Research Highlights

Metallic State of Sequence-Controlled Oligomer Conductor that Models Doped PEDOT Family

Mori and Ozaki Groups

Organic conducting materials are attracting attention because of their flexibility and solution processability, characteristics not found in inorganic semiconductors and metals which are currently the mainstream materials. Among them, conductive polymers such as doped poly(3,4ethylenedioxythiophene) (PEDOT) are widely used organic conducting materials because of their easy solutionprocessability and high conductivity. However, the large molecular-weight distribution of polymers during processing causes less-crystallinity and less-accessible to atomic-level structural information and makes it difficult to elucidate the conduction mechanism and design polymers based on the crystal structure. In this study, we focused on oligomers to challenge these issues. Oligomers have high degrees of freedom in molecular design controlling three parameters (hetero-sequence, chain length, and terminal group). In addition, since oligomers possess single-crystallinity, detailed structural information can be accessible, the conduction mechanism based on crystal structures can be clarified and materials design are possibly proposed.

So far, Mori group has developed 3,4-ethylenedioxythiophene (EDOT, O) oligomeric salts nO-X [1-3]. EDOT dimer salts $2O \cdot X$ (X = BF₄, ClO₄, PF₆) have a relatively wide calculated bandwidth of around 1 eV [1], but are Mott insulators with 1/2-filled band structure. To deviate from the Mott insulating state and to improve the conductivity, two strategies for reducing the Coulomb repulsion (U_{eff}) between carriers have been reported. The first is band-filling modulation from the 1/2-filled state [2]. The second strategy is the extension of conjugate length, namely elongation of oligomer length. The trimer salt $3O \cdot PF_6(CH_2Cl_2)$ has been synthesized for oligomer-length elongation, which leads the reduction of resistivity by about one order of magnitude than that of dimer salt $2\mathbf{O} \cdot \mathbf{PF}_6$ [3]. From the above results, the realization of high conductivity and metallic state in oligomeric organic conductors can be achieved by reducing $U_{\rm eff}$ through conjugate expansion, band-filling modulation, and suppressing stacking dimerization with improving dimensionality of the electronic structure.

Although conjugate-length expansion of oligomers is effective in reducing $U_{\rm eff}$, it has been difficult to synthesize long-chain oligomers without introduction of solubility auxiliary groups due to instability against oxidation and solubility issues of oligomers consisting of a single EDOT unit. In this study, we utilized heterogenious units, i.e., 3,4-ethylenedithiothiophene / 3,4-(2',2'-dimethylpropylenedioxy)thiophene (S/P), to synthesize long chain oligomers in solid state. The long-chain oligomers were designed and



Fig. 1. Chemical structures, molecular arrangements, and temperature dependence of resistivities for doped oligomers, a Mott insulator 20·PF₆ and metallic $4PS \cdot (PF_6)_{1,2}(solvent)_m$, modeled the famous conductive polymer PEDOT-PSS. The resistivity of $4PS \cdot (PE_6)$ (calculated and the second sec 4PS·(PF₆)_{1.2}(solvent)_m reached 36 Scm⁻¹, which is lower by 10⁻⁶ than that of $2O \cdot PF_6$.

newly synthesized without the introduction of solubilitysupporting groups that inhibit intermolecular interactions in solids. In the neutral 4PS (P-S-S-P), stability and solubility can be imparted by introducing an S-S structure in the center, which is a truncated and twisted structure of the conjugated system. This twisted structure is eliminated by oxidation. By introducing bulky unit **P** at both ends, dimerization is suppressed by increasing the dimensionality of the electronic structure, and band-filling modulation is achieved by creating a space where excess anions can exist (Fig. 1).

Subsequently, single crystals of 4PS•(PF₆)_{1.2}(solvent)_m were prepared by constant-current electrochemical oxidation of tetramer donor 4PS. Band calculations show a quasi-onedimensional band structure (W = 0.41 eV) with band dispersion mainly in the stacking direction, confirming the acquisition of dimensionality. The room temperature resistivity in the stacking direction is 36 S cm⁻¹, which is six orders of magnitude lower than that of 2O•PF₆, and metallic conduction behavior is observed in the high temperature region above 280 K (Fig. 1). The IR reflection spectrum reveals a plasma edge, and the first metallic state in a single-crystalline EDOT-based oligomeric organic conductor is observed [4].

This result demonstrates that molecular arrangements and electronic functionalities in the solid state can be controlled by the type and sequence of oligomer units, which is a characteristic molecular design freedom of oligomers, and realizes a new concept in the development of conductor materials. This concept is expected to create a new trend in the development of organic conducting materials.

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Broken-Symmetry Quantum Hall States in Organic Dirac Fermion Systems

Osada Group

Recently, the v = 1 quantum Hall (QH) plateau was observed in the Hall resistance of an organic conductor α -(BETS)₂I₃, which has been known as a two-dimensional (2D) massless Dirac fermion (DF) system with finite spinorbit coupling (SOC), under high pressure [1]. In general, the 2D DF systems show the QH effect at the LL fillings $v = \pm 2$, ± 6 , ± 10 , ... when their Landau levels (LLs) have four-fold spin and valley degeneracy. The v = 1 QH effect is expected only when both spin and valley degeneracy are broken in the N = 0 LL. The spontaneous valley symmetry breaking is caused by the exchange interaction. We have studied the spatial order of the broken-symmetry QH states in α -type organic DF systems, α -(ET)₂I₃ and α -(BETS)₂I₃.

In order to clarify the broken-symmetry QH state of the α -type organic DF system with four molecular sites (A, A', B, and C) in the unit cell, we have studied its electronic state under magnetic fields using the four-band tight-binding model including Peierls phase factors. Figure 1 shows the magnetic field dependence of the energy levels (Hofstadter butterfly) for the spinless case (no Zeeman effect and no SOC). The Chern number for each gap confirms the validity of the conventional DF picture in these materials.

The four-component envelope functions of the N = 0LL with valley degeneracy were investigated based on the Hofstadter calculation. The site-resolved probability density of the LLs is shown in Fig. 2. When the SOC is considered, it breaks the spin degeneracy of the N = 0 LL and opens a spin-split gap. We can see that the degenerating $-\mathbf{k}_0$ - and



Fig. 1. (left) Band dispersion of an *a*-type organic conductor α -(ET)₂I₃ under pressure at zero magnetic field. (right) Magnetic field dependence of energy levels (Hofstadter butterfly) in an α -type organic conductor α -(ET)₂I₃ for the spinless case. The energy gap between quantized levels is colored according to the Chern number $N_{\rm Ch}$.



