and Mono phases for the cases with/without strain and Vo charging. Figures 3(a) and 3(b) respectively correspond to the cases of (111) tensile strain and (001) compressive strain. It can be seen that both the strain and the Vo charging work cooperatively to stabilize the Ortho phase. In these ways, we can conclude that not only the substrate-induced strain but also the ionization of Vo are important factors to grow and stabilize the ferroelectric Ortho phase.

Finally, we consider the ferroelectricity of Ortho HfO₂. It is well known that the polarization charge of ferroelectric material can be calculated by the Berry phase method using the bulk unit cell. The result by this method corresponds to the free standing ferroelectric film located isolate in the vacuum. However, in experiments, such material is grown on some substrates. In order to study the effect of the substrate on the ferroelectricity, the



Fig.4. Calculated local-potential profile around Ortho HfO_2 (001) thin film. To correct the periodic boundary condition of the repeated slab geometry, the artificial electrodes are inserted in vacuum region so as to keep the horizontal potential.

calculation method using the thin film geometry should be developed. Thus, we try to calculate the polarization charge using the conventional repeated-slab unit cell.

Due to the cancellation of electric fields caused by the front and back surfaces of the film, the potential should be flat outside the ferroelectric film. To realize such situation, we arrange the artificial electrodes (dipole) in the vacuum region in the unit cell, as shown in Fig.4. Then, we calculate the polarization charge using the Ortho HfO₂(001) thin film. The calculated polarization charge is about 53μ C/cm², which agrees with the values by the Berry phase method around 40-50 μ C/cm² and the observed values around 40 μ C/cm². In the future, we will use this method and study how the polarization charges with varying the substrate.

All these calculations were performed using the xTAPP, VASP, and our original pspwf codes. In order to realize the calculations for the present thin-film systems, because the system is made of a large number of atoms (1000-2000 atoms), the advanced computing facility having multi-task and higher-speed CPU (more than 1280 cores \times 2.0G Hz), 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.

Elucidation of surface structure and reactive property of (100) exposed CeO₂ nanocubes through first-principles calculation

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CeO₂ nanocubes with (100) facet exposed have been synthesized by supercritical method, and it was found to have high oxygen storage capacity. In this study, the stabilization of the (100) facet by organic modification was studied by using first-principles calculations.

Another approach to improve oxygen storage capacity of CeO_2 is metal doping into the structure. In this study, Cr-doping into CeO_2 was also studied. The structural effects by doping were investigated.

In this study, first principles simulations based on density functional theory (DFT) was conducted. Plane wave basis DFT simulations were conducted using VASP code. Structures of CeO₂ at surface and bulk were calculated with generalized gradient approximation proposed by Perdew, Burke, and Ernzerhof (PBE) [1]. The valence configurations of the pseudopotentials were $5s^25p^64f^45d^16s^2$ for Ce, $3s^{2}3p^{6}3d^{5}4s^{1}$ for Cr, and $2s^{2}2p^{6}$ for O. The DFT+U method introduced by Dudarev et al. [2]was used to treat electron localization. The parameter U-J was set to 3.5 eV for Cr3d, 5.0 eV for Ce4f, and 5.5 eV for O2p states, respectively, based on previous studies of Cr_2O_3 and CeO_2 [3]. The Monkhorst-Pack kpoint mesh of 4×4×4 was used for the unit cell of CeO2. The defect simulations were conducted with supercell of 2 × 2 × 2 extension (96 atoms).The slab model exposing (100) facet includes 60 atoms, and that for (111) facet includes 108 atoms. The Monkhorst -Pack kpoint mesh for the slab model was 4×4×.

Figure 1a and 1b show $CeO_2(100)$ and (111) surface structure. The (111) facet of CeO₂ is nonpolar, contrary to the polar surface of (100). For the (100) facet model, half of the oxygen was moved to the other side to exclude polarity keeping the CeO_2 composition. The surface energy obtained from these calculations were 1.46 J/m² for (100) and 0.78 eV/m² for (111). The CeO_2 (111) is more stable than CeO_2 (100). The instability of (100) is the origin of high activity as catalysts. When CeO2 is synthesized with organic surfactant, it is known that (100) facet exposes. In Figure 1c, structure of carboxylic acid attachment on CeO2 (100) is shown. When calculating carboxylic attachment, dipolar correction implemented in VASP was used. After the deprotonation of the carboxylic acid one oxygen of COO locates between two

Ce atoms and the other oxygen locates on one Ce atom. The adsorption energy was found to be -26.6 kJ/mol. The apparent surface energy including the adsorption energy of the surfactant is lower in (100) than (111).



Fig. 1 Surface structures of CeO_2 . a) CeO_2 (100), b) CeO_2 (111), c) Carboxylic acid adsorption on $CeO_2(100)$.

The bulk calculation was conducted to obtain the oxygen vacancy formation energy in the Cr-doped system. The supercell consisting 96 atoms were used. Figure 2 shows the local structure around oxygen vacancies. The information about the structures is summarized in Table 1. Figure 2a shows the pure CeO₂, which includes an oxygen vacancy. Two Ce³⁺ ions exist in the next nearest neighbor (NNN) of the oxygen vacancy. The oxygen vacancy formation energy was 2.00 eV. Figure 2b shows the structure of Cr doped CeO₂, which one of the Ce are substituted with Cr. The doping concentration is corresponding to 3 at%. In this case four oxygen atoms coordinates Cr, and Cr exists as 4+. Figure 2c shows the structure that one of the oxygen coordinating Cr (O-1 in Figure 2b) was removed. As a result of the vacancy introduction, local structure around Cr changed to six-coordination, and Cr became 3+ state, and the oxygen vacancy formation energy was 0.99 eV. The significant decrease in oxygen vacancy formation energy was observed. Also in this case, Ce3+ exits in the next nearest neighbor of oxygen vacancy. Further oxygen removal (O-2 in Figure 2c) occurred with lower oxygen vacancy formation energy as 0.65 eV. The local structure and the valence of Cr did not change, and two more Ce3+ are formed at the next nearest neighbor of the oxygen vacancy. At the vicinity of Cr dopant oxygen vacancy can be formed easily. Moreover, an oxygen atom, which is not at the next of Cr surrounded by four Ce⁴⁺ (O-3 in Figure 2d) was removed. As a result, the structure shown in Figure 2e was obtained. For the three oxygen vacancies, one Cr3+ and 5 Ce3; was formed. Five Ce3+ locates not at the nearest neighbor (NN) of oxygen vacancy but at the next nearest neighbor of the oxygen vacancies. The oxygen vacancy in this case was 1.20 eV, and significantly lower than pure CeO2 although the local structure was similar. This is not the oxygen vacancies around dopant. Doping affects whole the structure occurring distortion, which results in the lower oxygen vacancy formation energy at far position from the dopant.



Figure 2 Structure of Cr 3% doped CeO₂ a)Non-doped CeO₂ with an oxygen vacancy, b) Cr4+ substituted CeO₂, c) \sim e) Cr doped CeO₂ with 1-3 oxygen vacancies

Structure	Bader charge, e					Vo positions	F	Co ³⁺ positions
	Ce ³⁺	Ce ⁴⁺	Cr ³⁺	Cr ⁴⁺	0	(distance from Cr)	[eV]	relative to V ₀
Non-doped CeO_2 with 1 V_O (Figure 6A)	+2.11	+2.44	n/a		-1.28 to -1.20	n/a	2.00	NNN (2Ce ³⁺)
Cr ⁴⁺ doped CeO ₂ (Figure 6B)	n/a	+2.45	n/a	+2.00	-1.24 to -1.16	No V _O	n/a	n/a
Cr^{3+} doped CeO_2 with 1 V_O (Figure 6C)	+2.15	+2.44	+1.86	n/a	-1.26 to -1.17	O-1 in Figure 6B (2 Å)	0.99	NNN (1Ce ³⁺)
Cr^{3+} doped CeO_2 with 2 V_O (Figure 6D)	+2.15	+2.43	+1.85	n/a	-1.27 to -1.20	O-1 in Figure 6B (2 Å) O-2 in Figure 6C (2 Å)	0.65	NNN (3Ce ³⁺)
Cr^{3+} doped CeO_2 with 3 V_O (Figure 6E)	+2.13	+2.42	+1.85	n/a	-1.37 to -1.20	O-1 in Figure 6B (2 Å) O-2 in Figure 6C (2 Å) O-3 in Figure 6D (6 Å)	1.20	NNN (5Ce ³⁺)

Table 1 Structural information about Cr 3% doped CeO₂

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"Atomistic Origin of High-Concentration Ce³⁺ in {100}-Faceted Cr-Doped CeO₂ Nanocrystals"

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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. 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 in-house program [1–6]. The peak in magnetization when applying an intermediate magnetic field along the hard axis of CrI₃, a well-known 2D material for the spintronic application, is successfully reproduced by using our program as shown in Fig. 1. The origin comes from the competition between magnetic anisotropy and external magnetic fields, where the temperature dependence of magnetic anisotropy energy plays the role. The finite magnetic anisotropy at slightly higher than Curie temperature is reproduced, where the magnetization anisotropy and anisotropic magnetic susceptibility is the crucial factor. The high accuracy in the estimation of anisotropic magnetic entropy change in CrI_3 paves the way to predict the magnetocaloric properties of new materials. In the next step, we have some ideas to enhance the accuracy and predict some novel properties of magnetic materials within the theoretical framework.

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Figure 1: Magnetization, magnetic anisotropy energy, and anisotropic magnetocaloric effect of CrI_3 [6].

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Electrochemical reaction analysis using density functional calculation + implicit solvation model 3

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We have studied electrochemical reaction systems using density functional combined with implicit solvation model, called ESM-RISM simulations [1–4]. This year, we focused on the adsorption structures of $Pt(111)-H_2O$ (see Fig. 1a). The understanding of this metal/water interface system is important for basic electrochemical reactions such as oxygen/hydrogen reduction/evolution reactions.

Fig. 1a shows the most stable structure, Pt(111) $\sqrt{39} \times \sqrt{39}$ -H₂O including 5- and 7membered rings, which is consistent with experiment. Fig. 1b shows the pair distribution functions of the obtained structure, which shows the Pt-O and O-O peaks of 2.3 Å and 2.5 Å. This small O-O distance could induce the redshift of OH vibrational frequencies. We also conducted the analysis of vibrational frequencies of the obtained structure. As a result, calculated vibrational frequencies were in good agreement with experiments. However, the adsorption energy of this structure is less than the activation energy of desorption from experiment, which indicates that the Pt-H₂O interaction should be improved by more sophisticated density functional.



Fig. 1: (a) Adsorption structure of Pt(111)-H₂O.(b) Pair distribution function of Pt(111)-H₂O.

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Study of Efficient Training Data Generation Method for Constructing Artificial Neural Network Force Field III

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Machine Learning Interatomic Potential (MLIP) not only achieves high accuracy by learning from first-principles molecular dynamics (MD) data, but also has low computational cost. Active Learning is the driving force behind the recent development of MLIPs. This approach primarily uses the uncertainty in the output of MLIPs to discover and generate unlearned data for efficiently constructing robust potentials. In this study, we continued to work on improving Active Learning. The MLIP using artificial neural network (called ANN potential) was used. In the previous studies, the use of standard deviation of atomic force is considered effective for finding unlearned data. We have also found that the method worked well.

On the other hand, we found that the MLIPs training method needs to be improved. The current standard training method does not guarantee the accuracy of pressure required for MD. We have demonstrated that the training of pressure is essential for ANN potentials to reproduce the solid-liquid phase transition [1]. Pressure training is also essential for thermal conductivity calculations using MLIPs. The heat flux in the Green-Kubo formula for ANN potentials is closely related to pressure. Thus, it has been found that without pressure training, obvious errors can occur in thermal conductivity [2].

Since the current MLIPs are trained not only with potential energy but also with atomic force and pressures, the cost function is composed of the corresponding terms. For efficiently training, adjustable coefficients are therefore introduced into these terms having different units and data size. Although previous studies did not emphasize the importance, we demonstrated that the coefficient adjustment was a significant effect on the accuracy of ANN potentials [3].

No matter how efficiently untrained data can be obtained, it becomes meaningless if the training is inadequate. As the application of MLIPs expands, the training of pressure and the coefficient adjustment would become essential.

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Structure stability and electronic structures of point defects in wide-gap oxide materials

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The wide-gap oxide materials such as Al_2O_3 and Ga_2O_3 have been attracted great interests in applications for power electronics devices. In this work, we have studied the structural and electronic properties of oxygen defects (vacancies or interstitials) in several amorphous oxides by the first-principles calculations.

The amorphous model structures of a-Al₂O₃ and a-Ga₂O₃ are generated by the firstprinciples molecular dynamics simulations and the melt-and-quench techniques. Figure 1 shows an example of the generated model structures using the 120-atom supercells. The mass densities are set to be 3.3 g/cm³ for a- Al_2O_3 and 4.5 g/cm³ for *a*-Ga₂O₃, which are in their respective experimental ranges and are lower than those of the α crystal phases (4.0) and 6.4 g/cm³ for Al_2O_3 and Ga_2O_3 , respectively). The O coordination numbers around Al are four (60.4%), five (29.2%), and six (10.4%) in *a*-Al₂O₃, and those around Ga are four (66.7%) and five (33.3%) in *a*-Ga₂O₃.



Figure 1: Amorphous structures of (a) a-Al₂O₃ and (b) a-Ga₂O₃ 120-atom supercell models.



Figure 2: Density of states (DOS) of a-Al₂O₃ with the excess O (O_i⁰). Total (black line with left scale) and O_i⁰ (red line with right scale) DOSs are shown. The inset shows the local structure near O_i⁰, forming the peroxy linkage.

The O defects are introduced by adding and removing O (interstitials O_i^q and vacancies V_O^q) in the pristine oxide models, considering the charged states q of defects. In the charge neutral state (q = 0), it is found that O_i^0 tends to form the O–O peroxy linkage, giving the π^* - and σ^* -type O₂-like states near the valence band top and the conduction band bottom regions, respectively (Fig. 2). It is also found that such the O₂-like states show interesting behavior by changing q, and similar properties of O_i^q are confirmed in a-Ga₂O₃ and in several oxide crystals. We also study electric properties due to V_O^q in oxides to discuss ReRAM [1].

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Theoretical study for magnetic-nano-particles formation from first-principles calculations

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There is a growing interest in searching novel materials that are not only thermodynamically stable, but also thermodynamically unstable for applications. Chemical synthesize techniques, which control nano particles precisely, are being developed in order to find new functional materials for technologies. Recently, Teranishi's group at Kyoto University found a new behavior of crystal structure transformation for an ionic nanocrystal [1], and a new Z3-type Fe(Pd,In)₃ crystal structure, which was synthesized by introducing a third element of In into $L1_2$ -FePd₃ [2].

In this report, we performed first-principles non-collinear calculations in order to explain the higher coercivity value in the Z3-Fe(Pd,In)₃ structure. We used the ab-initio code, OpenMX [3], for calculating the magnetic anisotropy energies of $L1_2$ -(Fe,In)Pd₃ and Z3-Fe(Pd,In)₃ structures and compared these energies to find easy axes. In each calculation, the spin directions of each atom in these systems were set from [001] to [100] when $\varphi = 0$ and from [100] to [110] when $\theta = 0$. We found that the magnetic anisotropy energies show $-1.38 \mu eV/atom$ for the $L1_2$ -(Fe,In)Pd₃ structure and -0.213 meV/atom for the Z3-Fe(Pd,In)₃ structure. The easy axis for Z3-Fe₈(Pd₂₀,In₄) is the c axis, as shown in the figure. The tendency which the Z3-Fe(Pd,In)₃ structure has higher coercivity values than the $L1_2$ -(Fe,In)Pd₃ structure is consistent with the experimental measurement. We assume that

added In atoms might be one of the reasons to increase the magnetic anisotropy of the Z3- $Fe(Pd,In)_3$ structure. Further theoretical studies are needed to explain the mechanism of the coercivity increase in the Z3-Fe(Pd,In)_3 structure.