Fig. 2. (left) Probability densities of LLs under the SOC at four molecular sites of α -(ET)₂I₃ at about 33 T. Zeeman shift is not included. The zero-field gapped dispersion is also shown over them. (right) Schematics of spontaneous valley splitting of the "N = 0↑" and "N = 0↓" LLs and the examples of the charge and spin density patterns of the broken-symmetry $\nu = \pm 1$ QH states when the SOC is dominant for the spin splitting.

+**k**₀-valley states have different probability weights on the A and A' molecules, which are connected by the inversion operation. This valley-site correspondence is recognized independently of the presence of the Zeeman effect or the SOC. When the spontaneous valley symmetry breaking, which is equivalent to the inversion symmetry breaking in this case, occurs due to the exchange interaction in the N=0 LLs, their valley splitting leads to the $v = \pm 1$ QH effects. These broken-symmetry QH states are accompanied by the spatial modulation of charge and spin densities at A and A' sites in a unit cell, as shown in the right panel of Fig. 2.

In graphene, which is the typical 2D DF system, the broken-symmetry QH states, especially the v = 0 QH states have been intensively studied both theoretically and experimentally. Since graphene has the ten times larger group velocity than the α -type organics, the spin splitting is almost negligible compared to the LL spacing, so that we have to consider the SU(4) symmetry breaking of the N = 0 LL. In fact, various QH states, the QH ferromagnet (QHF), the canted antiferromagnet, the charge order, the Kekule distortion, etc. have been proposed as the v = 0 QH state. On the other hand, in the α -type organic DF system, the spin splitting resulting from the Zeeman effect and the SOC is sufficiently large compared to the LL spacing. The v = 0 QH state is considered to be the QHF state without spontaneous symmetry breaking (SSB) as previously pointed out [3]. Therefore, only the $v = \pm 1$ QH states are accompanied by the SSB in the organic DF system.

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Magnetic Modulation and Thickness Dependence of Second Harmonic Generation in Two-Dimensional Multiferroic CuCrP₂S₆

Ideue Group

Two-dimensional van der Waals multiferroics are emerging material platforms for realizing unique magnetoelectric/ magneto-optical properties and also important building blocks for functional van der Waals devices. Although they provide a new opportunity of controlling multiferroic properties in the atomic layer limit, research on few-layer multiferroic crystals is limited and the effect of thickness dependent symmetries on multiferroic properties are less explored.

In this work, we studied the symmetries and magnetoelectric responses in exfoliated samples of novel van der Waals multiferroic CuCrP₂S₆ by optical second harmonic generation (SHG).

CuCrP₂S₆ is a layered material composed of the honeycomb lattice of distorted CrS₆ octahedra and CuS₃ triangles and pairs of P ions inside the honeycomb, and shows the structural and magnetic phase transition at $T_{\rm C} = 190$ K and $T_{\rm N}$ = 32 K, respectively. At $T > T_{\rm C}$, it shows centrosymmetric crystal structure with C2/c space group (Fig. 1 (c)), in which Cu ions can move and ion conductor behaviors have been reported. With decreasing the temperature, movement of Cu ions start to freeze at T = 190 K and is completely settle down at T = 145 K, which cause the structural transition to the non-centrosymmetric phase with Pc space group (Fig. 1 (b)). Below $T < T_N$, A-type antiferromagnetic order develops, in which spins of Cr^{3+} align along the *a*-axis (Fig. 1 (a)). Because both the spatial inversion symmetry and timereversal symmetry are broken, CuCrP₂S₆ shows the magnetoelectric effect in this low-temperature phase.

Figures 1 (d)-(e) show the polarization-resolved SHG



Fig. 1. (a-c) Crystal and magnetic structures of CuCrP₂S₆ at $T < T_N$ (a), $T_N < T < T_C$ (b), and $T_C < T$ (c). (d-f) Polarization-resolved SHG patterns in CuCrP₂S₆ at T = 5 K (d), T = 100 K (e), and T = 300 K (f). (g) Temperature dependence of SHG intensity along the polarization angle $\theta = 10^{\circ}$ and 90°. AFM indicates antiferromagnetic phase.

patterns at T = 5 K (Fig. 1 (d)), T = 100 K (Fig. 1 (e)), and T = 300 K (Fig. 1 (f)), respectively. At T = 300 K, small SHG signal has been observed (Fig. 1 (f)), which can be attributed to the surface or electric quadrupole terms. In the intermediate temperature region, SHG intensity along the a-axis is enhanced (Fig. 1 (e)). Since inversion symmetry is broken in this phase, electric dipole term of SHG is allowed and this additional component is generated in the SHG. In the antiferromagnetic phase, SHG intensity along the *b*-axis is also developed (Fig. 1 (d)), which can be explained by the magnetic dipole term. In Fig. 1 (g), we plot the temperature dependence of the SHG intensity along the polarization angle $\theta = 10^{\circ}$ and 90°. Here, $\theta = 0^{\circ}$ is defined as *a*-axis. This temperature variation clearly indicates that SHG intensity along the a-axis (b-axis) originating from electric dipole (magnetic dipole) term reflect the structural (magnetic) phase transition in CuCrP₂S₆.

In order to understand the effect of magnetoelectric properties on SHG, we measured SHG under the magnetic field. Figure 2 (a) (red) shows the SHG pattern under the magnetic field (B = 1.2 T) at T = 5 K. The magnetic field is applied to the *b*-axis. SHG pattern changes dramatically, showing the large enhancement along the a-axis. In CuCrP₂S₆, the application of the magnetic field along the *b*-axis will generate the electric polarization along the *a*-axis due to the magnetoelectric effect. This electric polarization induced by the magnetoelectric effect is considered to generate a large SHG. Furthermore, the thickness dependence of the SHG induced by the magnetoelectric effect was investigated. Figure 2 (b) shows the SHG patterns under magnetic field (B = 1.2 T) along the *b*-axis for samples of various thicknesses. For thicker samples, the SHG pattern is mirror symmetric with respect to the *a*-axis. This is because that bulk sample has the glide symmetry with respect to the ac-plane. However, as the thickness is reduced, this glide symmetry is lost, resulting in modulation of the SHG pattern. These results indicate that symmetry change by thinning can modulate the magnetoelectric effect in two-dimensional van der Waals multiferroics.



Fig. 2. (a) Polarization-resolved SHG patterns in CuCrP₂S₆ under the magnetic field (B = 1.2 T) along the *b* axis (red). SHG measured under zero magnetic field (black) is also shown. Insets show the schematics of magnetic structures and directions of the magnetic field and electric polarization induced by the magnetoelectric effect. (b) Thickness dependent SHG patterns under the magnetic field (B = 1.2 T) along the *b*-axis. All the data were measured at T = 5 K.

In summary, we have observed magnetic modulation and its thickness dependence of SHG in $CuCrP_2S_6$. This work clarifies the unique magnetoelectric properties in $CuCrP_2S_6$ and also provide a new design principle of two dimensional multiferroics.

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Chirality-Induced Phonon-Spin Conversion at an Interface

Kato Group

Chirality has been an important concept not only in highenergy physics but also in solid state physics for long time. The chirality in materials has attracted much attention after the discovery of chirality-induced spin selectivity (CISS) in DNA and peptides [1]. Indeed, the discovery of CISS has stimulated many theoretical and experimental studies on spin-related phenomena in chiral materials since it may reveal a way of developing spintronic devices without using heavy elements.

Recently, thermal phonon transport in a chiral crystal, α -quartz (SiO₂), induces spin current into an adjacent normal metal [2] as shown schematically in Fig. 1 (a). This observation is quite remarkable since α -quartz is nonmagnetic and includes no heavy elements, which induce spin-orbit interactions. While this CISS phenomenon due to phonon transport is naively explained by angular momentum transfer from chiral motion of nuclei to spins of conduction electrons, its microscopic origin remains unanswered because of the lack of understanding of the microscopic description underlying interfacial phonon-spin conversion.

The key idea to solve this problem is reconsideration on microscopic spin-phonon coupling. Usually, it is derived from energy change of electrons induced by lattice displacement in combination with the spin-orbit interaction. In our work [3], we focused on a previously overlooked mechanism derived from the gyromagnetic effect [4], considering the coupling between local microrotations and electron



Fig. 1. (a) Schematic setup. Heat current in the chiral insulator generates a spin current in the normal metal through an interface. The generated spin current can be observed by a voltage in the NM induced by the inverse spin Hall effect. (b) Schematic illustration of energy dispersion splitting for chiral phonons. The red and blue lines represent the energy of the right-handed ($\lambda = -$) chiral phonon modes, respectively.

spins. The gyromagnetic effect has been studied originally as the interconversion phenomenon between spin and macroscopic mechanical rotation. We have now extended it to microscopic rotation, revealing a nontrivial spin-phonon coupling. Starting with a microscopic model for a bilayer system composed of a normal metal and chiral insulator, we derived the effective Hamiltonian describing the interfacial coupling between the electron spins and chiral phonons due to the spin-microrotation coupling. In our study, chirality is characterized by time-reversal symmetry and lack of the parity(mirror) symmetry with respect to spatial inversion. This feature is reflected by splitting of the phonon dispersion $\omega_{q\lambda}$ as schematically shown in Fig. 1(b), where q is the wavenumber and $\lambda = \pm$ is the chirality of phonons. When the phonons propagate along the chiral axis, their energy becomes different $(\omega_{q^+} \neq \omega_{q^-})$ due to the chirality of the crystal. The phonon dispersion lacks the parity symmetry $(\omega_{q\lambda} \neq \omega_{-q\lambda})$, while it keeps the time-reversal symmetry $(\omega_{q\lambda}$ $= \omega_{-q\bar{\lambda}}$ where $\lambda = \mp$ indicates the chirality opposite to λ .

By treating this interfacial coupling perturbatively, we formulated the spin current injected from the chiral insulator into the normal metal. The results suggest that an imbalanced distribution among the chiral phonon modes, e.g., due to a temperature gradient, drives the interfacial spin current into the normal metal. By a simplified calculation assuming the relaxation time approximation, the spin current into the normal metal is obtained as

$$I_s^z \propto \sum_{\boldsymbol{q}(\boldsymbol{q}_z > 0)} q_z^2 \frac{\partial}{\partial q_z} \left(\omega_{\boldsymbol{q}+}^4 - \omega_{-\boldsymbol{q}+}^4 \right) \left(-\frac{\partial_z T}{T} \right)$$

Combining this result with chiral property of phonons described above, we can show that nonzero spin current is generated across the interface only for chiral insulators.

Our findings clearly illustrate the microscopic origin of the spin current generation by chiral phonons without the spin-orbit interaction and may lead to a breakthrough in the development of spintronic devices without heavy elements.

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Gapless Detection of Broadband Terahertz Pulses Using a Metal Surface in Air Based on Field Induced Second-Harmonic Generation

Yoshinobu and Matsunaga Groups

Terahertz (THz) time-domain spectroscopy has been attracting much attention in many research areas such as imaging, molecular spectroscopy, and solid-state physics because the energy covers various elementary excitations in solids and molecules. Various methods for detecting the phase-locked THz electric field have been developed, such as electro-optic (EO) sampling and photoconductive antennas. Because most of these detection methods use insulating solid crystals, phonon absorptions and the phase matching condition in the crystals largely disturb the timedomain waveform of the THz pulse, particularly between 5 and 15 THz. To realize a gapless detection for broadband THz pulses, Air-Biased Coherent Detection (ABCD) has been utilized; it is based on the interference between the THz electric field-induced second harmonic (TFISH) light from air molecules and an electric-field-induced second harmonic light by the electrodes with high bias voltage above 1 kV. Recently, to reduce the voltage value, Solid-State-Biased Coherent Detection (SSBCD) using insulators such as silica or diamond instead of air was developed; however, it still requires sub-kV bias and microfabrication processes. Therefore, a much simpler geometry for gapless broadband THz pulse detection is highly demanded.

We have developed a new detection method, termed as Air-Metal Coherent Detection (AMCD), where we utilize a metal surface instead of the vias voltage in ABCD. The schematic of our experimental setup is depicted in Fig. 1(a). Second-harmonic generation (SHG) light from a Pt surface in air under broadband THz pulse irradiation was investigated. An output of the Ti:sapphire regenerative amplifier was divided into two beams for THz generation and for a near-infrared pulse as a fundamental light of SHG lights. Here, the THz pulse was generated from the two-color laserinduced air plasma filamentation, and we confirmed its broad bandwidth up to at least several tens of THz by using mid-infrared-sensitive power meters. Both P-polarized pulses were collinearly focused on the Pt surface in air, and THz pulse-modulated SHG intensity $\Delta I_{2\omega}$ was measured by a photomultiplier tube. The time profile of $\Delta I_{2\omega}$ and the amplitude spectrum obtained by fast Fourier transform of the time trace were shown in Figs. 1(b) and 1(c), respectively. For comparison, the spectrum evaluated by using a conventional EO sampling method with a GaP crystal is also added in Fig. 1(c). The spectrum evaluated by EO sampling (red) was restricted only below 7 THz due to the phonon resonances and phase-matching conditions in the GaP crystal. By clear contrast, the spectrum obtained from the time trace of $\Delta I_{2\omega}$ measurement (blue) detected the broadband frequency components without gaps. Because the THz field inside the metal is sufficiently weak, the TFISH generation in the metal



Fig. 1 (a) Schematic illustration of the experimental setup. (b) The time profile of $\Delta I_{2\omega}$ measured for the Pt single crystal using the broadband THz pulse. (c) The blue line corresponds to the amplitude spectra obtained by fast Fourier transformation of the time trace of (b). As a reference, the amplitude spectrum detected by the EO sampling method with the GaP crystal was added as the red line

is negligible. As a result, the effect of phonons is absent for the ΔI_{20} measurements, enabling a gapless detection of broadband THz pulses in the region of 0.2-20 THz as shown in Fig. 1(c). We also confirmed that this method works well even with a gold mirror instead of the Pt surface.