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Fe(Pd,In)3 structure depending on the spin directions.

Evolutionary algorithm for simulation of fast chemical reaction process

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1 Introduction

One methodology in the quantum materials informatics, based on density functional theory to evaluate many-body correlation effects, has recently been used to determine the electronic phase diagram of oxides [1], to design hightemperature superconductors [2], and spinelectronic devices based on atomic layer material [3]. Materials design of measurementbased quantum computing devices [4, 5], and the elucidation of unknown photo-induced phase transitions based on measured data [6] were performed. We have also designed an activation method of catalytic properties and evolutionary operations for detonation processes.

2 Alkane dehydrogenation on nanographene catalyst

To support designed activated nanographene catalysts for dehydrogenation of alkane, several dehydrogenation reaction pathways were determined based on density functional theory calculations. The catalytic effect of vacancy created graphene surfaces is simulated using the alkane decomposition reaction as an example.

The effect of the atomic defects was investigated, and the effect of lowering the reaction energy barrier due to substitution by nitrogen and other group V elements was confirmed. Furthermore, the characteristics of the nanographene catalyst, in which multiple active sites are involved in the reaction, confirm that propylene generation from propane on our catalytic structure has the effect of significantly lowering the endothermic reaction heat.

At the same time, in-situ AI analysis of timedependent small-scale data during the synthesis of catalytic materials was requested to elucidate the experimental procedures. Theoretical analysis of emission spectra during the material conditioning (activation process by high-energy particle irradiation) was performed. As a result, it became possible to develop a measurement method to support insitu observation of molecular desorption by adopting machine-learned classification using ResNet.

3 Algorithms for elucidation of detonation reaction paths

We are also promoting the elucidation of the detonation reaction mechanism by combining evolutionary algorithms, which reveals oxidation and reduction reactions in the TNT-RDX composite that produces the detonation diamond. An evolutionary algorithm systematically generates intermediate states of chemical reaction processes.

Stable crystals initiate rapid chemical reactions triggered by mass transport. We introduced mass transport into the evolutionary algorithm. The basis for the continuation of the reaction was found by structural optimization calculations, first-principles molecular dynamics calculations, and the migration paths of radicals within the crystal.

Consider that radical species are supplied to adjacent material phases in the processes of redox reactions. To determine the initiation process of this chain reaction, we applied the accelerated chemical reaction simulation using the generational operation of the evolutionary process. We applied this method to oxidation of RDX and reduction of TNT, and confirmed that our acceleration method works

The initiation point of the detonation process is considered to be the formation of OH radicals by electron transfer excitation. The OH radicals pull out hydrogen atoms and rapidly destabilize RDX. RDX then decomposes to form NO₂. (Figure 1 (a), (b))

Hydrogen radicals are supplied to TNT from the destabilized RDX. When a certain amount of hydrogen radicals are added, the nitro groups of TNT are decomposed to generate water, resulting in nitroso groups. This nitroso group functions to join adjacent carbon skeletons. (Figure 1 (c)) From these carbon skeleton linkages, the formation of clusters with larger carbon skeletons may follow.

By confirming that the supply of hydrogen radicals to TNT and OH radicals to RDX initiate rapid reactions, and by successfully drawing the initial reaction cycle, we confirmed that our method has potential for providing insight into real-time evolution problems.

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Figure 1: Molecular structures arising from operations of evolutionary algorithms. (a) RDX, which is destabilized by the addition of hydroxyl radical, generates (b) a water molecule and simultaneously releases of NO₂. (c) TNT destabilized by hydrogenation can generate carbon clusters bridged by NO groups.

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Study on Hydration Process of Cellobiose by First Principles Calculations Tomomi Kondo^{1,2}, Daisuke Akazawa^{1,2}, Takehiko Sasaki¹, Motoyuki Shiga²

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Cyclization dehydration reaction of polyalcohol in hot water has been proven to be efficient method for utilization of biomass materials [1]. For this purpose we proposed a new method of refinement (improved metadynamics method: Refined MTD), and applied it to cyclization dehydration of 2,5-Hexanediol (HDO) [2]. Based on these results we studied cyclization dehydration process of dsorbitol (SBT) yielding 1,4-Anhydro-d-sorbitol (1,4-AHSO), 2,5-Anhydro-d-sorbitol (2,5-AHSO) and 1,5-Anhydro-d-sorbitol (1,5-AHSO) as shown in Fig. 1.



Fig. 1 Cyclization dehydration process of d-sorbitol.

Calculations were conducted using software PIMD [3] working with DFTB or VASP. The calculation system consists of 1 SBT 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 defined for each product as shown in Table 1. Fig. 2 shows the illustration for 1,4-AHSO3 as one example. 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. Reaction processes in HCl(aq), H₂CO₃ (aq) and pure water were examined.



Fig. 2 Illustration for CV of 1,4-AHSO3

Table 1Definitions of CVs

CVs	1,4-AHSO3	1,4-AHSO6	1,5-AHSO2	1,5-AHSO6	2,5-AHSO2	2,5-AHSO5
Difference of the bond length d	O_6, C_3, O_3	$\mathrm{O}_3,\mathrm{C}_6,\mathrm{O}_3$	$\mathrm{O}_6,\mathrm{C}_2,\mathrm{O}_2$	O_2,C_6,O_6	O_5,C_2,O_2	$\mathrm{O}_2,\mathrm{C}_5,\mathrm{O}_5$
Dihedral ϕ	O3-C3-C4-C5	O6-C6-C5-C4	O2-C2-C3-C4	O6-C6-C5-C4	O2-C2-C3-C4	O5-C5-C4-C3
Difference of the Coordination number of H D_n	O ₃ , O ₆	O ₆ , O ₃	O ₂ , O ₆	O_6, O_2	O ₂ , O ₅	O_5, O_2

According to DFTB based calculations over 3 ns dehydration reaction was observed and the

transition state was found on the free energy contour map at CV with $\phi = 155^{\circ}$, d=0.0 and n=2.1. Molecular dynamics calculations were conducted around this transition state so that the real time mechanism is visualized. After proton is bonded on the oxygen atom (Fig. 3 ①) the dehydration (Fig. 3 ②) and the formation of O-C bond (Fig. 3 ③) occur almost simultaneously, indicating that the five-membered ring is formed via S_N2 process.



Fig. 3 Reaction process from SBT to 1,4-AHSO



Fig. 4 Dehydration mechanism for SBT.

The mechanism is summarized in Fig. 4. The simulation results predict that the reaction is faster in HCl solution than in carbonic acid solution, due to the acid-catalyzed mechanism. In most of the calculated conditions, the reaction

barriers for two of the pathways leading to the five-membered ring products, 1,4-AHSO and 2,5-AHSO were found to be lower than those leading ot the six membered ring product, 1,5-AHSO. This is in agreement with experiments where only the five-membered ring products were detected. The reaction pathway to the fivemembered ring products goes through a metasbable state of SBT in the confined conformation. These results were published in [4].

We also calculated ab initio molecular dynamics (MD) simulations for cellobiose aqueous solution using PIMD and CP2K program and the subsequent C-K edge XAS spectra simulation using CP2K. Experimental XAS spectra can be interpreted by water molecules interacting with the cellobiose molecule [5].

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Ab initio calculation for structural stability of transition-metal-oxide superlattice

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In this study, we investigate the structural stability of transition-metal-oxide superlattices using first-principles calculations. We consider superlattices built by polar and non-polar transition-metal oxides. The polar type is a transition-metal oxide in which the charge neutrality of the constituent parts is not maintained, but the entire charge neutrality is maintained. For example, in a perovskite $LaAlO_3$, it is made as the stacking structure consisting of a LaO plane charged with +1 valence and an AlO₂ plane charged with -1 valence. On the other hand, in the non-polar type, the charge neutrality is maintained including the partial system; for example, in $SrTiO_3$, it consists of charge-neutral SrO and TiO_2 planes. We consider 10 types of superlattices consisting of SrTiO₃, SrVO₃, $BaTiO_3$, $LaAlO_3$, $CaCuO_2$. In the present report, we focus on $SrTiO_3/SrVO_3$ (STO/SVO) and $CaCuO_2/SrTiO_3$ (CCO/STO) superlattices. Also, we write the superlattice as A_n/B_n where A and B specify materials, and n is their number. We used xTAPP [1]

To discuss the structural stability of the superlattice, we calculate the *n* dependence of the following standard enthalpy of formation $\Delta H(n)$ as

$$\Delta H(n) = \Delta H_I(n) + \Delta H_S(n), \qquad (1)$$

where $\Delta H_I(n)$ and $\Delta H_S(n)$ are defined as

$$\Delta H_I(n) = \frac{E[\mathbf{A}_n/\mathbf{B}_n]}{n} - \left[E(\mathbf{A}, a_n^{\parallel}) + E(\mathbf{B}, a_n^{\parallel})\right], \quad (2)$$



Figure 1: Calculated standard formation enthalpy $\Delta H(n)$ (black lines) for the (a) $(\text{STO})_n/(\text{SVO})_n$ and (b) $(\text{CCO})_n/(\text{STO})_n$ superlattices. Red and blue lines are an interfacial contribution $\Delta H_I(n)$ due to the interface formation, and a strain-storage one $\Delta H_S(n)$ due to the lattice mismatch.

and

$$\Delta H_S(n) = \left[E(\mathbf{A}, a_n^{\parallel}) - E(\mathbf{A}) \right] + \left[E(\mathbf{B}, a_n^{\parallel}) - E(\mathbf{B}) \right], \quad (3)$$

respectively. $\Delta H_I(n)$ is an interface energy due to the interface formation, and $\Delta H_S(n)$ is a strain-storage energy due to the lattice mismatch. Also, a^{\parallel} is an in-plane lattice parameter of the superlattice.

Figure 1 shows our calculated standard formation enthalpy $\Delta H(n)$ (black lines), as well as its decomposition $\Delta H_I(n)$ (red lines) and $\Delta H_S(n)$ (blue lines). Panels (a) and (b) are the results for STO/SVO and CCO/STO superlattices, respectively. The case $\Delta H_I(n) >$ $\Delta H_S(n)$ indicates that superlattice does not develop epitaxially; the STO/SVO superlattice is stable with the epitaxial growth, while the CCO/STO superlattice is unstable.

About the optimized structure of the superlattice, the following trends were observed:



Figure 2: Ferroelectric displacement occurred in the CCO-based superlattice.

- 1. In the superlattices composed only of the perovskite-type oxides, an in-plane lattice constant a_{\parallel} shows a tendency to converge to an averaged value of the two materials that make up the superlattice.
- 2. The average *c* length of of each block constituting the superlattice basically reflects the bulk parameters.
- 3. In the superlattice of polar and insulating non-polar transition-metal oxides, a significant ferroelectric displacement occurs in the non-polar side (Fig. 2).

To understand the tendency of the standard formation enthalpy (Fig. 1) and the ferroelectric displacement in the CCO-based superlattice (Fig. 2), we calculated an effective potential for electrons in the superlattice along a stacking direction z. Figure 3 (a) displays results for the CCO/STO superlattice. From the figure, we see that a potential gradient is occurring in the STO side (blue arrow), leading to the electric field from TiO₂/Ca to CuO₂/SrO interfaces. From the behavior of this effective potential, the CCO/STO superlattice can be regarded as dielectric inserted into a capacitor [Fig. 3 (b)]. With this view, the interfacial charge can be estimated from the classical elec-



Figure 3: Left: Calculated effective potential for electrons in the superlattice, along the stacking direction z. Right: A schematic figure for the resulting electric field.

Table 1: Interfacial charge in the CCO-based superlattice. Unit of e.

	Interfacial charge					
n	2	3	4	5		
CCO/STO	0.33	0.30	0.28	0.27		
CCO/BTO	0.33	0.33	0.31	0.29		
CCO/LAO	0.38	0.31	0.28	0.26		
LAO/SVO	0.25	0.20	0.19	0.16		

tromagnetism as

$$Q = \sqrt{\left(\frac{\epsilon}{\epsilon_0}\right)\epsilon_0 \frac{dv(z)}{dz}\Delta S}.$$
 (4)

Table 1 shows our estimated interfacial charges for the CCO-based superlattice, we show an n dependence. The resulting charge is near 0.3 e, which gives the electric field of 0.87 VÅ⁻¹.

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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 for ultraprecision optical components for scientific and industrial applications, especially in extreme ultraviolet (EUV) and X-ray regimes. Using short-wavelength light, scientific imaging of cutting-edge materials/biological samples and nanoscale lithography has become possible thanks to the ultra-precision optical components. Si is the material of choice for optical components, thanks to its attractive properties, such higher cleanliness, as machinability, and workability. 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 the 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 a hydrolysis reaction, in which the catalyst assists water dissociation and stabilization of the hypervalent state, increasing the 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 calculations. 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 conditions. 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). Similar results are observed on a Si(100).



Fig. 1: Mechanistic reaction pathways of the Ptcatalyzed water etching of Si(111).

To investigate the effect of oxidation for an HF-treated Si(100) surface, Si(100) with an H-terminated surface was used. Si-H and Si-OH exchange reaction is investigated, as shown in Fig. 2. The activation barrier is 0.75 eV.



Fig. 2: Oxidation effect of Si(100) by water

To investigate the effect of oxidation by oxygen at the terrace and step-edge sites, Si(111) is employed, as illustrated in Fig. 3. The corresponding activation barriers are 0.46 and 0.15 eV, respectively (Fig. 4).



Fig. 2: Si(111) oxidation effects by oxygen at the terrace and step-edge sites (top-view).

The obtained results indicated that the oxidation occurs readily in the air at a step-edge site but not at a terrace site. The obtained results are consistent with the previous study [4]. The obtained results also explained why the wettability of the Si surface could last for several hours in the ambient conditions in the previous experimental study [5].



Fig. 4: 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 the oxidation effect of a Si surface by oxygen or water. Oxygen plays a main role in surface oxidation. Moreover, the combined oxidation effects of oxygen and water might be an important factor to be considered in future studies.

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Ab initio molecular dynamics study on ion-conduction mechanisms of perovskite-type oxide

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We have investigated the mechanism of photoinduced oxygen dynamics in cobalt double-perovskite crystal using density functional theory (DFT) based quantummolecular-dynamics (QMD) simulations.

We adopted the LR-TDDFT for calculating light-absorption spectra, which are calculated as folded oscillator strengths



of EuBaCo₂O_{5.39} crystal

We found that the photoexcitation with an energy exceeding 3 eV provides the oxide ion with excess energy, arrowing it to pass through the barrier. The oxide ion may travel to the crosswise position from the potential valleys of the ground state via intersection of the potential energy curves in the excited and ground state at \sim 1 Å. Figure 2 shows the ionic configurations of the oxide ion (O1) as it moves from the diagonal to the crosswise position. The oxide ion is subjected to the repulsive and attractive forces from the other oxide and cobalt ions, respectively.



Fig. 2. Ionic configurations during the travel of the oxide ion

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Atomic structure of metal-oxide interfaces and oxide grain boundaries

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The atomic structures of $SiO_2/4H-SiC$ (0001) [Si face] and $(000\overline{1})$ [C face] interfaces were analyzed by first-principles molecular dynamics (MD) calculations combined with aberration-corrected scanning transmission electron microscopy (STEM). MD simulations were performed using the Vienna ab initio Simulation Package (VASP). The generalized gradient approximation (GGA) in the form of the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was implemented. A kinetic energy cutoff of 450 eV was used for the expansion of the charge density, and all calculations were performed using a Brillouin zone sampling with $2 \times 2 \times 1$ kmesh. The cell sizes are 1.070 nm (~ 4 unit cells of SiC) along the $[1\overline{1}00]$ axis and 0.926 nm (~ 3 unit cells of 4H-SiC) along the [11 $\overline{2}0$] axis where 6 Si-C bilayers along the [0001] axis were involved as the 4H-SiC substrates. SiO₂ structures were constructed by randomly distributed 30 Si and 60 O atoms on each faces as the initial models. The opposite side of the 4H-SiC {0001} slabs was passivated by hydrogen atoms to eliminate the effects of dangling bonds, and a vacuum slab with a thickness of 1.5 nm along the [0001] axis was embedded into the outer side of SiO_2 amorphous layer to avoid unwanted interactions. The supercell includes 246 atoms in total, including 102 silicon, 72 carbon, 60 oxygen and 12 hydrogen atoms. The initial model was heated at 3500 K for 15.0 ps, cooled at -355 K/ps, and then relaxed at 300 K for 9.0 ps. Finally, the atomic positions were fully relaxed until the maximal force on each atom decreased to below 0.05 eV/Åand the total energy converged to less than $1.0 \times 10^{-4} \text{ eV/atom.}$

We observed the interfacial O atoms on the amorphous SiO_2 layer on the Si face show clear atomic ordering with a rigid O-Si bridge structure across the $SiO_2/4H$ -SiC interface, which indicates a slow oxidation rate. The C face interface, on the other hand, was atomically rough and formed many dangling bonds with high oxidation rate. We concluded that the formation of a stable and flat oxidation front by O atom ordering and the suppression of interface defects or residual C will be useful for designing high-performance 4H-SiC MOSFET devices [1].

Polycrystalline ZnO is widely used and its properties are largely influenced by grain boundaries (GBs). We systematically investigated [0001]-symmetrical tilt GBs in polycrystalline wurtzite ZnO by first-principles calculations and atomic-resolution aberrationcorrected STEM. The Zn sites form an octahedron capped by Zn tetrahedra, with O atoms located at the center, forming a Zn octahedron which can be regarded as a hexagon viewed along the $\mathbf{c} = [0001]$ -axis. The misorientation of ZnO [0001]-symmetrical tilt GBs is defined by the dihedral angle 2θ between the $(11\overline{2}0)$ planes in adjacent grains, where θ is the dihedral angle between the $(11\overline{2}0)$ and $(p q \overline{p+q} 0)$ -GB planes.

The stable structures of the $\Sigma 7 (12\overline{3}0)$ at

21.79°, $\Sigma 13$ (2570) at 27.80° and $\Sigma 13$ (1340) at 32.20° CSL GBs were independently simulated. The upper crystal was shifted toward the lower crystal by 0.01 nm along the x-, y-, and z-directions. Static lattice calculations were carried out with General Utility Lattice Program (GULP) using the Buckingham-form two-body interatomic potential for ZnO. The local minima were then optimized in the firstprinciples calculations with the plane-wave basis projector-augmented wave method included in VASP. The GGA was used for the exchangecorrelation potentials in the PBE form and the cutoff energy was 400 eV for all plane-wave basis sets. All ionic positions as well as the supercell volume were relaxed such that all forces were $< 1.0 \times 10^{-5} \text{ eV/Å}$, and the residual force on each relaxed atom was < 0.05 eV/Å under the constant pressure of 0 Pa and constant temperature of 0 K. The Brillouin-zone integrations were performed over a $4 \times 2 \times 4$ kpoint mesh generated by the Monkhorst-Pack scheme.

The GB and bulk structural units found in this study are similar to capped trigonal prisms (CTPs) and octahedra, corresponding to octagons and hexagons viewed along the **c**-axis, respectively. After relaxation, the stable atomic structures were obtained for the $\Sigma7(12\overline{3}0)$ GB at 21.79° concave octagons are aligned periodically and are filled in by two hexagons. On the other hand, the stable atomic structure for the $\Sigma 13 (13\overline{4}0)$ GB at 32.20° was alternative arrangement of a hexagon and a concave octagon in a period. The stable atomic structure calculated for the $\Sigma 13$ (2570) GB is composed of four hexagons alternately arranged with three octagons, which is reportedly a one-to-one combination of the $\Sigma7 (12\overline{3}0)$ GB at 21.79° and the $\Sigma 13 (13\overline{4}0)$ GB at 32.20° . These hexagons and concave octagons are fundamental structural units to describe [0001]-symmetrical tilt GBs in wurtzite ZnO, and we found that the arrangement of structural units changes around the critical angle of 32.20° , where the $(13\overline{4}0)$ GB at 32.20° is considered a singular GB. The zigzag arrangements are achieved because of the octagons inclined at $\pm 30^{\circ}$ to the GB plane above 32.20° , exhibiting the same core structure as the $\Sigma7 (12\overline{3}0)$ GB at 21.79° [2].

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Structure and Property of Basalt Melt and Glass

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Knowledge of the macroscopic physical properties of silicate melt (magma) under high temperature and high pressure is extremely important for understanding the phenomena of terrestrial planets such as the formation of the early Earth, the transport of volatile elements, and volcanic eruptions.

We study the influence of the microscopic structures (structural factors, radial distribution function, coordination number, network topology, etc.) of basalt melts and basalt glasses, which are related to the history of earth formation, on their macroscopic physical properties (density, diffusivity, viscosity, thermal conductivity, etc.), paying particular attention to the medium-range structure, trace elements, and entropy effect (temperature effect).

Transport properties like diffusivity and viscosity of melts dictated the evolution of the Earth's early magma oceans. We reported the structure, density, diffusivity, electrical conductivity and viscosity of a model basaltic (Ca₁₁Mg₇Al₈Si₂₂O₇₄) melt from first-principles molecular dynamics calculations at

temperatures of 2200 K (0 to 82 GPa) and 3000 K (40–70 GPa). A key finding is that, although the density and coordination numbers around Si and Al increase with pressure, the Si-O and Al-O bonds become more ionic and weaker. The temporal atomic interactions at high pressure are fluxional and fragile, making the atoms more mobile and reversing the trend in transport properties at pressures near 50 GPa. The reversed melt viscosity under lower mantle conditions allows new constraints on the timescales of the early Earth's magma oceans and also provides the first tantalizing explanation for the horizontal deflections of superplumes at ~1000 km below the Earth's surface [1, 2].

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First principles calculations of two-dimensional ordering process at organic/inorganic materials interface

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We have studied dynamic processes at the interface between the organic and inorganic semiconductor materials by means of the first-principles calculations and the kinetic Monte Carlo simulations. All the first-principles calculations were conducted within the density functional theory (DFT) via the Vienna ab initio simulation package (VASP), version 5.4.4 in the ISSP's massively parallel supercomputer system.

In this project, a system of 3,4,9,10 - perylene tetracarboxylic dianhydride (PTCDA) molecules adsorbed on a Ge(001) surface was employed as a prototype of the organicinorganic semiconductor interface. Previously, we found that a solely adsorbed PTCDA molecule is not mobile at 500K but is mobile at 700K. Furthermore, it was found that the PTCDA molecules diffuse concertedly with the dynamics of Ge(001) surface, involving the flipflop motion of the Ge buckled dimers. [1]

First, we explored the diffusion process of PTCDA molecules under the intermolecular interactions. As a result, it was found that the diffusion mechanism of PTCDA molecules under the intermolecular interactions is similar to that of the lone adsorbed molecule, and the PTCDA molecules were found to be mobile even under the intermolecular interactions at 500K. The kinetic Monte Carlo simulation at 500K using the energy barriers obtained by the DFT calculations generally reproduced the experimental observation.

Toward a more accurate simulation, we investigated the flip-flop motions of surface buckled dimers both for the clean Si and Ge(001) as elementary processes because their flip-flop motions are well known for their dynamic properties on both surfaces. It was found that the flip-flop motion is not a simple seesaw motion but a two-step motion. In addition, by considering the flip-flop motion, the diffusion barriers of a PTCDA molecule on Ge(001) were reduced by about 20%.



Fig. 1. (a) Adsorption of PTCDA on Ge(001) surface. (b) The flip-flop motion of the Si and Ge(001) surfaces.

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RSDFT 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 force microscopy (nc-AFM). In atomic 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 as shown in Fig. 1. In this study, to explicate the mechanism of the phenomena, the forces between Si tip and Si(111)-(7×7) surface were calculated using real-space density functional theory (RSDFT) [2]. 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 structure of a Si(111)- (7×7) reconstructed surface consisting of 298 Si atoms, the back surface of which was terminated with 49 H atoms, and the structure of a [001]-oriented Si tip by RSDFT; the tip consisted of 30 Si atoms having a Si dimer at the tip apex, the back side of which was terminated with 18 H atoms, named "dimer tip" [3]. Next, we calculated the structure changes and the forces acting between the tip and the Si surface during tip approaching and retracting over the hollow



Fig. 1 Model of backbond breaking and formation during a tip approach and retraction cycle with a hysteresis loop in the forcedistance curve, which is estimated from experimental results.

site at the separations between the tip apex atom and the Si adatom on the surface from 5.0 to 2.0 Å, as shown in Fig. 2. On the approaching at 3.5 Å, one of the three backbonds of the adatom was broken, and the adatom was pulled toward the tip. At 2.2 Å, the force between the tip and the surface turned to repulsive. At 2.05 Å, the tip apex atom bonded with the rest atom under a strong attractive force. Starting from the structure of the tip and the Si surface, we calculate the optimized structure by retracting the tip by 0.1 Å step, which was the separation between the H-terminated Si planes of the tip and the Si surface. Up to the separation of 2.8 Å, the attractive force became stronger, and at 2.9 Å the structure and the force almost reverted to those at 2.9 Å on the approaching. When being further retracted, the structure and the force were the same as those on approaching. The force-



Fig. 2 Force–distance (separation) curve with the optimized structures of the Si tip and Si(111)- (7×7) surface, calculated by RSDFT.

distance curves with hysteresis loop were obtained by RSDFT calculations. The greyed area surrounded the curves in Fig. 2, corresponding to the nonconservative dissipation energy, was about 1.6 eV. This value was larger than the value of about 0.4 eV that was experimentally measured in ref. 1. This means that the initial structure of the tip should be reconsidered to clarify the mechanism for the dissipation energy of the tip–sample system.

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Elucidation of Photocatalytic Reaction Mechanism by Ab Initio Calculations

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We have studied the reaction mechanism of photocatalytic oxidation in TiO_2 [1] using cp2k program package (MPI parallelization with multiple threads). We focused on the energetics and dynamics during the polaron migration. This is a collaborative work with the Prof. Satoshi Yamauchi at Ibaraki University, who conducted the LPCVD experiment.

This experimental and theoretical study clarifies dependence the facet 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 density functional theory (DFT) calculations using the constrained DFT method [2-3] and the hybrid functionals show that the (112) surface stabilizes the adsorbed water molecule most strongly.

We are extending this study to analyze the dynamical properties by the constrained DFT[1-3] and the dynamical reaction path

analysis, [4] and compute the band structure in titania and the other photocatalysts.



Fig. 1: Molecular mechanism of hole migration.

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Theoretical Analysis of Metal Film Growth Mechanism in Chemical Vapor Deposition

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We have studied low-pressure chemical vapor deposition of Cu on Ru substrate using CuI using cp2k and VASP program packages (MPI parallelization with multiple threads). In this year, we also studied the mechanism of Cu nanoparticles by reducing spinel type oxides. This is a collaborative work with the experimentalists [1-3] (Prof. Satoshi Yamauchi and Assistant Prof. Shohei Tada at Ibaraki University), who conducted the 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 density functional theory (DFT) molecular dynamics (MD) simulations by cp2k. In addition, the charge and chemical environment around Cu atoms in spinel type oxide Cu-doped MgAl₂O₄. Figure 1 shows the proposed formation mechanism of Cu nanoparticles after reducing inverse spinel-type Cu-doped MgAl₂O₄.

Based on this study, we are developing the computational method to compute the surface acidity on solid oxides, [4-5] and improving the catalytic performance by chemically modifying the catalytic reaction field.



Fig. 1: Formation mechanism of Cu nanoparticles by H₂ reduction of inverse spinel type Cu-doped MgAl₂O₄.

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

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Among hydrogen-bonded systems consisting of small organic molecules, some shows ferroelectricity or antiferroelectricity [1]. They contain neither toxic nor rare elements and are expected as environmentally friendly materials. Spontaneous polarization, which is one of the most important properties for the ferroelectrics, can be predicted by electronic-structure calculations together with the Berry phase theory. We calculated polarization values for seven representative hydrogen-bonded ferroelectrics (croconic acid (CRCA), 2-phenylmalondialdehyde (PhMDA), 3-hydroxyphenalenone (HPLN), cyclobutene-1,2-dicarboxylic acid (CBDC), 2-methylbenzimidazole (MBI), 5,6-dichloro-2-methylbenzimidazole (DC-MBI), and 3anilinoacrolein anil (ALAA)) and the obtained results are in excellent agreement with the experimental results [2]. These calculations were performed using experimentally obtained crystal structures with only hydrogen positions computationally optimized. It is well known that hydrogen positions are difficult to accurately determine by x-ray diffraction analysis. Accurate experimental structure data are not always available. In such cases, computational optimizations for all of the crystal structure parameters are necessary. Nonetheless, the van der Waals interaction, which is often crucial in organic solids, cannot be accurately described by the local density approximation (LDA) or the generalized gradient approximation (GGA). In the present study, we apply van der Waals density-functional theory (vdW-DFT) calculations to reproduce crystal structure parameters of the seven compounds mentioned above. For the vdW-DFT method, we used two forms: the van der Waals densityfunctional consistent-exchange (cx) method [3] and the revised Vydrov-van Voorhis (rVV10) method [4]. Calculations were performed using the QMAS code.

Figure 1 shows the deviations of the calculated structure parameters (lattice parameters a, b, and c, and hydrogen-bond length d, namely, the $O \cdots O$ or $N \cdots N$ distance) (a) from room-temperature experimental results and (b) from 0-K extrapolated values, as well as (c) their averages and bounds [5]. The calculated results obtained by the LDA and the PBE version of the GGA are also shown. The experimental structures are at room temperature, whereas the calculation results correspond to 0 K. Unfortunately, only a limited number of low-temperature structures have been reported and the 0-K values were extrapolated using them to prepare Fig. 1 (b). The vdW-DFT results show good agreement with experimental results, implying that an important step for the computational materials design of organic ferroelectrics has been achieved. Spontaneous polarization values obtained by the vdW-DFT calculations are again in good agreement with the experimental results. The success in reproducing the structure parame-



Figure 1: Deviations of calculated structure parameters (a) from room-temperature experimental results and (b) from 0-K extrapolated values, as well as (c) their averages and bounds (S. Ishibashi, S. Horiuchi, and R. Kumai, "Hydrogen-bonded single-component organic ferroelectrics revisited by van der Waals density-functional theory calculations", Phys. Rev. Mater. 5, 094409 (2021), DOI: 10.1103/PhysRevMaterials.5.094409).

ters also enables the simulation of electromechanical responses. Direct and converse piezoelectric coefficients are evaluated for CRCA, PhMDA and DC-MBI and the resultant values show acceptable agreement with the experimental values if possible objective factors are considered [5].

Organic antiferroelectrics also are promising. For example, their applications as highpower electrical energy storage materials are expected utilizing electric-field-induced phase changes. Usually, they consist of two or more polar subunits. For squaric acid (SQA), we have demonstrated that the polarization of the electric-field-induced phase can be estimated by proper summation of the subunit polarization vectors [6]. By applying this procedure, we have successfully predicted polarization values for the electric-field-induce phases of several organic antiferroelectrics and the obtained results are in excellent agreement with experimental results [7].