In this study, a new gapless detection method was developed for broadband THz pulses by using a metal surface in air without any high voltage electrodes. The present AMCD method does not suffer from phonons or phase matching in insulating solid-state optics and does not require any power supply, bias voltage, or fabrication process, but offers a simple and gapless sampling method for broadband THz pulses.

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Fabrication of Orientation-Controlled Orthoferrite Films

Lippmaa and Nakatsuji Groups

YFeO₃ is an orthorhombic antiferromagnet with a distorted pseudocubic perovskite structure. The spins are slightly canted, giving the material a small spontaneous residual magnetic moment. Single crystals of YFeO3 have been shown to have a magnon decay length of several hundred nm. As the spin ordering temperature is about 640 K and YFeO₃ has no spin-flop transitions below the ordering temperature, it can be a useful material for designing roomtemperature antiferromagnetic spintronic devices. The choice of suitable antiferromagnets is small, with most experimental work focusing on hematite α-Fe₂O₃. However, device design generally requires thin films and it is known for α -Fe₂O₃ that the magnon decay length in a thin film is much shorter than in a single crystal. In Fe₂O₃, this reduction of the decay length may be related to the small grain size and high defect density, which is an intrinsic problem with iron oxides due to the existence of multiple crystalline phases with the same nominal film composition. Compared to hematite, the orthoferrite phase is more stable and it should thus be possible to fabricate films with single-crystallike quality, at least in terms of the magnetic structure. In particular, large magnetic domains are desirable with few grain boundaries. However, when orthorhombic films are grown on common cubic substrates, such as SrTiO₃, the film would spontaneously form various twinned structures due to the unequal lengths of the pseudocubic in-plane axes of the film. We have successfully grown YFeO₃ films with large magnetic domains and a well-defined in-plane orientation of the crystallographic axes by using an orthorhombic NdGaO₃ substrate. The (110) surface of a NdGaO₃ crystal has a tetragonal in-plane unit cell, which can work as a growth template for a fully-strained epitaxial film, ensuring that the orthorhombic *c*-axis is in the plane of the film and that there are no 90° in-plane twin boundaries. To achieve such growth, the substrate has to have an atomically flat surface. The substrates were therefore annealed in air at 1000°C to

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Fig. 1. Atomic force microscope image of a YFeO₃ film surface. A defect-free step-and-terrace surface was observed over large length scales. X-ray reciprocal space mapping of a YFeO₃ film on a NdGaO₃ substrate shows that the film does not contain twin domains.

Fig. 2. MOKE imaging of the direction switching of the weak residual magnetic moment of a YFeO₃ film during a gradual increase of an external magnetic field. The magnetic domain size appears to be larger than 100 μ m.

obtain a step-and-terrace NdGaO₃(110) surface. The YFeO₃ films grown by pulsed laser deposition also exhibited a clean long-range step-and-terrace morphology (Fig. 1a), indicating that the films did not have 90° twin grain boundaries. The structural quality was confirmed through x-ray reciprocal space mapping (Fig. 1b), which showed that the films did not have a multi-domain structure. The magnetic ordering temperature of the films was verified to be close to 640 K by measuring the small residual ferromagnetic component of the canted spin structure. Hysteresis loops associated with the switching of the spontaneous residual magnetic moment were only observed when the magnetic field was applied in the plane of the film along the YFeO₃ c-axis. The magnetic domain size was analyzed by magneto-optic Kerr rotation (MOKE) imaging. By slowly increasing the magnitude of the applied field, a gradual domain formation and domain wall movement could be observed in a narrow field range of 342 to 360 Oe (Fig. 2). The MOKE imaging showed that the magnetic domain size was on the scale of 100 µm or more. The magnon decay length in single crystals has been shown to be on the order of 0.5 µm, which means that for the purpose of device design, the films can be considered to have a single-domain structure. The well-ordered flat surface of the films provides a good starting point for constructing devices with very well defined interfaces. The YFeO₃ films can be easily combined with various oxide ferromagnets, such as (La,Sr)MnO₃ or metal layers.

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Coupled Electron-Proton Transfer Dynamics in Electrochemical Media

Sugino Group

Protons couple with water molecules in solution to form a hydronium ion (H₃O⁺(aq)), which is sometimes regarded as a small polaron. At low voltages, instead, they prefer to combine with an electron near the electrode and are adsorbed thereon as a neutral species (H⁰(ads)). This is a prototypical electrochemical reaction called Volmer step. This change in the proton state is called coupled electron-proton transfer dynamics; its microscopic elucidation, however, has long been a challenge of theoreticians. A few decades ago, Schmickler modeled it by adding solvent phonons coupled harmonically with protons to a surface adsorption model called Newns-Anderson model. The resulting Newns-Anderson-Schmickler model, consisting of a hydrogen atom, electrons in electrode, and solution, has been regarded as one of the standard models for the electrochemical step.