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Global search for the stable structures of two-dimensional materials based on Gaussian process regression

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Silicene, a silicon analog of graphene has drawn a great deal of attention not only as a promising candidate for topological insulators from a scientific point of view, but also as an atomically thin semiconductor material from an application point of view. On the Ag(111) surface, however, the sp^3 -like buckling nature of its honeycomb lattice leads to the emergence of a varieties of phases characterized by different patterns of buckling structures as compared with the freestanding structure predicted theoretically [1], hindering the elucidation of the whole picture of the electronic and structural properties of silicene supported on solid surfaces.

First-principles calculation based on the density functional theory (DFT) is a powerful technique to predict stable structures of new materials, but its performance depends on the initial guesses, and the global search for stable structures is computationally demanding in most cases. To tackle the difficulty in the global structure search by the DFT calculation, we adopt an efficient machine-learning technique named global optimization with first-principles energy expression (GOFEE) [2], which is based on Gaussian process regression and evolutionary algorithms. As an example, we here apply GOFEE to the global search for the stable structures of silicene supported on the Ag(111) surface. Our results reveal that GOFEE not only reproduces successfully the stable structures identified so far, but also predicts the existence of a variety of metastable structures which are too subtle to determine experimentally.



Figure: Obtained structures corresponding to the $4\times4-\alpha$ and β (top left and right) and the $\sqrt{13}\times\sqrt{13-\alpha}$ and β (bottom left and right) phases of silicene on the Ag(111) surface.

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First-principles study on the origin of phase stability of Mg–Zn–Y alloys with long-period stacking order

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The design of alloys based on magnesium (Mg) has attracted much attention since Mg is the lightest substance element for structural metals. A dilute Mg alloy containing one at.% of Zn and two at.% of Y showed high-strength properties with a tensile yield strength of ~ 600 MPa [1]. This strength is coupled with the appearance of a unique crystal structure called long-period stacking order (LPSO). In the LPSO-based Mg alloy, solute atoms of Zn and Y are enriched in a few layers of the (0001) plane of the hexagonal closepacked (HCP) Mg matrix [2]. Shockley partial dislocation (stacking faults) occurs in the solute atoms enriched layer, which orders periodically along the [001] direction of the hexagonal lattice. Furthermore, structural analysis using scanning transmission electron microscopy (STEM) revealed that $L1_2$ -type clusters of solute elements (Zn and Y) are embedded in the Mg matrix near the stacking fault [3].

In this study, the electronic origin of the phase stability of Mg–Zn–Y based alloys with LPSO is studied based on first-principles density-functional theory (DFT) calculations. In particular, we aim to understand the role of the Zn atom in 18R–Mg₅₈Zn₇Y₈ alloy, and the possible realization of Zn vacancy formation is studied using a convex hull energy diagram. The heat of formation as a function of the number of Zn vacancies is calculated, and we show how the electronic structure near the Fermi level affects structural stability. In the present DFT calculations used a pseudopotential tech-

nique with plane-wave basis sets adopting the projected augmented-wave method implemented in Quantum ESPRESSO. The exchange-correlation functional is the generalized gradient approximation proposed by Perdew, Burke, and Ernzerhof.

For calculating the heat of formation, the number of Zn atoms in Mg₅₈Zn₇Y₈ is deduced using the fixed number of Mg and Y atoms to understand whether the Mg-Zn-Y alloy includes Zn vacancies that can be formed from the elemental metals of Mg, Zn, and Y. The obtained scatter plot of the heat of formation as a function of the Zn composition ratio indicates that all phases, including Zn vacancies, are thermodynamically unstable and decomposed into $Mg_{58}Zn_7Y_8$ (x = 0) and elemental metals of 58Mg+8Y phases. Nevertheless, the hull distance decreases as vacancies (x) decrease. Therefore, we consider the state in which Zn_7Y_8 clusters with an $L1_2$ structure are already formed and plot the convex hull diagram. Zn vacancies with x = 1 and 3 are on the convex hull. These states should be observed below the decomposition temperature. Therefore, we conclude that the Zn atoms in the LPSO alloy are stable even if they are about half of the number of Y atoms.

In general, the density of states (DOS) for HCP metal is characterized by a deep valley or dip near the Fermi level (E_F) , where E_F is at the lowest position of the valley. The depth of the valleys in the DOS represents the magnitude of splitting the prominent peaks of the DOS between those in occupied and unoccupied states. The width of the valley or dip appears as a difference in the enthalpy of formation (or cohesive energy) between different metals [4, 5]. By focusing on the partial DOS of Zn and its neighboring Mg, we find that the formation of the bonding state between Zn and the surrounding Mg atoms has a crucial role in stabilizing the LPSO structure.

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Metastability of 2D and 3D binary ordered alloys

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It is well-known that the fcc (hcp) metals in the hcp (fcc) structure are dynamically stable, while the fcc (bcc) metals in the bcc (fcc) structure are unstable [1]. To understand the metastability relationship between different crystal structures, we calculated phonon dispersions for 2D and 3D systems using densityfunctional perturbation theory implemented in Quantum ESPRESSO [2]. The calculations were done using system B and C.

In our previous work, we showed that if the elementals metals in the 2D hexagonal structure is dynamically stable, then the fcc and hcp structures are also dynamically stable, showing that 2D structures serve as building blocks for constructing the 3D structures [3]. In the present work, we extend this investigation to binary ordered alloys of CuX with X being 46 metallic elements [4, 5]. We showed that if the CuX in the AB layer structure is dynamically stable, then that in the AB and ABC stacking structures is also dynamically stable (see Fig. 1 for the crystal structures). In addition, we calculated phonon dispersions for the CuX, AgX, and AuX in the AB layer structure, and found that 48 out of 135 ordered alloys are dynamically stable, predicting that those alloys in the AB and ABC stacking structures are also dynamically stable [5]. The present work has shed light on the 2D structures as a building block for computational material design.

We also predicted potential substrates that allow immiscible metals (Pb and Sn) to form the surface alloys by using density-functional theory [6]. The prediction of their surface geometry is left for future work.



Figure 1: Schematic illustration of 2D and 3D structures.

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Ab Initio Molecular Dynamics Study on Static Structure of Glass Materials

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We have studied a condensed matter system which are crystal, liquids, and amorphous. In this project, we focused on the static structure of amorphous V_2O_5 state. The *ab initio* molecular dynamics (AIMD) simulations were performed with our original QXMD code [1].

In order to investigate the static structure of amorphous V_2O_5 , we employed the machine learning method using artificial neural network (ANN) to construct the interatomic potential [2]. The Aenet package [2] was used for training



Fig. 1: (Left) Root mean square errors and (right) partial radial distribution functions.

based on the AIMD simulations of liquid and amorphous V₂O₅. Figure 1 shows the root mean square errors (RMSE) and partial radial distribution functions $g_{\alpha\beta}(r)$ ($\alpha, \beta \in V, 0$) of liquid V₂O₅. According to our previous study [3], considering not only energy but also atomic force and virial tensor improves ANN potential better. Based on the learning condition, our MD simulation using the ANN potential basically represent the FPMD simulations except for the unreasonable peak of $g_{00}(r)$ at approximately r = 0.4 Å. In the future work, we develop the training method by other technics, e.g., active learning from the result of MD simulations with ANN potential for liquid systems.

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Atomistic simulations for excited materials by strong laser

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We have performed investigations that describe nonequilibrium electron-ion dynamics realized by strong laser fields irradiation. Complex pathways accompany these dynamics along different phases depending on time and positions. These multi-physical and nonequilibrium characteristics prohibit direct measurements for the intermediate processes of the dynamics. Our investigation is aimed to understand what processes could happen in the laser-excited materials, including insulators and metals, via theoretical simulations.

We have accumulated simulated electronic structure data just after ultrashort laser pulse by using SALMON code [1] based on timedependent density-functional theory [2]. This data is the key quantity of the laser-excited dynamics' initial process, which triggers whole subsequent processes. We reported Rabi-type absorption oscillation in bulk Al with resonant excitation by increasing the intensity of the electric field [3]. By analyzing the occupation evolution as a function of the intensity, the electron occupation shows symptom of multiple Rabi-flopping to higher energy bands for bulk Al.

We have developed a semiclassical theoretical framework for electron-ion coupled dynamics under a strong laser field [3]. Freeelectronic behavior of metal is accurately reproduced with more than 50-times lighter computational cost than TDDFT. The lightweight cost allows us to simulate spatially larger systems, including non-uniform structures, such as surfaces or impurity, and electron-ion coupled dynamics for the laser-excited material response.

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Study on structural elementary excitations at semiconductor surfaces and interfaces

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In this project, we have been focused on physical properties of structural elementary excitations of semiconductor surfaces and interfaces. In this year, we have focused on the physical properties of defects in SiO_2 . The calculations were performed based on the first-principles calculation. Program package PHASE/0 was employed. [1]

Defects in SiO_2 have been widely studied because they are the source of device performance degradation for MOS field-effect transistors (MOSFETs), which is widely used for the integrated circuits. The gate insulator of MOSFET is made of silicon oxide SiO_2 . Those studies revealed that O vacancies, one of typical defects, can trap charges, assist gate leak current, and also lead to the formation of eternal gate leakage paths. They also revealed the role of post oxidation annealing. However, recent progress of integrated circuit technology have forced the MOSFET device structure from planar to three dimensional. If we consider the vertical body-channel-MOSFET with silicon oxide gate insulator, the oxide can be strained because of the device formation process. The interface oxide might be compressed and the surface oxide be expanded due to the thermal oxidation of silicon for the gate formation process. The compressive and expanded strain are expected as much as 3% in the worst case. Such strain should affect on the physical properties of defects in silicon oxide gate insulator

Therefore, we first focused on the O vacancy

and studied strain dependence of its formation energy and diffusion barrier. Based on these results, in this year, we have studied stability of various defects including the O vacancy, the charging effects on them, and their strain dependences. Some of the vacancies we have studies are fully terminated by H atom or OH group, and other are partially terminated. We modeled the host SiO_2 by alpha-quartz crystal with supercell containing 24 Si and 48 O atoms.

First, we have found a novel O vacancy defect which has only two -OSi bonds. This defect is unique because the widely known O vacancy defect has three -OSi bonds. This new O vacancy defect is stable because it accompanies a three-Si-member ring within the model, while ordinary alpha-quartz just contains only six-Si-member rings. Next, we have found that a dangling bond of Si can surely assist the gate leakage current because they show charging levels in the middle of band gap. Then, we have found that the compressive strain makes it easier to release the terminators H or OH, while it does not significally change the charging level positions. From these results, we have confirmed that strain in the gate insulator silicon oxide surely enhances the device performance degradation. Careful device formation process must be necessary.

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Ab-initio molecular-dynamics calculations for moleculemodified nanointerfaces

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Surfaces and/or interfaces of oxide materials are often modified by other molecules in order not only to stabilize their structure against deterioration but also to control surface morphology. Calcium carbonate (CaCO₃), which is widely used as filler in resins, plastics, and rubber materials to improve their physical, mechanical, and thermal properties, is a typical example of such phenomena. To control particle morphology and to improve affinity with base materials, calcium carbonate is often surfacetreated with organic compounds. This activated calcium carbonates (ACCs) not only exhibit excellent application properties, but also can be applied as eco-friendly inorganic-organic hybrid materials. It has been reported [1] that surface deposits with ~ 5 nm thickness exist on the (104) surface of calcite covered with stearic acid (SA). Since this thickness corresponds to about twice the length of a SA molecule, it is suggested that SA bilayers may be formed on the calcite (104) surface, but the detailed adsorption state has not been clarified to date.

In this study, we performed first-principles calculations based on density functional theory using the Vienna Ab initio Simulation Package (VASP). We created a simulation model for three types of SA-SA and two types of calcite-SA interfaces as shown schematically in Fig. 1 A-E. First-principles molecular dynamics (FPMD) simulations with canonical ensembles at room temperature were performed for these models, and the presence or absence of adsorption was verified by observing changes in the interface structure in each model. We also verified the stability of the interface structures by analyzing the energetic properties in the relaxed system.

According to the results of the FPMD simulations, we considered that the interface structure in the A, B, and E models are intrinsically unstable because the interatomic distance of the bonding part in each model



Fig. 1 Schematic illustration of the simulation models for SA-SA (A-C) and calcite-SA (D, E) interfaces.

gradually increased at room temperature . On the other hand, such behavior has not been observed in the C and D models. Comparing of the potential energy of the C model with that of two isolated SA molecule, it was found that the energy of the C model was 0.4 eV lower. This result indicates that the C model is energetically favorable and stable interface structure may be formed with an adsorption with C model. From these results, it is considered that despite the first SA layer is favorable with D model, some molecules on the first layer may be inverted (or "alternately aligned") in order to adsorb the second layer with C model in the SA bilayer on calcite (104) surface[2]. Further computation with larger system size is necessary to validate this hypothesis. Development of an effective interatomic potential based on a Deep-Learning (DL)-based molecular design methods [3] is in progress for simulations of the bilayer system.

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First-principles Calculations of Magnetic Insulators Under Uniform Electric Fields

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This year, we tried to focus on electric field effects of magnetic insulators. We have developed a linear-combination-of-pseudo-atomicorbital (LCPAO) scheme of a finite electric field method based on the modern theory of polarization [1] and implemented it to the OpenMX code [2], a first-principles calculation code based on the density functional theory (DFT). Through the scheme, one can consider electric field effects even for periodic systems such as bulk insulators. We improved our implemented code this year. The socalled egg box effect causes numerical errors due to the real space grid, especially in the LCPAO method, and it disturbs evaluation of the forces, dipole moment and stress tensor. It can be resolved by the grid cell sampling to repeat the evaluations for the shifted grid several times based on the frozen LCPAO density matrix, and we implemented the function in the previous year. We found that a solution was the "one-shot" grid cell sampling, that is, the forces under the fine grid were evaluated from the density matrix obtained from the rough grid without the grid shifts. We calculated electronic and static dielectric constants and Born effective charges of III-V and II-VI semiconductors and group IV insulating materials. The calculated values coincided with the reported computational values even in the GGA case that the density gradient is sensitive to the egg box effect, and they were an agreement with the experimental values. In addition, we also debugged the implemented code for the non-collinear spin density functionals applicable to materials that spin-orbit interaction (SOI) is important. We also found that the SOI has a non-negligible influence on the dielectric constants of cases including the heavy elements. For the magnetic insulator cases, we confirmed that the debugged code worked well for the antiferromagnetic NiO for different U parameters based on the DFT+Uscheme through the comparison to the previous study. For some insulators with noncollinear spins, the self-consistent-field (SCF) calculations were difficult to get converges because the careful mixing during the SCF calculations were essential. Our implementation will become a powerful tool to expand subjects of researches on materials in investigating the electric field effects.

We also developed the new evaluation scheme for the anomalous Hall and Nernst conductivity without constructing the Wannier functions or explicit evaluation of the Kubo formula [3]. We reproduced the intrinsic contribution of the typical metals such as bcc iron. Our scheme has advantages of efficiency and stability: it is the non-iterative scheme unlike Wannierization and can avoid numerical instability such as the k-space Dirac monopole. The scheme is more appropriate for not only large scale cases but also high-throughput calculations than a Wannier function method.

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Optical conductivity of Ca5Ir3O12 by first-principles calculations

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We have studied the title compound Ca₅Ir₃O₁₂ which have attracted attention due to the its strong spin-orbital interaction (SOI) [1]. Such strong SOI is affected to the physical This compound properties. shows an antiferromagnetic ordering below 7.8 K, a second order phase transition at 105 K and nonlinear conductivity along *c*-axis and so on. We performed synchrotron radiation-based infrared (SR-IR) spectroscopy to reveal the its electronic property for single crystal of $Ca_5Ir_3O_{12}$. From this measurement, we observed reflectivity and optical conductivity. Then, we investigated reflectivity and optical conductivity of Ca₅Ir₃O₁₂ by first-principles calculations to discuss about our experimental results.