It is found that the terms added to consider the solvation effect can be apparently removed by applying the Lang-Firsov transformation, often used in studying polaron dynamics. This technique allows us to apply the non-equilibrium approaches so far developed for the Newns-Anderson model. Based on this recognition, we provided an analytical expression for the Volmer dynamics and revealed the non-adiabaticity caused by the moving hydrated protons, i.e. the deviation from the adiabatic Born-Oppenheimer (BO) state [1]. This is an extension of our previous work on the Volmer dynamics based on first-principles BO dynamic simulation [2] although the model used therein has been greatly simplified in the present Schmickler model. Importantly, however, it is possible for the model to consider the energy dissipation channels; (a) electron-hole excitation in the electrode or the electronic friction channel, and (b) vibrational excitation in the solvents. The former channel opens mainly when the proton affinity level aligns with the Fermi level and is increasingly important as the velocity of the proton increases, while the latter channel is constantly active under the conditions we have assumed. Our solution to

Fig. 1. Electrode-solution interface. Green circles represent the atoms constituting the electrode, and the red and while circles represent, respectively, the oxygen and hydrogen atoms constituting the hydronium ion. The hydrogen atom nearest to the electrode is moving towards the electrode, and this motion is coupled to transfer of an electron in the electrode. The Newns-Anderson-Schmickler model represent the coupled proton-electron transfer dynamics, for which an analytical solution has been provided in our research.

the time-dependent News-Anderson-Schmickler model can be used to explain qualitatively the experiments regarding how the reaction rate depends on the electrode potential. The solution can also be used to show how the kinetic energy of the hydrated protons is dissipated into the dissipation channels, which should be important for the chemical-toelectric energy conversion efficiency. As far as we know, the two channels have not been studied together although each of them has been studied separately; the electrode problem thus provides a novel target for non-equilibrium statistical physicists.

Our simulation is currently based on assumed trajectories of the proton although the trajectory can be assumed only for fast-moving protons; in the present case, however, protons are moderately accelerated in the electric double layer, possibly on the order of several tens of meV. In the future step, therefore, the trajectory will be determined by solving the proton's equation of motion considering self-consistently the two dissipation channels as described above. We will consider in addition the quantum effect of protons, such as tunneling and interference, that may play a role as discussed in the literature. Those are the target of our long-term project "Establishing a Quantum Theory of Electrodes". Our study has enabled us to take an important step in this direction. **References**

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Extremely Large Magnetoresistance in Multipolar Kondo System PrTi₂Al₂₀

Nakatsuji Group

The multipolar Kondo systems $Pr(Ti, V)_2Al_{20}$ provide unprecedented opportunities to design new quantum phases and functionalities beyond the spin-only paradigm. They host a nonmagnetic crystal-electric-field ground state in which the magnetic dipole moment is absent while higher-order quadrupolar and octopolar moments are active; the substantial Kondo entanglement between these multipolar moments and the conduction electron sea serves as the root for strange

Fig. 1. Transverse magnetoresistance (MR) curves of $PrTi_2Al_{20}$ obtained at various temperatures. While conventional B^2 behavior is observed at high *T* (inset), unsaturated quasi linear MR is observed at low *T* up to 16 T (main panel).

Fig. 2. Low-*T* Hall coefficient $R_{\rm H}$ (a) and χ , $\chi\rho$ and $\chi\rho^2$ (b) as a function of *B*. $R_{\rm H}$ cannot be scaled by either χ , $\chi\rho$ and $\chi\rho^2$, indicating the anomalous Hall component associated with the magnetization is negligibly small.

metal behavior, quantum criticality, and exotic superconductivity observed in these systems. Here, we discover extremely large magnetoresistance (XMR) exceeding $\sim 10^{3}$ % in the pure ferroquadrupolar ordered state of PrTi₂Al₂₀ and identify the key role of Fermi surface topology in generating this XMR. Large magnetoresistance lays the foundation for various technological applications; a well-known example is the magnetic field sensor based on giant magnetoresistance (GMR). Our findings demonstrate that a multipolar ordered state, without involving spin degrees of freedom, can realize large magnetoresistance. These findings provide essential insights that may facilitate revealing unified mechanisms behind large magnetotransport phenomena and thereby widen the material platforms for their applications.

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Giant Anomalous Nernst Effect in

Polycrystalline Thin Films of Co₂MnGa Nakatsuji Group

Co₂MnGa is a Heusler compound that exhibits the largest anomalous Nernst effect at room temperature. This effect arises from its topological band structure, namely, the Weyl cone. Previously, the large anomalous Nernst effects in thin films of Co₂MnGa were obtained via epitaxial growth using a single-crystal substrate or an interface with an easily crystallized material such as AlN. Here, by improving the deposition process, we have succeeded in obtaining the anomalous Nernst effect of $-5.4 \,\mu$ V/K in Co₂MnGa

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Fig. 1. Schematic illustrations for the thermoelectrical transport measurements (Seebeck and anomalous Nernst effect) and magnetic field dependence of the anomalous Nernst effect in the Co₂MnGa film at 300 K.

Fig. 2. Column chart of absolute values of room-temperature anomalous Nernst effect ($|S_{yx}|$)) obtained in magnetic materials. Each group is categorized as follows: bulk single crystals (green), bulk poly-crystals (brown), film deposited on a single crystalline substrate (blue), singlelayer films deposited on an amorphous template (red), and multilayer films deposited on an amorphous template (purple).

polycrystalline films directly deposited on an amorphous template of SiO₂/Si substrates, which are cheaper and readily available. The key aspect of this method is that Co₂MnGa grains with the $L2_1$ structure were realized by high-temperature deposition. This film deposition technique can facilitate the commercial advancement of thermoelectric devices using the anomalous Nernst effect and the development of spintronics devices by interfacing with widened material classes.

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Magnetic Anisotropy of Fe/MgO Interfaces Inserted with Alkali Halide Layers

Miwa Group

Fe/MgO-based systems have attracted attention for magnetic tunnel junction applications because of the simultaneous existence of robust perpendicular magnetic anisotropy (PMA) and giant tunnel magnetoresistance (TMR). Recently, it was demonstrated that a few monolayers of LiF insertion can enhance the interfacial PMA at the Fe/MgO interface while TMR and the voltagecontrolled magnetic anisotropy effect are maintained [1]. It was also shown the PMA enhancement originates from increased Fe orbital magnetic moment anisotropy, and a higher electronegativity of F compared with O seems to contribute to the enhancement [2]. Motivated by these findings, in this study, we investigate the influence of alkali halide layers with different anion electronegativity and spin-orbit interaction on the magnetic anisotropy at the Fe/MgO interface [3]. Here we chose LiF, CsI, and NaCl as a fluoride, an iodide, and a chloride since they could be grown epitaxially on Fe, considering their similar lattice constants ($a_{\rm Fe} = 0.286$ nm, $a_{\rm LiF}/\sqrt{2} = 0.285$ nm, $a_{\rm CsI}/\sqrt{2} = 0.318$ nm, $a_{\rm NaCl}/2 = 0.282$ nm).