We performed density functional calculations by using Quantum ESPRESSO code [2]. These results were used to calculate reflectivity and optical conductivity by using RESPACK code [3]. In Quantum ESPRESSO, we use the norm-conserving pseudo potentials generated by the code ONCVPSP (Optimized Norm Conserving Vanderbilt PSeudopotential), and are obtained them from the PseudoDojo [3]. The exchange-correlation function is used

Perdew-Burke-Ernzerhof type. Γ-pointcentered $5 \times 5 \times 13$ and $10 \times 10 \times 25$ k-points samplings is set to be compared.. We use the energy cutoff of 96 Ry for the wave function, a convergence criterion for the electronic selfconsistency loop of 10^{-10} Ry, and the Gaussian smearing method with a smearing width of 0.002 Ry. We included the SOI effect. In RESPACK, the polarization function is calculated within random phase approximation. For this calculation, we set cutoff energy for polarization function of 6 Ry. Smearing value used in tetrahedron calculation is set to 0.01 eV. Lattice parameters of Ca5Ir3O12 is referred to previous report [5].

Fig 1 shows band structure of Ca₅Ir₃O₁₂ from $5 \times 5 \times 13$ and $10 \times 10 \times 25$ k-point sampling. E = 0 is fermi level. Both results are consistent with previous report []. As shown previous report, this material is metal on this level of density functional calculation. This metallic trend is different from experimental observation which shows as semiconducting electrical properties. This is limitation of this level calculation. From this result, we use 5×5 $\times 13$ k-point sampling for polarization function calculation because this calculation is time consuming.

Fig. 2 shows the calculated reflectivity of $Ca_5Ir_3O_{12}$ parallel to c-plane and c-axis. This shows reflectivity R = 1.0 at $\omega = 0$ because of metallic behavior in our results. The broad peak is shown around 5000 cm⁻¹.

Fig. 3 shows the calculated optical conductivity of $Ca_5Ir_3O_{12}$ parallel to c-plane and c-axis. These have two peaks at about 1000 cm⁻¹ and about 5000 cm⁻¹ for parallel to *c*-plane and *c*-axis. We considered that the peak of about 1000 cm⁻¹ is shown due to the metallic behavior in the calculation. Experimental result has the peak at about 4000 cm⁻¹. This seems to be good agreement with our 5000 cm⁻¹ peak. However, we note that the calculation and experiment have difference of metal or semiconductor.

We need to more discussion by using these results, and also improvement such as metallic behaviour in the calculation. Using ISSP Supercomputer, we achieved the first principles calculation of optical properties such as the compound $Ca_5Ir_3O_{12}$.

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Fig. 1 Band structure of $Ca_5Ir_3O_{12}$ from different *k*-point sampling. E = 0 is fermi level.



Fig. 2 Calculated reflectivity of $Ca_5Ir_3O_{12}$ parallel to *c*-plane and *c*-axis.



Fig. 3 Calculated optical conductivity of $Ca_5Ir_3O_{12}$ parallel to *c*-plane and *c*-axis.

Critical exponent of metal-insulator transition in doped semiconductors and spin ordering

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Impurity doping have an important effect on the conduction properties of semiconductors. Evaluating electrical conductivity at a zero temperature, the material becomes an insulator at low impurity concentrations, a metal at high impurity concentrations, and a metalinsulator transition occurs at some concentration in between. This metal-insulator transition is known to occur in many materials regardless of semiconductor or impurity type and is a general and fundamental property of quantum transport.

Electrons in semiconductors are scattered by randomly aligned impurities and the phase shifts of wavefunctions are distributed randomly. When those waves overlap, they cancel each other out and a localized state appears. This is Anderson localization, and the metalinsulator transition mentioned above is considered to be the Anderson transition between the Anderson localized phase and the delocalized phase. Continuous transitions such as the Anderson transition can be classified according to the critical exponent. The critical exponent ν characterizes the divergence of the correlation length $\xi \propto |n - n_c|^{-\nu}$ at the transition point $(n \text{ and } n_{c} \text{ are impurity concentrations and the})$ critical concentration). It is universal and independent of the details of the system. The critical exponent represents the universality of the phase transition, therefore, deriving its exact value is an essential problem.

Two different values for this critical exponent have been reported from experiments, $\nu \approx 0.5$ and ≈ 1.0 , but the origin of this discrepancy has not been clarified. This problem is called the exponent puzzle. To solve this exponent puzzle, the actual situation in the doped semiconductor needs to be simulated from first-principles.

In this study, we consider a system of randomly distributed P impurity donor ions in Si. For the analysis of its electronic structure, we used a program we implemented that self-consistently solves the Kohn-Sham equation based on density functional theory. Experiments suggest that the spin order changes near this metal-insulator transition point, and thus, the present calculations take into account the spin degrees of freedom.

We generated random impurity configurations. The impurity concentration is ranged from $\approx 0.8 \times 10^{18} \text{cm}^{-3}$ to $\approx 2.1 \times 10^{18} \text{cm}^{-3}$, and the system size is taken by 228.6, 285.8, 342.9, and 400.1 Å. The critical concentration has been predicted by convolutional neural network [1]. We sampled $\approx 180,000$ data in the vicinity of the predicted concentration, and solved the electronic state self-consistently.

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Exploration of exotic surface sites for catalyst informatics Yoyo HINUMA

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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.

Computational exploration of previously unknown reactive sites is a powerful strategy for emergence of new catalytic reactions. Exotic surfaces theoretically can be investigated, but there are very few, if any, computational models of high index orientations that considers reconstruction of the surface. A workflow to efficiently obtain a set of accessible terminations by removing those that are metastable against macroscopic facet formation and by comparing cleaved surfaces and surfaces suggested by a genetic algorithm (GA) for promising orientations is proposed and demonstrated using 34 orientations of β-Ga2O3 and θ -Al₂O₃. Seven and six terminations considered experimentally accessible are found for β -Ga₂O₃ and θ - Al₂O₃, respectively, where the highest surface energy was roughly twice of the lowest. The lowest surface O vacancy formation energy (EOvac) in an accessible surface is 3.04 and 5.46 eV in the (101) and (20-1) terminations for β -Ga₂O₃ and θ -Al2O3, respectively, where the decrease in E_{Ovac} from the most stable surface is 1.32 and 1.11 eV, respectively. The E_{Ovac} in accessible surfaces showed a good correlation with descriptors of the local coordination environment, suggesting that exploiting surface O in an unfavorable environment in an accessible termination would enhance O vacancy-related catalyst performance even in materials that do not show reactivity on the most stable surface.

Analysis of the electronic structure of ferromagnetic shape memory alloy and ferrimagnetic spinel oxide

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We have investigated the electronic and magnetic structure of the magnetic shape memory alloy of Ni₂MnGa and ferrimagnetic spinel oxide of NiCo₂O₄. In these materials, the LDA/GGA investigation level showed inconsistency with experimental facts, such as the period of martensite modulation due to Fermi surface nesting and the properties of electrical resistivity, respectively. Since these discrepancies may originate from electron correlation effects, we employed the quasiparticle self-consistent GW (QSGW) approach, which is one of the beyond LDA/GGA methods, to investigate the electronic structure of those materials. The first-principles calculation package ecalj [1] is used for this study.

(A) Ni₂MnGa

The Ni₂MnGa ferromagnetic shape memory alloys, which have magnetic and shape memory properties, have been attracted as magnetic actuator materials. We applied the QSGW to the high-symmetry (cubic) and low-symmetry (tetragonal) phases of Ni₂MnGa. We found that the Fermi surface of the cubic phase expands compared to GGA, resulting in the reduction of vector length in Fermi surface nesting. The obtained nesting vector from the generalized susceptibility is consistent with the experimentally observed crystal structure at low temperatures, such as 10M or 14M long-period modulated structures [2]. We also estimated the effect of Mn's on-site Coulomb interaction on the tetragonal phase [3].

(B) NiCo₂O₄

The NiCo₂O₄ spinel has drawn much attention for its material application due to its low cost, high electronic conductivity, redox reaction, and high electrochemical activity. However, its electronic structure is not well understood. We investigated the inverse spinel β structure by QSGW. We found that the e_g orbital of Co tetrahedral site appears on the Fermi-level and splits due to the uniaxial crystal symmetry, stabilizing $3z^2$ and destabilizing x^2-y^2 orbitals.

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First-principles calculations of complex metallic alloy surfaces

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We studied the adsorption of pentacene on the 2-fold surface of an icosahedral Ag-In-Yb quasicrystal [1](QC). An STM experiment reported that pentacene molecules adsorbed in a quasiperiodic manner on this surface[2].

The QC surface has approximated by a diskshaped atomic cluster with a radius of 2.2 nm (Fig. 1). Atomic positions of the QC surface has extracted from the structural data of an X-ray diffraction experiment for the isostructural $Cd_{5.7}$ Yb quasicrystal[3], where Ag and In atoms occupy the Cd sites in the Ag-In-Yb QC. In the calculations, the molecular axis of pentacene is constrained to be parallel to the surface, and all atomic positions, including the substrate atoms, are fixed. Calculations are carried out with the VASP code mainly on the system-B as bulk jobs using 72 nodes.

First, we carefully checked the cluster thickness dependence of the adsorption energy. And we confirmed that the thin film composed only of the top layer atoms well describes the interactions with pentacene. Thus, we describe the results below using the thin film as the substrate.

The adsorption energy of pentacene shows strong orientational dependence on the molecular axis of pentacene. Figures 2(a) and (b) show the adsorption energies of pentacene with its molecular axis aligned to two different 2fold axes, 2f-90° and 2f-180°, which are parallel to the surface and perpendicular to each other. It is clearly shown that pentacene favors one of them (2f-90° direction shown in Fig. 2(a)). Comparably stable orientational configurations are found when the molecular axis is aligned to two 5-fold axes on the surface. Obtained orientational dependence of the adsorption energy well explains the result of statistical analysis from an STM experiment[2].



Figure 1: Adsorption energy of pentacene with the molecular axis parallel to the 2-fold (a) 90° and (b) 180° directions.

We also studied the adsorption of oxygen atoms on the (111) surface of the PdZn intermetallic compound. We used the VASP code with a slab model consisting of six atomic layers. Using a 2x2 unit cell containing eight atoms in the top layer, we investigated the adsorption structures for various oxygen coverages between 0.125 - 1.0 monolayer (ML). Calculations were mainly carried out on the system-C as flat MPI jobs with 4-9 nodes. At high oxygen coverages, we found that Zn atoms form a Zn-O layer with a hexagonal ring reminiscent of the Wurtzite ZnO. PdZn is known as a candidate catalyst for the methanol steam reforming (MSR) because of its higher thermal stability than the traditional Cu-based catalyst. It has been reported that a ZnO patch is formed on the PdZn catalyst during the MSR reaction, and considered that the high CO_2 selectivity of PdZn in MSR is due to the formation of the ZnO patch[4]. However, there is still no report of the first-principles calculations about the formation of the Zn-O layer.

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Atom exchange of fcc metal surfaces

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The migration of an adsorbed atom (adatom) impinged from gas phase to a surface is one of the fundamental processes for crystal growth. In some adatom-surface combinations, instead of migration of an adatom on the surface, an adatom may be embedded in the surface layer by displacing the surface atom, and the released atom migrates on the surface, which is often called "displacive adsorption". Such substitutions between adatoms and surface atoms are frequently reported by using field ion microscopy (FIM) [1].

We have investigated adatom migration and adatom-surface atom substitution from theoretical point of view. We chose the Ni(100) and Ni (110) surfaces as model systems and investigated the migration and the substitution of Ni and Cu atoms based on first-principles calculations. We employed a popular firstprinciples calculation code VASP, and the nudged elastic band (NEB) method was applied to the evaluation of adatom migration and exchange potentials [2].

Surface models are shown in Figs. 1. We employed 7-layer slab model with ~0.8 nm

vacuum layer for both sides for both the Ni(110) and Ni(100) surfaces. After fully relaxed atomic structures of slabs for pristine surfaces, Ni or Cu adatom was located and adsorbed surfaces were again relaxed by keeping atomic positions of bottom 4 layers fixed. Electronic and ionic iteration parameters are listed in Table 1. The NEB method was performed for 5 images with both the initial and final structures being fixed (IMAGE=4). Near the potential maximum, the migration potential was further evaluated by dividing these images.

The obtained migration potential barriers are listed in Tables 2 and 3. For the Ni(110) surface, a simple surface diffusion of adatom along [110] direction, path A in Fig. 1(a), had a



Fig. 1: Adatom migration pathways for (a) Ni(110) and Ni(100) surfaces. The unit cells used in the structural calculation are shown by the dotted lines. Initial adatom position is indicated by blue circle, and path A, B, and C on the Ni(110) surface and path A and B on the Ni(100) surface are indicated by purple, green, and yellow, respectively.

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VASD Version	535		
VASI VEISIOII	Ni(110): 4: 2 17 1		
slab geometry	Ni(110): 4×2 unit 7 layer		
Sinc geometry	Ni(100): 3×3 unit 7 layer		
le nointe	Ni(110): 12×16		
k-points	Ni(100): 12×12		
potential	PBE [3]		
cut off energy	384.08 eV		
	Methfessel & Paxton		
Fermi level smearing	$\sigma = 0.12 \text{ eV}$		
1:4:	Electronic: 10 ⁻⁶ eV		
convergence condition	Ionic: 0.01 eV/Ang.		
	AMIX = 0.02		
	BMIX = 0.0001		
SCF mixing parameters	$AMIX_MAG = 0.08$		
	$BMIX_MAG = 0.0001$		
	(linear mixing)		
Time period	POTIM = 1.0		
Number of core	576 (192/image)		

Table 1 Parameters for present calculation

lowest energy. Atom exchange processes such as path B and C have higher energy than path A. Experimentally, only path C was seen by FIM study [1]. Although the present calculation of the energy barrier of path C gave 0.36 mV lower than that of path B, but we failed to reproduce the experimentally observed large difference in the exchange probability between path B and C [1]. This seems to indicate the thermal effect, i.e., collective motion of adatoms and surface atoms is crucial to the atom exchange process and molecular dynamic study should be required for understanding this discrepancy.

For the Ni(100) surface, adatom diffusion along the [110] direction, path A in Fig. 1(b), again had a lower energy than atom exchange process path B, in agreement with the previous

Table 2 Migration potentials of Ni adatom corresponding paths shown in Figs. 1

face	path	Potential energy [eV]
Ni(110)	Path A	0.321
	Path B	0.444
	Path C	0.443
Ni(100)	Path A	0.728
	Path B	1.105

Table 3 Migration potentials of Cu adatom corresponding paths shown in Figs. 1

face	path	Potential energy [eV]
Ni(110)	Path A	0.309
	Path B	0.426
	Path C	0.428
Ni(100)	Path A	0.523
	Path B	1.080

report.[4]

In conclusion, the present calculation showed that in addition to the surface migration of adatom such as Ni and Cu, atom exchange may be possible on the Ni(110) surface, but slightly higher energy, i.e., higher temperature is needed for replace surface atom with adatom on the Ni(100) surface.

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Development of the first-principles method for calculating T_c based on density functional theory for superconductors

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The first-principles prediction of the superconducting transition temperature T_c of metals is a challenging goal in the condensed matter physics. For phonon-mediated superconductors, accurate calculation schemes is now available on the basis of the Eliashberg theory and density functional theory for superconductors (SCDFT) [1, 2]. In this year, we conducted a development of a first-principles method with the latter theory.