The schematic of the samples is shown in Fig. 1(a). Epitaxial multilayers consisting of MgO (5 nm)/V (30 nm)/ 0.6, and 1 nm)/MgO (5 nm)/SiO2 (5 nm) were grown on single-crystalline MgO (001) substrates by molecular beam epitaxy, where LiF, CsI and NaCl were introduced as alkali halide layers. The crystallinity of each surface was evaluated by performing reflection high-energy electron diffraction (RHEED) measurements. The RHEED patterns of the 0.2-nm-thick LiF, CsI, and NaCl layers are shown in Fig. 1(b), 1(c), and 1(d), respectively. The streaky pattern in LiF indicates the epitaxial growth because of the good lattice matching. The spotty pattern in CsI represents a rough surface, and the additional 2×2 streaks may originate from only half Cs/I atoms in the CsI monolayer compared to the Fe layer. The pattern of NaCl shows a superlattice because of two models of pseudo epitaxial growth of NaCl: either NaCl[110] or [100] direction is parallel to the Fe[100] direction.

The magnetic properties were characterized by using the polar magneto-optical Kerr effect (polar-MOKE). The LiF thickness dependence of the normalized magnetization curves for the Fe 0.7-nm region is shown in Fig. 2(a). The shape of the magnetization curves is modified by the inserted LiF layers, revealing that the LiF insertion strengthens PMA, and the PMA becomes the strongest at a LiF thickness of 0.4 nm.

We estimated the total PMA energy $(K_{\rm eff})$ from the magnetization curves, and we characterized the contribution from the interfacial magnetic anisotropy $(K_{\rm I})$ to the PMA energy by employing the linear fitting: $K_{\rm eff}t_{\rm eff} = \left(K_{\rm V} - \frac{1}{2}\mu_0 M_{\rm eff}^2\right)t_{\rm eff} + K_{\rm I}$. The interfacial magnetic

Fig. 1. (a) Schematic of the multilayers. RHEED patterns of the alkali halide layers: (b) LiF 0.2 nm, (c) CsI 0.2 nm, and (d) NaCl 0.2 nm

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Fig. 2. (a) LiF thickness dependence of the normalized magnetization curves for the Fe 0.7-nm region. (b) Interfacial magnetic anisotropy energies as a function of alkali halide thickness for the LiF, CsI, and NaCl samples

anisotropy energies as a function of alkali halide thickness for the LiF, CsI, and NaCl samples are shown in Fig. 2(b). For the LiF sample, the $K_{\rm I}$ slightly increases in the 0–0.4-nm regions but starts to decrease in the 0.4-1.0-nm regions. It is suggested that the high electronegativity of F is beneficial for interfacial PMA probably because of the weaker Fe-F hybridization and stronger electron localization at the interface. For the CsI and NaCl cases, the interfacial PMA decreases monotonically with CsI or NaCl thickness. Despite their strong spin-orbit interactions, the finite magnetic dead layers suggest an intermixing of the alkali halide and Fe layers, which contributes to the interfacial PMA degradation.

In summary, we studied the effect of alkali halide insertions on magnetic anisotropy at the Fe/MgO interface, and our study shall serve as a guiding principle for designing a new dielectric layer to achieve stronger PMA in ultrathin Fe films.

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X-Ray Magnetic Circular Dichroism **Study of Enhanced Interfacial Perpendicular Magnetic Anisotropy** in LiF-Inserted Fe/MgO Interface

Miwa Group

Fe(CoB)/MgO interfaces are crucial for spintronics applications such as magnetoresistive random access memories (MRAMs) due to their giant tunneling magnetoresistance (TMR) effect and strong interfacial perpendicular magnetic anisotropy (PMA). Strong PMA is key to shrinking the size of magnetic cells while keeping thermal stability intact, and improving PMA is one of the most significant challenges in MRAM development.

Recently, Nozaki et al. demonstrated that inserting an ultrathin LiF layer between the MgO and Fe layers significantly boosts interfacial PMA while preserving or even enhancing TMR ratio [1]. Although this discovery is promising, the cause of the enhancement remains elusive, and clarifying its origin is of great importance for further improvements in PMA. For such purpose, we conduct x-ray magnetic circular dichroism (XMCD) measurements on Fe/ LiF/MgO multilayers [2].

The Fe/LiF/MgO structures were grown on singlecrystalline MgO (001) substrates using molecular beam epitaxy. The sample structure is illustrated in Fig. 1(a). XMCD measurements were conducted at the BL-16A beamline in the Photon Factory.

Figure 1(b) presents an out-of-plane magnetic hysteresis loop measured with the magneto-optical Kerr effect. The loops are perfectly square, indicating that the Fe/LiF/MgO multilayers exhibit PMA. The coercive field becomes larger with LiF thickness up to 0.4 nm but slightly declines when the LiF layer reaches 0.6 nm, in agreement with the previous study [1]. This suggests that PMA energy increases with LiF insertion.

To uncover the origin of the enhanced PMA, we measured XMCD spectra with both out-of-plane and nearly in-plane (70°) magnetic fields. Figure 2(a) compares the XMCD spectra for samples without LiF and with a 0.4-nmthick LiF layer. The XMCD spectra are normalized to the Fe L_2 -edge maxima. The XMCD spectra consists of broad single peak for each L_3 and L_2 edge, confirming the absence of Fe oxides or fluorides at the interface. The intensity of the XMCD is stronger for the out-of-plane magnetic fields than for the in-plane magnetic fields. This intensity anisotropy becomes more pronounced with LiF insertion, indicating that the orbital magnetic moment becomes more anisotropic.

To be more quantitative, we estimated spin and orbital magnetic moments using XMCD sum rules. Figure 2(b)

Fig. 1. (a) Schematic sample structure. (b) Hysteresis curves measured using magneto-optical Kerr effect.

Fig. 2. (a) X-ray magnetic circular dichroism spectra for the samples without LiF and with 0.4-nm-thick LiF, measured with out-of-plane $(\theta = 0^{\circ})$ and nearly in-plane $(\theta = 70^{\circ})$ magnetic fields. The measurement geometry is depicted in the inset. (b) Anisotropy in the ratio of the Fe orbital magnetic moment to the Fe spin magnetic moment as a function of LiF thickness. The coercive fields are also plotted for comparison.

shows the obtained anisotropy of the orbital to spin magnetic moment ratio, defined as $\Delta(m_{\rm orb}/m_{\rm spin}) = (m_{\rm orb}/m_{\rm spin})_{\theta=0^{\circ}}$ – $(m_{\rm orb}/m_{\rm spin})_{\theta=70^{\circ}}$. This anisotropy increases with LiF thickness. This strengthened orbital moment anisotropy is consistent with the PMA enhancement because the PMA energy is proportional to the orbital moment anisotropy in the simplest approximation. Indeed, the coercive fields behave similarly to the orbital moment anisotropy, as displayed in Fig. 2(b). The $\Delta(m_{\rm orb}/m_{\rm spin})$ values seem saturated at the LiF thickness of 0.2 nm, the origin of which may be attributed to the fact that the Fe layer is almost fully covered by a monolayer of LiF (~0.2 nm).