In the conventional superconductors, the phonon-mediated attraction is the dominant source of the electronic pairing interaction, where the electron-electron Coulomb repulsion has only a secondary role that it partially cancels the attraction. On the other hand, as the Coulomb interaction becomes stronger, there emerges a chance for it to affect the superconductivity in a different way. A prominent example is the plasmon-mediated pairing mechanism [3, 4]: the frequency dependence of the screened Coulomb interaction enhances the pairing. Another is the spin-fluctuation mechanism, where ferromagnetic fluctuation strongly suppress the singlet pairing [5, 6, 7, 8]. We have developed an SCDFT based method to calculate $T_{\rm c}$ with the plasmon and spin fluctuation effects included. In this project, we made further progress along this line. In the SCDFT, the superconducting $T_{\rm c}$ can be evaluated by solving the following gap equation

$$\Delta_{n\mathbf{k}} = -\mathcal{Z}_{n\mathbf{k}}\Delta_{n\mathbf{k}}$$

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

The kernels \mathcal{K} and \mathcal{Z} represent the effect of the electron-phonon and electron-electron Coulomb interactions. By developing new forms of \mathcal{K} we can in principle incorporate novel interaction effects. β is the inverse temperature and $E_{n\mathbf{k}}$ is the Kohn-Sham energy eigenvalue.

First, we constructed a formalism of the exchange-correlation functional in the SCDFT based on the adiabatic connection formula [9]. We formally confirmed that this formalism reproduces the previous one.

Next, we extended this formalism and derived a formula for the exchange-correlation kernel beyond the local density approximation. As this is numerically too demanding, we are continuing exploration of efficient numerical implementation of the newly developed formula.

We also tested an implementation of the SCDFT-based T_c calculation in SUPERCON-DUCTING TOOLKIT [10] to see if the previously published values [8], calculated with another in-house code, are well reproduced. The calculated values (Table 1), though fairly agreeing with the previously published ones, were generally larger. The overestimation is likely attributed to a subtle implementation details like how to numerically integrate the internal frequencies. These calculation were performed in System B (Ohtaka) with parallelization within a single node. The elapsed time for each T_c was approximately less than 30 minutes.

Table 1: Superconducting transition temperature $T_{\rm c}$ (K) calculated with the SCDFT gap equation Eq. (1) using SUPERCONDUCTING TOOLKIT, with and without the spin fluctuation effects. In RPA and LDA, the exchange correlation kernels entering the \mathcal{K} formula [7] are ignored and incorporated, respectively.

	RPA		LDA		
	w.o. SF	w. SF	w.o. SF	w. SF	
V	20.5	2.8	18.1	2.5	
Al	1.2	0.6	0.9	0.4	

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Calculation of photoelectron angle distribution in the photoexcitation process on the organic molecules adsorbed surface

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In recent years, it has been reported electronic and physical properties of organic molecules which interact with the surface using Wave number space resolved Photoelectron Spectroscopy. We have investigated the copper (II) phthalocyanine (CuPc) monolayer substrate system. Monolayer TiSe₂ have two typically phases depending on the temperature. A (1×1) structure (normal phase) is shown at room temperature and a (2×2) superstructure (CDW phase) is realized under the 200 K. Each phase has band gap of 83 meV and 153 meV, respectively [1, 2]. We have adopted this interesting thin film as the substrate and reported the structural changes depending on the temperature in the previous year. In this year, we investigated the electronic state of a (1×1) monolayer TiSe₂. Based on these results, we optimized the structure of CuPc adsorbed on TiSe₂.

1. Band calculation of TiSe₂ monolayer

We performed density functional theory (DFT) calculations using the Vienna Ab Initio Software Package (VASP) version 5.4.4 [3,4]. The exchange correlation effects were described by the Generalized Gradient Approximation (GGA) within the PerdewBurke-Ernzerhof (PBE) formalism. We used a unit cell with lattice constants a = b = 3.53 Å, c = 20.0 Å, $\alpha = \beta = 90^{\circ}$ and $\gamma = 120^{\circ}$, and planewave basis set with the projector augmented wave (PAW) approach with an energy cutoff of 380 eV. The Brillouin zone integration was performed on a Monkhorst-Pack of $18 \times 18 \times 1$ grid of k-points. The energy convergence criterion was chosen for the self-consistency cycle was 1×10^{-7} eV. To account for Fermi surface broadening, temperature parameter σ for Methfessel-Paxton smearing was applied [5].

We investigated a local Coulomb repulsion of Ti 3d electrons and the effect of the electronic smearing parameter σ on the band gap. We calculated band gaps with different sets of Coulomb repulsion U and σ . Fig. 1(a) show a negative bandgap without considering U and σ . On the other hand, fig. 1(b) and (c) have positive bandgaps close to 0. It is found that both σ and U increase the gap between the top of Se 4p band (Γ , red point) and the bottom of Ti 3d band (M, blue point). However, the rise in σ push up the upper end of the Se4p band above the fermi surface, so Fig. (b) is also excluded. As a result, we find the parameter set $(U = 3.9 \text{ eV} \text{ and } \sigma = 0.01 \text{ eV})$ which reproduce experimental result [6]. We used these parameters for optimization of CuPc / TiSe₂ structure.



Figure 1 Band dispersion of the (1×1) monolayer TiSe₂ with different electronic smearing parameter σ and effective Hubbard parameter U for Ti.

2. Structural optimization of CuPc/TiSe2

We expanded above model for an 8×8

structure of the monolayer TiSe₂ with lateral dimensions of 693 Å². For Cu atom of CuPc, U value was adjusted to 4.0 eV which could reproduce the qualitative orbital ordering of isolated CuPc. In addition, CuPc had an unpaired electron, thus we considered spin polarization. Ionic positions were optimized until the residual force on each ion was less than 1×10^{-2} eV/Å. When starting with a random wave function, it took about 12 hours to converge one electronic state using 5 nodes with total 144 cores. From this structure optimization calculation, it is found that the adsorption distance between molecule and substrate is 3.16 Å, resulting in a flat molecule structure.

We have reached the stage where it is possible to calculate the Wave number space resolved Photoelectron Spectroscopy. We are planning to perform this calculation next year.

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Physical properties of layered graphene

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Graphene is one of the most promissing materials for electronics devices including field effect transistors and molecular sensors. Bilayer of graphene would have rich properties because electronic structures of graphene change depending on how two layers interact with each other. Here, we study the stackingpattern effects on the electronic transport and molecular adsoprtion of bilayer graphene using a first-principles density-functional calculation [1, 2, 3].

It has been reported that the bilayer graphenes with three different stacking patterns (AA, AA', and AB) have been synthesized and observed experimentally. Table 1 lists the adsorption energies and the binding distances between the B atom and the adsorbed molecule for various molecules on the B-doped bilayer graphenes with three different stackings. For all stacking patterns, CO and CO_2 molecules are adsorbed not strongly but weakly, whereas NO and NO_2 molecules can bind strongly with the large adsorption energies and the short binding distances. O_2 and N₂ molecules weakly bind with small adsorption energies. Therefore, only NO and NO_2 molecules in air are adsorbed with chemical bonds on the B-doped bilayer graphene without depending on the stacking patterns.

We study electronic transport of the pristine bilayer graphene for the three different stackings. The conductance for the AB stacking has the linear dispersion near E = 0 eV as in the case of the monolayer. On the other hand, unlike monolayer, the slope of the conductance curve between 0 eV and $\sim \pm 0.25$ eV is different from that between $\sim \pm 0.5$ eV and ± 1.0 eV, respectively. Due to the difference of the slope of the conductance curve in different energy ranges, the transport properties induced by the adsorption of molecules would be different from that of the monolayer. The finite conductivity in the AB-stacked bilayer graphene was reported theoretically and observed experimentally. The conductance of the AA-stacked bilayer graphene seems to have constant value from the energies E = -0.25 eV to +0.25 eV, and it increases linearly below -0.25 eV and above +0.25 eV. Unlike the AA-stacked bilayer graphene, the conductance of the AA' stacking shows asymmetric behaviors near the Fermi energy. Thus, it is interesting that the conductances of the bilayer graphenes with AA, AA' and AB stackings are different from one another.

We study the molecular adsorption effects on the transport of the B-doped bilayer graphenes for three different stackings, and define $\Delta G(E) = (G_a - G_b)/G_b \times 100(\%),$ where G_a and G_b are the conductances of the B-doped bilayer graphene with and without molecules, respectively. When NO and NO_2 molecules are adsorbed on the AB-stacked bilayer graphene, the conductances at the energy E = 0 eV change with $\Delta G(0) = +8.2\%$ and +3.0%, respectively. For the AA stacking, the adsorptions of NO and NO_2 molecules can induce $\Delta G(0) = +2.1\%$ and -17.4% in the conductances, respectively. In the case of the AA' stacking, there are sizable conductance changes of -17.2% and -47.7% for the adsorptions of NO and NO₂ molecules, respectively.

In summary, the stacking-dependent behaviors of the transport and the adsorption properties of molecules of bilayer graphene have been investigated for various molecules including environmentally polluting or toxic molecules and common molecules (NO, NO₂, CO, CO₂, O₂, and N₂) using a first-principles density-functional study. Irrespective of stack-

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Stacking		NO	NO_2	CO	$\rm CO_2$	O_2	N_2
AA	E_a	-1.20	-1.12	-0.12	-0.04	-0.16	-0.28
	d	2.15	1.60	2.90	2.87	1.76	2.96
AA'	E_a	-1.22	-1.15	-0.12	-0.04	-0.19	-0.28
	d	2.15	1.60	2.90	2.87	1.75	2.96
AB	E_a	-1.19	-1.13	-0.12	-0.03	-0.20	-0.27
	d	2.14	1.60	2.89	2.84	1.75	2.93

Table 1: Adsorption energy E_a (eV) and distance d (Å) between molecule and B atom for each molecule adsorbed on B-doped bilayer graphenes with AA, AA', and AB stackings.

Table 2: Percentage of changes in the conductance at the Fermi energy E = 0 [$\Delta G(0)$] for each molecules adsorbed on B-doped bilayer graphene with AA, AA', and AB stackings. The changes in the conductance are calculated with respect to the B-doped bilayer graphene.

	$\mathbf{A}\mathbf{A}$	AA'	AB
NO	2.1	-17.2	8.2
NO_2	-17.4	-47.7	3.0

ing patterns, only NO and NO₂ molecules in air can bind strongly on B-doped bilayer graphene. It is found that the conductance curves of bilayer graphenes change depending on the stacking patterns and the presence of the NO/NO₂ molecule, and the variation of the conductances induced by molecular adsorptions could be used by gas sensing devices such as field-effect transistors under low bias voltages.

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Computational materials design of Ag and Cu chalcogenide based thermoelectric materials

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The development of compact, wearable, and especially self-charging personal electronics has become more feasible in recent years. As a continuous power supply for an uninterrupted operation, it is desirable that these electronic devices can convert directly the waste heat of the human body or environment into electricity via flexible thermoelectric (TE) generators. A recent study discovered the extraordinary ductility of the inorganic semiconductor silver sulfide (Ag_2S) [1] paving the way for flexible TE developments. In this study, we use firstprinciples calculations combined with the Boltzmann transport theory to investigate the electronic and transport properties of Ag and Cu chalcogenide materials.

First of all, we have chosen the exchange correlation functional SCAN+rVV10 in order to reproduce band gap energy and lattice constants of α -Ag₂S reasonably. According to the calculations of the formation energy of typical intrinsic defects, it is found that the intrinsic defects greatly affect the system's conductivity where Ag vacancy and interstitial Ag act as p-type and n-type defects, respectively [2]. The effects of the doping of transition metal impurities were investigated and the results were consistent with the experimental observations [2]. We have also found that experimental transport properties were reasonably reproduced by using the electron-phonon coupling method, showing the suitability of this scattering model in estimating the relaxation time [3].

In addition to Ag chalcogenides, we have also applied our calculation procedures to Cu sulfide systems and found that the defect formation energy and transport properties can be simulated by using the acanthite-like structure for this material. Based on these knowledges, we will extend our computational materials design for (Ag_{1-x}, Cu_x) $(S_{1-y}, Se_y)_2$ chalcogenides to realize flexible TE materials.

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Thickness-Dependent Electronic Properties of Atomically Thin Boron Monosulfide

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Rhombohedral boron monosulfide (r-BS) is a meta-stable phase of binary boron-sulfer system obtained under high-temperature and high-pressure condition [1]. Recently, Kondo et al. have succeeded to exfoliate atomically thin layers of r-BS from its bulk.

We have studied the electronic structures of thin layers of r-BS using the first-principles density functional theory calculations. The calculations have been performed using the massively parallel computers in ISSP, University of Tokyo.

From the electron localization function (ELF) analysis, we have found that B and S atoms are covalently bonded in each S-B-B-S unit layer (Fig. 1). The valence-band maximum (VBM) states are consisted of hybridized B-p_z and S-p_z orbital states. By the stacking of layers, the VBM states exhibit splitting, resulting in the systematic narrowing of the band gap (Fig. 2). This band-gap narrowing has also been observed in the optical experiment [2] and is suggesting the potential application of r-BS as 2D semiconductos with tunable band gap.

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Figure 1: Electron localization function along the atomic bonds in (a) r-BS, (b) h-BN, and (c) MoS₂.



Figure 2: Calculated band gap values of thinlayer $(1 < N < \infty)$ and bulk $(N = \infty)$ r-BS.
Large-Scale Molecular Dynamics Simulations on Non-Equilibrium Phenomena Using First-Principles Calculation and Machine Leaning

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Artificial neural network (ANN) potential, which is an interatomic potential constructed by machine-leaning, attracts attention as a promising method to achieve extra-large-scale molecular dynamics (MD) simulation with first-principles accuracy [1]. Application of this ANN-MD to far-from-equilibrium phenomena, such as fracture and pressure-induced 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 [2] 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 [3]. 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 [4]. 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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Defect formation energy and band structure of Pb-based topological insulators

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PbBi₂Te₄ topological insulator (TI) is considered as one of the promising candidates for future spintronics material with a large spin current density. However, experimental studies of its surface transport properties have not yet been reported, owing to a lack of bulk insulating crystals. So far, we achieved bulk insulating states in Pb(Bi,Sb)₂Te₄ topological insulators by tuning compositional ratio of Bi and Sb [1]. Although such control of compositional ratio leads to a change in the type and concentrations of intrinsic point defects, the Fermi level is not necessarily well tuned. For further success in achieving the bulk-insulating state, not only the reduction of absolute amount of charged defects but also the enhancement of the activation energy is required. Recently, it was reported that Sn doping for Bi₂Te₂Se TI is effective for lowering carrier concentrations and activated resistivities, with a localized impurity band that acts as a charge buffer occurring inside the bulk band gap.

We carried out band structure calculation of PbBi₂Te₄ based on density functional theory

(DFT) using Vienna ab-initio simulation package (VASP) version 6.2.1. We adopted generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof (PBE) as the exchange correlation energy functional. For all calculations, we included spin-orbit coupling (SOC). We obtained band gap of 115 meV for PbBi₂Te₄, which is much lower than experimentally reported value ~230 meV. In order to estimate band gap more accurately, the Heyd-Scuseria-Ernzerhof (HSE06) and HSE03 hybrid functional was employed. As a result, band gap was further underestimated. We found that the HSE is not effective for accurate estimation of band gap of narrow-gap semiconductors.

In 2022, we plan to calculate defect formation energies using GGA-PBE including SOC.

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Electronic structure of the interfaces between diamond and alkali metals

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The interaction between diamond surfaces and liquid alkali metals has been little investigated. We observed the etching process upon heating and the change in fluorescence of nitrogen impurities (NV⁻ centers). DFT calculations using the ISSP supercomputer were performed to investigate the electronic structure, and it was shown that the experimental results can be explained by the difference in band bending.