We infer that the enhancement of the orbital moment anisotropy arises from the more robust interfacial electron localization and electron-electron correlation, due to the highly ionic nature of LiF and weak Fe-F hybridization, or from improved interface quality with fewer defects.

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Influence of Alkali-Fluoride Insertion Layers on the Perpendicular Magnetic Anisotropy at the Fe/MgO Interface

Miwa Group

Fe/MgO-based systems have attracted significant attention because of their strong perpendicular magnetic anisotropy (PMA) and giant tunneling magnetoresistance (TMR). Recently, it was reported that an ultrathin LiF layer insertion at the Fe/MgO interface could enhance the interfacial PMA while maintaining the TMR ratio [1, 2], and the following study showed that inserting other alkalihalide layers, such as NaCl and CsI, degrades the interfacial PMA [3]. Such findings suggest the importance of the strong electronegativity of fluorine atoms. However, since LiF has better lattice matching with Fe than MgO ($a_{\text{LiF}} = 0.403 \text{ nm}$, $a_{MgO} = 0.421 \text{ nm}, \sqrt{2} a_{Fe} = 0.405 \text{ nm}), \text{ it remains unclear}$ whether the presence of fluorine atoms on the Fe atoms or the improved lattice matching between Fe and LiF layers contributes more significantly to the PMA enhancement. In this study, we insert an ultrathin NaF layer with suboptimal lattice matching to Fe at the Fe/MgO interface and characterize the PMA energy to disentangle the effects of strong electronegativity and lattice matching [4]. NaF, LiF, and MgO share the same NaCl-type crystal structure with lattice constants of 0.462, 0.403, and 0.421 nm, respectively.

The schematic of the multilayer structure is shown in Fig. 1(a). The multilayers consist of single-crystalline MgO (001) substrate/MgO (5 nm)/V (30 nm)/Fe $(t_{Fe} = 0.3 - 0.9 \text{ nm})/\text{NaF} (0 - 1 \text{ nm})/\text{MgO} (5 \text{ nm})/\text{SiO}_2 (5 \text{ nm}).$ We performed reflection high-energy electron diffraction (RHEED) measurements to examine the surface crystallinity. The RHEED images of the 0.6-nm-thick Fe layer,

Fig. 1. (a) Schematic of the multilayers. (b) RHEED patterns of the multilayers: 0.66-nm-thick Fe layer, 0.1- and 0.6-nm-thick NaF layers, and MgO overlayer on 0.1-nm-thick NaF layer. (c) Normalized reciprocal of the distance between streaks (1/d) in V, Fe, and NaF epilayers obtained from pixel analysis.

0.1- and 0.6-nm-thick NaF layers, and the corresponding MgO cap layer on the 0.1-nm-thick NaF layer, are shown in Fig. 1(b), respectively. The sharp streaks observed in the RHEED pattern indicate the well-epitaxial deposition of each layer.

To evaluate the lattice matching properties, we estimated the in-plane lattice constants of the NaF with various thicknesses by measuring the distance between the streaks in the RHEED patterns [represented as d in Fig. 1(b)]. As the in-plane lattice constant is inversely proportional to d, we plotted 1/d values for the Fe and NaF layers normalized to that for the V layer in Fig. 1(c). The lattice constant of the Fe underlayer is plotted in blue at a NaF thickness of 0 nm. The 1/d value remained constant with a 0.1-nm-thick NaF insertion but drastically increased when the NaF thickness exceeded 0.1 nm. The in-plane lattice constant of the 0.6-nmthick NaF layer is estimated as ~0.323 nm, approaching its unconstrained bulk lattice constant ($a_{\text{NaF}}/\sqrt{2} = 0.327 \text{ nm}$). These results indicate that a NaF layer epitaxially forms islands on the Fe layer when the NaF layer is thinner than a monolayer. However, for thicker NaF layer insertions, accumulated internal stress overcomes the epitaxial stress and creates interfacial defects, and therefore, the lattice constant approaches the bulk lattice constant.

The magnetic properties were characterized by polar magneto-optical Kerr effect (polar-MOKE) measurement. The magnetic dead layer thickness of the NaF sample and the compared LiF sample are shown in Fig. 2(a). The dead layer exhibits robustness after LiF insertion and remains unchanged with a 0.1-nm-thick NaF insertion. However, it drastically increases as the NaF thickness becomes thicker, suggesting interlayer mixing between NaF and Fe layers. We estimated the magnetic anisotropy energies from magnetization curves and extracted the interfacial magnetic anisotropy energies (K_I) of NaF and the compared LiF samples are shown in Fig. 2(b). The 0.1-nm-thick NaF insertion shows a slight enhancement of K_I which is similar to the LiF case, except for the critical thickness difference probably originating from

Fig. 2. NaF and LiF thickness dependence of the (a) dead layer and (b) interfacial magnetic anisotropy energies (K_1) .

the difference in lattice matching conditions. Despite the suboptimal lattice matching, the $K_{\rm I}$ enhancement in the Fe/NaF interface underscores the importance of fluorine atoms on the Fe atoms.

In summary, we have investigated the influence of NaF insertion on magnetic anisotropy at the Fe/MgO interface to disentangle the effects of fluorine electron negativity and lattice matching. Our result deepens the understanding of the effects of fluorine insertion on magnetic anisotropy at the Fe/MgO interface.

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Pressure-Induced Superconductivity in Polycrystalline La₃Ni₂O_{7-δ}

Uwatoko Group

High- $T_{\rm c}$ superconductors have been at the forefront of scientific exploration due to their immense potential for transformative technological applications. The groundbreaking discovery of high- T_c cuprates, where superconductivity (SC) emerges through doping Mott insulators with strong electron correlations, has motivated numerous endeavors in the past decades to unveil its mechanism and to find more superconducting families with high $T_{\rm c}$. Through sharing striking structural and electronic similarities with cuprates, the nickelates with $Ni^+(3d^9)$ electron configuration offer a tantalizing avenue for uncovering new high-T_c superconductors. However, SC was not experimentally realized in nickelates until 2019, when the infinite-layer $Nd_{1-x}Sr_xNiO_2$ thin films were found to show SC with $T_c \approx 9-15$ K [1]. Since then, considerable dedication has been directed toward finding more nickelate superconductors with higher $T_{\rm c}$.