Experimental observation revealed that the etching of diamond occurred in heated lithium. K and Na did not show etching. The fluorescence of the NVcenter was significantly reduced only in contact with molten K. This is understandable if we consider that the negatively charged NV⁻ that emits fluorescence is lost due to upward band bending. Although the extent of band bending depends on the doping state of the semiconductor, the amount and direction of band bending can be estimated by determining the positional relationship between the Fermi level of the undoped semiconductor (in this case diamond) and the metal using DFT calculations. We used VASP[2] with PBE

functional. The initial structure for the optimization was created considering the bulk lattice constants of the Li, Na, and K. $3 \times 3 \times 4$ unit cells of the diamond with 4 layers of alkali metal atoms on both sides were employed. We tried several starting structures do the alkali metals (lattice constant, orientation and shift), and the final structures were almost the same. The results are shown in Fig. 1. An upward shift in the density of states of interfacial carbon is observed, and it is stronger at the interface with (c) K.



Fig.1 Density of states of carbon at diamond interfaces with various materials [1].

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Automatic generation of first-principles effective models based on MLO

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To the goal of material informatics, automatic generation of data is the central part of calculations. According to the density functional theory (DFT) and local density approximation (LDA), we can calculate electronic structure, which generally controls the most part of material properties, systematically without any empirical inputs. The DFT calculation itself is not so much demanding in computational resources as long as we consider tens of atoms per unit cell. Therefore, DFT calculations have been taken advantage of material informatics.

The band structure within few eV measured from Fermi energy is effective for material properties at low temperature. In other words, whole band structure contains excess information. Even the drastic development of computational power, the computational cost beyond the DFT calculations, for example many body calculations, are still sometimes demanding. Therefore, for mining new functional material such as magnets and/or superconductors driven by electronic many body effects, it is convenient that we can automatically construct a model which only contains the low-energy part of electronic

structure. Historically, we already have the technique of Maximally Localized Wannier Function (MLWF) [1], however, MLWF contains several difficulties or automation especially for the system spanned by s- and p-orbitals like semi-conductors. Therefore, for calculating mixed system (superlattice and so on) containing not only the localized electrons such as d-electron but also (s- or p-) delocalized electrons, MLWF is not a perfect method.

For the goal of automation, we have already constructed a new method named Muffin-tin Like Orbital (MLO). MLO is given as a linear combination of atomic basis functions, which is used for the first-principles calculations based on LMTO algorithm. Thanks to the PMT method [2], we can take into account the effects of extended electron orbital such unoccupied states can be considered in the localized basis. Here, PMT is a mixed basis function for firstprinciples calculation between Plane-wave and Linear Muffin-Tin orbital. By a kind of weighted sum method, we can take into account the effect of unoccupied orbital to the lowenergy models's energy eigen values numerically.

For the benchmark materials, we have

chosen four simple samples: Si(already shown Fig.1 of the 2020's report), SiO2(cubic), SrTiO3, and graphene. For all samples, the automation of model construction is succeeded. For SrTiO3, components described by planewave (namely, interference of unoccupied orbitals to the low-energy model) bases is few. This can be interpreted that LMTO is a sufficiently accurate basis function for SrTiO3. For graphene, we can obtain a two-orbital model which contains only C-pz' π -bond orbitals forming the Fermi surface (or, Dirac cone). Surprisingly, it is revealed that such π bonds contains much plane-wave components. For SiO(cubic), we find that an empty sphere in a relatively large interstitial region is necessary to reproduce the extended orbital shaping like a

free electron's Bloch orbital.

For the future work, we have to simplify and sophisticate MLO algorithm to save the computational times and to adopt for more larger system such as superlattice, hetero junctions, and surfaces.

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Theoretical Study on Electronic Properties in New Nanoscale Surfaces and Interfaces

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We theoretically studied the electronic structures of VSe₂ monolayers. Recently monolayers of transition-metal dichalcogenides (TMD) are extensively studied. Much attention is paid to magnetic properties of TMD monolayers in recent years. Room temperature ferromagnetism was reported for VSe₂ monolayers in 2018 [1]. However, there is a controversy over its emergence. A recent experiment suggested that VSe₂ monolayers are on the verge of ferromagnetism [2]. We performed a density-functional calculation on this system.

We used the program package VASP for the density-functional calculation. Figure 1 shows the calculated result. Figure 1(a) and (b) show band structures of the VSe₂ monolayer in non-magnetic (NM) and antiferromagnetic (AFM) states, respectively. The magnetic structure of the AFM state is shown in Fig. 1(c). We used a $\sqrt{3} \times \sqrt{3}$ supercell of the primitive cell in the calculation. Γ is the center in the two-dimensional Brillouin zone. M is the point at the half of a primitive reciprocal lattice vector. We found that the band structures of NM and AFM states are very similar.

In addition to the VSe₂ monolayers we performed calculations of electronic structures of V_5 Se₈. We unfolded the calculated band structures in order to compare with experimental band structures obtained from angle-resolved photoelectron spectroscopy.

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Figure 1: Band structures of a VSe_2 monolayer in nonmagnetic (a) and antifferomagnetic (AFM) (b) states. The magnetic structure of the AFM state is shown in (c). Red and green circles show V and Se atoms, respectively. Arrows express the spin structure.

First-principles calculation of graphitization of diamond surface and its exfoliation process

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Diamond has a wide bandgap electronic property and high mechanical strength; application of diamond to semiconductor electronic devices or to mechanical cutting tools are expected [1]. In electronic device applications, polishing is required to produce a flat surface, but diamond is the hardest material and it is not easy. On the other hand, in tool applications, a serious wear property in cutting iron-based materials is reported. By utilizing this wear phenomenon, it may be possible to realize a novel diamond surface flattening method. Currently, two possible causes of wear are proposed: graphitization of diamond surface, and diffusion of C atoms into metal. This issue remains unclear, particularly in the mechanism how strong C-C bonds break.

In this study, we investigated weakening of C-C bond by the effect of Fe atom to confirm graphite layer peeling. Figure 1 (a) and (b) shows side views of the surface structures of diamond (221) with and without Fe atom, and (c) peeled structure with Fe atom. (Peeled in pristine structure is also perfomed but not shown.) A DFT-based STATE code is employed to obtain stable structures and energies. Peeled structures are obtained by pulling-up terminal atoms (shown in (a) and (b)). This is carried out by artificially adding a constant value of 0.002 Bohr to z axis of the terminal atoms in every quenched MD step with optimizing along x and y directions for the atom and other surface atoms. This procedure is repeated until saturated. The bond breaking energy 2.1eV is obtained by the energy difference between (b) and (c), while corresponding value of pristine surface is much larger energy of 3.2 eV. This indicates C-C bond is effectively weakened by a Fe atom.

It is concluded that a Fe atom can play a catalytic role in peeling graphite layer formed on diamond surfaces. Further investigations will be required to evaluate metal element, atomic environment effect, etc.



Fig. 1: Peeling of graphite layer formed on diamond (221). Bright, dark and small atoms indicate C, Fe and H atom. Atoms directed by arrow are pulled-up to obtain peeled structures.

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AB type 2D materials search by high-throughput DFT calculations

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Recent rapid research progress of twodimensional (2D) materials have revealed that 2D materials are expected to be good candidates for future applications and devices. In our previous research, we construct a structure map [1] and a web-based database [2] of AB₂ type monolayers by high-throughput DFT calculations using OpenMX [3].

In this project, a structure map for AB type monolayers of 2016 compounds which are all the combinations of 63 elements selected from the periodic table (except for noble gases, lanthanoids and actinoids) is constructed by high-throughput calculations based on the DFT (GGA-PBE) with the symmetry-unconstrained geometry optimizations and variational cell optimizations starting from several structures such as ferromagnetic planar square lattice and planar honeycomb lattice structures as initial states. We classified the converged structures by planarity, the number of atoms in a unit cell, 2D Bravais lattice and space-group symmetry. The classification makes it clear that most of the AB type monoatomic layers are understood as basic planar structures and their derivation patterns such as the shape of the primitive cell,



Fig.1: Examples of basic planar structures of AB type monolayers.

distortion, buckling and so on.

The genealogical classification helps us to understand phase transitions caused by lattice matching with a substrate, stacking layers, external bending, tensile and compressive stresses, and so on, when we invent new devices.

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Charge storage mechanism of $Ti_3C_2Ch_2$ (*Ch* = O, S, Se, Te)

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We have investigated the charge storage mechanisms of transition metal carbides (MXene) based on density functional theory (DFT) calculations. This year, we focused on the dependence on termination function group of a $Ti_3C_2T_x$ monolayer.

DFT calculations were performed with the Vienna ab initio simulation package (VASP). The projected augmented wave method and a plane basis set implemented in the VASP code were utilized with a cutoff energy of 520 eV and *k*-point sampling on a $4\times4\times2$ grid.¹ The generalized gradient approximation of the Perdew–Burke–Ernzerhof exchange-correlation functional was used.² To prepare the slab model

of Ti₂₇C₁₈*Ch*₁₈ (*Ch* = O, S, Se, Te), all Al atoms and a Ti₃C₂ monolayer were removed from Ti₆Al₂C₄, which was obtained from the Materials Project (ID: mp-3747), and expanded to a superstructure of $3\times3\times1$ (**Fig. 1a**). Structure optimization calculations were carried out before and after adsorption of Zn atom on A–C sites (**Fig. 1b**). Bader charge analysis was performed using the script provided by Henkelman's group.³

Adsorption at A and B sites are preferred to that at C site (**Fig. 2a**) due to more coordination number with *Ch* atoms (3 for A and B site *vs.* 1 for C site). Averaged adsorption energy, which would be inversely proportional to



Fig. 1 (a) The model structure of $Ti_{27}C_{18}Ch_{18}$ (*Ch* = O, S, Se, Te) and (b) absorption sites on the $Ti_{27}C_{18}Ch_{18}$ monolayer. These structures were described using VESTA.⁴

charge/discharge rates, was in the order of Te < Se < O < S. Net charge transfer through Zn adsorption increased in the order of Te < Se < S < O (**Fig. 2b**), which likely arises from more electronic interaction with more electronegative atoms. These results imply that Ch = O is the most preferable to achieve both a large capacitance and fast charge/discharge rates simultaneously in electrochemical capacitors using Zn²⁺ ion as an adsorbed species.

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Fig. 2 (a) Adsorption energy and (b) net charge transfer for Zn atom on the $Ti_{27}C_{18}Ch_{18}$ (*Ch* = O, S, Se, Te) monolayer.

Diffusion behavior of hydrogen in tungsten-rhenium alloy

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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 the 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.

By the way, rhenium (Re) is created in the W specimen by nuclear transmutation in the neutron irradiation circumstance in fusion reactors. The effects of Re addition on the W specimen were investigated. Fortunately, the material properties are improved by the Re addition. For example, the H retention is decreased because vacancy nucleation is suppressed by the presence of Re. Besides, the plasticity is also improved. Therefore, the application of W-Re alloys are positively considered for the PFMs instead of pure W.

In the present work, properties of H in W-Re alloys is investigated. In particular, diffusion behavior of H in the W-Re alloys.

Simulation Method

The stable positions of H in the W-Re alloys and their energy levels are calculated in terms of first-principle calculations based on density functional theory. We use Vienna ab-initio simulation package (VASP). Large simulation cell composed of 5x5x5 bcc lattice (250 atoms) are used to avoid the effects of periodic boundary condition imposed on the simulation cell. The cut-off energy of plane wave is 350eV. Re density is assumed to be low (less than 0.8 atomic percent) in the W-Re alloys. Besides, energy profiles of H along the migration paths in the W-Re alloys are estimated by nudged elastic band (NEB) method.

We investigate energy profiles of H in two type of W-Re model alloys, including one and two Re atoms, as shown in FIG. 1 and 2, respectively.

Results

H atom in the pure W and W-Re alloy is suited at tetrahedral interstitial site (T-site). Migration energies are estimated as barrier heights for H to move to the neighboring T-sites. In pure W lattice, migration energy for H is estimated to be about 0.21eV. In FIG. 1, T-sites (a-i) in the vicinity of a Re atom and migration path of H from T-site (a) to (i) are shown. T-site (a) and (b) situated nearest to the Re atom are geometrically equivalent. Energy profiles of H at the T-sites and along the migration path A are shown in FIG. 3. H located at T-site (a) and (b) are about 0.1 eV unstable, compared with that located far enough away from the Re. Therefore, T-sites close to Re are supposed to be unfavorable for H.

FIG. 2 shows likely migration path of H in the W-Re alloy including two Re atoms. The path is assumed to avoid T-sites close to the Re atoms. FIG. 4 shows energy profile of H along the migration path B from T-site (1) to (12). The migration path B keeps an appropriate distance from the two Re atoms. So, the migration energies of H to move the neighboring T-site are estimated to be 0.21-0.22 eV, which is almost same as that in pure W.

Summary and Discussion

According to H energy profile, H will keep away from Re in the W-Re alloys. Therefore, the higher Re density becomes, the lower H solubility becomes. If Re density is low, the migration energy of H in the W-Re alloy is estimated to be about 0.21eV, which is similar to that in pure W. However, the room available for H diffusion becomes smaller by the Re addition. So, H diffusivity in W-Re alloy would be lower, compared with that in pure W.



FIG. 1: Schematic view of W-Re alloy including one Re and H migration path A.



FIG. 2: Schematic view of W-Re alloy including two Re and H migration path B.



FIG. 3: Energy profile of H along the path A in FIG. 1.



FIG. 4: Energy profile of H along the path B in FIG. 2.

Clarification of atomistic mechanism application of process design for adhesion interface between metal and plasmatreated fluoropolymers using first principles calculation

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Recently, increasing frequency of the digital signals is necessary because the amount of information communication is increasing. However, the higher the frequency, the greater the transmission loss is. Therefore, polytetrafluoroethylene (PTFE) which has low relative dielectric constant and dielectric loss tangent is considered as suitable as dielectrics of high frequency printed wiring boards. However, PTFE has low adhesion property, so adhering PTFE to Cu is difficult. We have achieved generation of oxygen-containing functional groups and adhesion strength of 0.94 N/mm between PTFE and Cu when PTFE was Heplasma-treated at over 200°C under atmospheric pressure^[1]. However, the factor improving adhesion property, such as the chemical reaction at PTFE/Cu interface and the value of adsorption energy has not been investigated. Therefore, in this study, in order to explore functional groups contributing to improvement in adhesion property, the reaction between Cu(111) surface and fluorinated molecules was analyzed and the adsorption energy was calculated by means of first-principles calculations.

Our calculations were performed using the STATE (Simulation tool for atom technology) code with plane-wave basis and ultra-soft pseudopotential^[2, 3]. The wave function and the charge density of cutoff energies were 36 and 400 Ry, respectively. Generalized gradient exchange-correlation functional based on Predew-Burke-Ernzerhof (PBE) was used for the exchange-correlation functional and DFT-D2 was used for the dispersion correction method^[2, 3]. Cu surface was modeled Cu(111) 4×4 slab composed of 3 atomic layers. As the model of as-received PTFE, CF3-CF3 was calculated. In addition, CF₂=CF₂, CF₃-CF₂-OO', CF₃-CF₂-OH, and CF₃-CF=O were calculated as the model of plasma-treated PTFE. These were the models of molecule containing oxygencontaining functional groups observed by C1s-XPS spectrum of the plasma-treated PTFE surface. Cu surface, fluorinated molecules, and adsorption systems were optimized then total energies were calculated. The adsorption energy was defined as the difference between the sum of total energy of Cu surface and fluorinated molecules and total energy of adsorption system.

Fig. 1 shows the optimized atomic geometries for CF₃-CF₃. CF₃-CF₃ was not bonded to Cu surface and the value of adsorption energy was 0.25 eV in case of both on top site and on bridge site. This is because C-F bonding energy of 5.02 eV^[4] is large and C-F bond is stable. After optimization for CF₃-CF₂-OO', O-O bond in CF₃-CF₂-OO' was broken and CF₃-CF₂–O' and O were bonded to Cu surface, respectively. In this case, the sum of adsorption energies of CF₃--CF₂-O' and O was calculated as the adsorption energy of CF₃-CF₂-OO'. Therefore, the calculation of adsorption energy of CF₃-CF₂-O' which is broken O-O bond at initial state was added. Fig. 2 shows the optimized atomic geometries for CF₃-CF₂-OO' and CF₃-CF₂-O'. The adsorption energy was 3.10 eV, and the highest adsorption energy was obtained. Table 1 shows the value of adsorption energies by calculation. The value of adsorption energies of CF₃-CF₃, CF₂=CF₂, CF₃-CF₂-OO', CF₃--CF₂--O[•], and CF₃--CF=O was 0.25 eV, 0.68 eV, 4.73 eV, 3.10 eV, 0.60 eV, and 0.74 eV, respectively. In case of molecules containing



Fig. 1 Atomic geometries for CF_3 - CF_3 model (a) on top site and (b) on bridge site.



Fig. 2 Atomic geometries for (a) CF₃–CF₂–OO[•] model and (b) CF₃–CF₂–O[•] model.

Table 1Value of adsorption energies onCu(111).

Molecule	Adsorption energy [eV]
CF ₃ –CF ₃	0.25
$CF_2 = CF_2$	0.60
CF ₃ –CF ₂ –OO'	4.73
(CF ₃ –CF ₂ –O [•]	3.10)
CF ₃ –CF ₂ –OH	0.60
CF ₃ –CF=O	0.39

COO', the adsorption energy was the highest and the molecule was stable.

In this study, the functional groups contributing to improvement in adhesion property were explored by calculating the adsorption energies by means of first-principles calculations. From the result of calculations, the adsorption energy of molecules containing COO' was the highest. Therefore, generating the functional groups containing COO' is possible to generate PTFE surface having high adhesion property. However, the calculations about Cu surface having different miller indices are needed because Cu surface has not only Cu(111), but also Cu(100) and Cu(110). In addition, the calculations copper oxide such as CuO and Cu₂O are also needed because Cu surface is likely to be oxidized.

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First-principles electronic structure calculation of double-perovskite photocatalyst

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Double-perovskite oxides, $A_2B'^{III}B''^{V}O_6$, have been extensively studied due to their intriguing physical and chemical properties originating in their mixed valence nature[1]. Above all, $Ba_2B' {}^{III}B'' {}^{V}O_6$ was found to show an efficient photo catalytic activity to dissolve water molecules into oxygen and hydrogen gases. While TiO_2 has been known to be an practical photo catalyst, it uses only the ultraviolet rays which is less than 3 % of the sunlight pouring on the earth surface. On the other hand, the catalytic function of $Ba_2B' {}^{III}B'' {}^{V}O_6$ double perovskite is activated under visible light and hence has a great potential as a photo catalyst in daily use. In this work, we study the surface electronic properties of Ba₂PrBiO₆ double-perovskites. We used the DFT code of Quantum ESPRESSO throughout our study. PAW potentials were employed to represent the core region and the PBE functional was applied for exchange correlation. We also used the HSE06 hybrid functional to evaluate the band gap values. We constructed slab system with three units along the z-axis exposing (001) surface. The vacuum region was taken to be 20 Å height. Where two types of surfaces can be exposed as the (001), namely, the Ba-O polar-surface and the Pr-Bi polar-surface. We calculated the surface band structures and identified the band gaps as well as their work functions for these polar-surfaces.

As an example, we show the Ba-O surface band structure calculated within the PBE exchange-correlation functional (Figure

1). Top components of the valence band are comprised of oxygen orbitals, while the isolated bottom part of the conduction band is derived from the Bi orbitals. The surface band gap value was estimated to be 1.93 eV within the HSE hybrid functional level. The band gap value of the bulk system with the HSE is found to be 3.70 eV, therefore we think that the bulk band gap is significantly modified at the surface region. However, experimentally obtained optical band gap value is 1.07 eV and which is still half of the surface band gap obtained in this study. We think the origin of the discrepancy is the B-site disordering $(Pr \leftrightarrow Bi)$. Now, we have been studying the effect of the B-site disordering by evaluating the band gap of the system.



Figure 1: Ba-O surface band structure.

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Electronic structure calculation for a transition-metal monoxide using a four-atom-configuration model

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We have studied an electronic property of a transition-metal monoxide. Recently, this monoxide was reported to have an indirect gap whose energy is ca. 0.2 eV [1]. It is well known that these compounds have been poorly described by the density functional theory (DFT) with using commonly used approximate functionals. It was very difficult for us to reproduce this insulating ground state of this monoxide, only with the simple DFT+Ucalculation. The word "simple" means an application of only the on-site Hubbard energy on the d electrons. In this work, we explain about several extensions [2] that we learned from literatures [2] and used to reproduce the insulating ground state. We used the pwscf codes included in the Quantum ESPRESSO (QE) package [3]. We performed the following jobs to obtain the theoretical electronic and vibronic properties.

Self-Consistent Field Calculation – No matter what physical quantity is calculated; one must first determine the electron density. We used a 50 Ry energy cutoff for the electronic wave functions and a small smearing width of 0.02 Ry which required a $6 \times 6 \times 6$ *k*-point mesh. Adopted pseudopotentials are based on the projector augmented-wave method.

Introduction of Hubbard U – It should be noted that in addition to the Hubbard U on the dorbital (U_d) in the transition-metal element, we introduced that (U_p) on the p orbital of the oxygen atom. An additional introduction of U_p is believed to be useful to open the gap (i.e., leading to a correct insulating ground state) due to the existence of the exchange-induced splitting. The value of $U_p(ca. 21 \text{ eV})$ has been determined by the self-consistent linear response approach. On the other hand, if we tried to decide the value of U_d self-consistently, we could not reproduce the insulating ground state theoretically. Therefore, as a compromise, we set U_d of ca. 4.4 eV. We did not adopt the magnetic exchange J parameter for this calculation.

Spin-polarized DFT+U – The primitive cell of the rock-salt structure is composed of two atoms (one is anion, while the other is cation). To implement the antiferromagnetic ordering,

we adopted four-atom-configuration including two cations with up and down spins. By adopting this configuration, we can expect an effective lowering of the symmetry which may be useful to open the gap.

Structural optimization – We also optimized the structure by using the Broyden-Fletcher-Goldfarb-Shanno method. This turned out to be essential to make the Fermi energy lie in the splitting region of the d electrons. Otherwise, one cannot reproduce the insulating ground structure with the experimental lattice spacings. This resulted in the structure with the symmetry C_{2h} (2/m). It is known that the theoretical ground state depends on the starting eigenstates (occupation) during the spin-polarized DFT+Ucalculations. In some of transition-metal monoxides such as cubic FeO and CuO, this adjustment is essential to reproduce the insulating ground state [2]. This is also true in our case. The example of the output is shown in Fig. 1.

Band dispersion and electronic DOS calculations –It should be noted that all of the above-mentioned extensions such as non-zero U_p , the spin polarization, structure optimization, and occupational adjustments turned out to be essential to open an indirect gap (0.55 eV) in our case with a transition between L and Γ points. This is qualitatively consistent with the experimental observation [1]. The ground state obtained in the four-atom cell has slightly lower energy per the cation-anion pair compared to the nonmagnetic and metallic two-atom primitive cell, and thus the antiferromagnetic insulating ground state is energetically favored. The result of the density-of-states calculation suggests that both the valence and conduction bands are mainly composed of the *d* electron, consistent with the narrow Mott-Hubbard gap [1].

atom	1 Tr[ns(na)] (up,	down,	total)	=
2. 48039	1.01275 3.49314			
spin	1			
eige	nvalues:			
0. 292	0. 292 0. 448 0. 449	1.000		
	1			
spin	2			
eige	nvalues:			
0. 151	0. 151 0. 192 0. 259	0.259		
	•			

Fig. 1: An example of the orbital level output after the initial eigenvalue settings are reflected.

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Interactions in transition-metal-phthalocyanine monolayer weakly bound to metal surfaces

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Phthalocyanine is a π -conjugated planar molecule with a size of $\sim 1.2 \times 1.2 \text{ nm}^2$. Two H atoms at the center of the molecule can be substituted by a variety of transition metal ions (M^{2+}) , yielding a transition metal phthalocyanine (MPc). The M^{2+} ions are coordinated by lone pairs of four N atoms arranged in a planar tetragonal geometry. The adsorption of MPc on transition metal surfaces [1, 2] has been widely studied experimentally.

We recently have studied experimentally the adsorption and ordering of metal phthalocyanine molecules on a bilayer indium film fabricated on Si(111) surface [3, 4, 5], on which the interaction of *M*Pc with the substrate is expected to be weaker than the transition-metals substrates. Our aim is to establish nearlyfree-standing transition metal phthalocyanine monolayers effectively decoupled from the substrate.

The experimental studies of *M*Pc adsorption on metal surfaces commonly show that the phthalocyanine molecules form monolayers with long range order, in which the symmetry axes of molecules are aligned at a particular azimuthal angle which is not parallel to the axes of the translational symmetry of the twodimensional lattice the molecules form. This has sometimes been ascribed to the direct interaction of nitrogen atoms (imide N) of the molecule with the substrate metal atoms.

Our computational result suggests that the electronic interaction between phthalocyanine and In substrate is indeed week due to a large van der Waals gap between the molecular plane and the topmost In atomic layer of the substrate and further to the weak electronic interaction of the π orbitals of the molecules with the *sp* electrons of the In bilayer.

In order to highlight the intermolecular interaction, we studied the "free-standing" MPc monolayer by first-principles calculation by VASP. The molecules were assumed to be ordered in a nearly square translational symmetry which exactly is the one observed on In/Si(111). Note that the characteristics of the molecular arrangement is more or less similar on other metal surfaces studied. The total energy of the molecular film was calculated as a function of the azimuthal rotation angle of the molecule. It was found that the total energy is minimized at an azimuthal angle close to that observed experimentally for the molecule adsorbed on many metallic surfaces. This implies that the molecular configuration in the MPc monolayer is governed by the intermolecular interaction. We have examined several possibilities of the physical origin of the inplane intermolecular interaction between MPcmolecules and succeeded in identifying the interaction that stabilizes the free-standing MPc monolayer.

We also studied the d electronic structure of M^{2+} ions in the metal phthalocyanine adsorbed on In/Si(111) surface to probe the interaction with the substrate sp electrons. A good correspondence between the density of states measured by photoemission experiments with those obtained by the calculation yielded an insight into the interaction between central metal ions and metallic substrate in this system.

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Electronic Structure and Fermiology of *d*-electron compounds

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The monocarbides of transition elements from the group-IVB, -VB, and -VIB columns of the Periodic Table are well known for their great hardness and strength, high melting temperatures, metal-like thermal and electrical resistivities, nonstoichiometry, and superconducting properties [1, 2]. Most experimental and theoretical efforts to understand the fundamental properties of these technologically important materials have focused thus far on the group-IVB and -VB carbides, all of which crystallize with the cubic rocksalt structure. The compound WC has two phases: a low temperature phase is hexagonal WC and a high temperature phase above 2525°C is cubic WC. We studied simple hexagonal WC with a space group of P6m2 which contains one molecule in the unit cell. The lattice parameters a and care 2.906 and 2.837 Å, respectively [1]. The calculation for the energy band structures was carried out by using the OpenMX code(http: //www.openmx-square.org/). First, we discuss the calculated results for WC as shown in Figure 1, in which we depict the energy band structure along the symmetry axes in the Brillouin zone, which is shown in Figure 1, in the energy region from -20.0 to 20.0 eV. The Fermi level $E_{\rm F}$ is at 0.0 eV. for WC and indicated by dashed lines in Figure 1. With respect to the energy band structure near $E_{\rm F}$, we emphasize that there is always hybridization between the W 5d and C 2p states in WC. The total number of holes is equal to that of electrons, which

represents that WC is a compensated metal. We move to discuss the Fermi surface of WC. Three bands cross the $E_{\rm F}$, therefore WC has three Fermi surfaces in Figure 2. The color on the Fermi surface illustrates the distribution of the Fermi velocity components. Fermi surfaces for WC centered at the A, K, and M points, respectively. The 5th band has one dog's bonelike hole sheet centered at the each Γ point. The Fermi surfaces were calculated with FermiSurfer [3].



Figure 1: The energy band structure for WC, the symmetry points and axis for the simple hexagonal-type structure. $E_{\rm F}$ indicates the position of the Fermi level.

ReO₃-type structures can be described as ABX_3 perovskites in which the A-cation site is unoccupied. They therefore have the general composition BX_3 , where B is normally a cation and X is a bridging anion. The chem-



Figure 2: The Fermi surface for WC centered at Γ point. Colors indicate the Fermi velocity components on the Fermi surface.

ical diversity of such structures is very broad, ranging from simple oxides and fluorides, such as WO_3 and AlF_3 , to more complex systems in which the bridging anion is polyatomic, as in the Prussian blue-related cyanides such as $Fe(CN)_3$ and $CoPt(CN)_6$. We found that the energy bands near the Fermi level are mainly because of the hybridization between the Re 5dand O 2p electrons in Figure 3. Since the lowest twelve bands are fully occupied, as shown in Figure 3, the next three bands are partially occupied, while higher bands are empty. This compound is compensated metal because of having two chemical units in the unit cell. The calculated total density of states (DOS) for ReO_3 is shown in Figure 4, in the energy region from -25.0 to 25.0 eV. The total density of states for ReO_3 is shown by the solid black line and the s, p, d and f states are shown by the solid color lines, respectively. This figure tells us that the DOS of the d states is higher than that of the f states at the Fermi level. The Fermi surface of ReO_3 is found to consists of two hole sheets and two electron sheets.



Figure 3: The energy band structure for ReO_3 . E_{F} indicates the position of the Fermi level.



Figure 4: The density of states for ReO₃. $E_{\rm F}$ indicates the position of the Fermi level shown by the dashed line.

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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.

For molecular dynamics simulation widely used to obtain atomic-level information on strength and deformation of materials, an interatomic potential is very important. In this study, a highly accurate interatomic potential of pure magnesium was developed based on artificial neural network (ANN)[1]. The reference data for training the ANN potential were systematically constructed using density functional theory (DFT) calculations. The developed ANN potential can accurately estimate lattice constants and elastic moduli. Additionally, generalized stacking fault energies of slip systems in magnesium calculated with the ANN potential are also in agreement with the DFT results. We also developed the ANN potentials for several kinds of magnesium alloys; Mg-Y, Mg-Ca, Mg-Al, Mg-Zn. The ANN potentials of magnesium alloys successfully described interactions between a basal dislocation and each solute

atom, consistent with the previous DFT study.

Several magnesium alloys include long period stacking ordered (LPSO) structures which consist of periodic arrangement of basal stacking faults and enrichment of solute atoms in the vicinity of the stacking faults. The soluteenriched layers give rise to a significant mass change as well as local stiffness due to the L12type solute clusters, which affect the lattice vibration properties of the LPSO structures. Our previous study showed that for a heavy enough mass change, a phonon-mediated interaction of the solute-enriched layers is attractive and stabilizes the periodic stacking of the solute-enriched layers. In this study, we analyze phonon states of LPSO magnesium alloys, using first-principles calculations. We calculate phonon density of states and phonon dispersion based on the density functional perturbation theory.

References

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