Recently, Sun et al. reported the signature of hightemperature SC in La₃Ni₂O₇ crystals with T_c up to 80 K at pressures above 14 GPa [2]. In contrast to the infinite-layer Nd_{1-x}Sr_xNiO₂, La₃Ni₂O₇ exhibits an exceptionally unique electronic configuration with the nominal oxidation state of Ni^{2.5+} as a mixed valence state of Ni²⁺($3d^8$) and Ni³⁺($3d^7$). According to the structural study under high pressure, a structural phase transition from the orthorhombic Amam to Fmmm space group occurs at about 10-15 GPa, where the interlayer Ni-O-Ni bond angle changes from 168° to 180° [2]. Subsequent high-pressure studies on La₃Ni₂O₇ crystals confirmed the presence of a zero-resistance state under better hydrostatic pressure conditions, yet revealed also some issues related with sample-dependent behaviors that remain unclear so far [3,4]. Such a remarkably high T_c has immediately ignited widespread theoretical investigations on the mechanism of high- T_c SC. The significance of interlayer exchange between the d_{z^2} orbitals and intra-layer hybridization of the d_{z^2} and $d_{x^2-y^2}$ orbitals on the nearest neighbor sites has received substantial attention. In contrast to the extensive

theoretical investigations, experimental progress appears to have lagged behind, presumably due to the challenges associated with obtaining high-quality La₃Ni₂O₇ single crystals with controlled and homogeneous stoichiometry. Depending on the post-annealing process, the oxygen content of La₃Ni₂O₇ can vary from O_{6.35} to O_{7.05}. In addition, other competitive Ruddlesden-Popper phases are easily formed in the crystals grown using the optical image floating-zone furnace under moderate oxygen pressures. It thus becomes an important issue to perform a comprehensive study on the samples with well-controlled quality. Additionally, an open question remains concerning whether superconductivity can be achieved in La₃Ni₂O₇ polycrystalline samples subjected to high pressure. Therefore, we are motivated to prepare phase-pure polycrystalline La₃Ni₂O_{7-δ} samples in which oxygen content and chemical homogeneity can be easily controlled, and then to study the pressure effects on its

Fig 1. (a) Rietveld refinements on the room temperature XRD pattern of La₃Ni₂O_{7-δ}. The obtained lattice parameters are shown in the figure. The bottom marks and line correspond to the calculated Bragg diffraction positions and the difference between observed and calculated data, respectively. (b) Thermogravimetric curves for La₃Ni₂O_{7- δ} in 10% H₂/ Ar. (c) Rietveld refinements on the NPD pattern of La₃Ni₂O_{7- δ}. (d) The SEM-EDS elemental mapping of La₃Ni₂O_{7-δ}.

Fig. 2. The T-P phase diagram of the La₃Ni₂O_{6.93} polycrystalline. The solid and open circles represent the DW-like transition measured at various pressures using PCC, CAC and MA. The solid and open squares and pentagons represent the onset and zero-resistance superconducting transition temperatures determined from the present measurements in CAC and MA. The solid and open hexagon represent the critical temperature for the strange-metal-like behavior, above which the (T) curve deviates from linearity.

electrical transport properties under high pressure.

In this work [5], we synthesized high-quality La₃Ni₂O_{7- δ} $(\delta \approx 0.07)$ polycrystalline samples by using the sol-gel method without post-annealing under high oxygen pressure (Fig. 1), and then measured temperature-dependent resistivity under various hydrostatic pressures up to 18 GPa by using the cubic anvil and two-stage multi-anvil apparatus. We find that the density-wave-like anomaly in resistivity is progressively suppressed with increasing pressure and the resistivity drop corresponding to the onset of superconductivity emerges at pressure as low as 6 GPa. Zero resistivity is achieved at 9 GPa below $T_c^{\text{zero}} \approx 6.6$ K, which increases quickly with pressure to 41 K at 18 GPa. However, the diamagnetic response was not detected in the ac magnetic susceptibility measurements up to 15 GPa, indicating a filamentary nature of the observed superconductivity in the studied pressure range. The constructed T-P phase diagram (Fig. 2) reveals an intimate relationship between superconductivity, density-wave-like order, and the strange-metallike behaviors. The observation of zero resistance state in the polycrystalline La₃Ni₂O_{7- δ} samples under high pressures not only corroborates the recent report of superconductivity in the pressurized La₃Ni₂O_{7- δ} crystals but also facilitates further studies on this emerging family of nickelate high-T_c superconductors.

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Investigation of the Atomic Coordinates of CeNiC₂ under Pressure: Switching of the **Ce-Ce First Nearest Neighbor Direction**

Uwatoko Group

CeNiC₂ is notable for its unique properties, including heavy fermion behavior and multiple magnetic orderings. As the temperature decreases, CeNiC2 undergoes an incommensurate antiferromagnetic transition (ICAF) at $T_{ICAF} \sim 20$ K, followed by a commensurate antiferromagnetic transition at $T_{CAF} \sim 10$ K, and ferromagnetic ordering below 2.2 K. T_{ICAF} increases with pressure, reaching a maximum around 7 GPa. Beyond 11 GPa, the ICAF order is suppressed, and a SC dome with a maximum $T_c \sim 3.5$ K appears. This SC state has a large upper critical field, $H_{c2}(0) \sim 18$ T, nearly three times the Pauli paramagnetic limiting field, indicating an unconventional nature of the SC state. CeNiC₂ has the highest T_c among Ce-based heavy fermion superconductors [1]. In NCS superconductors, antisymmetric spin-orbit coupling can occur due to the lack of inversion symmetry, favoring spin-triplet Cooper pairing with large $H_{c2}(0)$. Also, NCS superconductors can host a mix of spin-triplet and singlet pairing. While CeNiC₂ has an NCS crystal structure at ambient pressure, it is unclear if this structure is maintained across the pressure range where the SC state appears. Subtle variations in interatomic distances under pressure can significantly affect the magnetic and electronic properties of heavy fermion materials. However, obtaining precise structural information under pressure is essential for understanding CeNiC₂'s properties, although challenging. This study investigates the effect of pressure on CeNiC₂'s atomic coordinates using single crystal X-ray diffraction (XRD) measurements at room temperature up to 18.6 GPa.

High-quality single crystals of CeNiC₂ were grown using the Czochralski pulling method in an Argon gas environment, with high-purity Ce, Ni, and C atomes. Single crystal X-ray diffraction at 293(2) K was conducted using a Rigaku XtaLab MicroMax007 HFMR with Mo-K α radiation and a HyPix6000 diffractometer. The crystal structure was solved using Olex2 with SHELXT 2018/2 and refined with SHELXL 2018/3. High-pressure experiments utilized a diamond anvil cell (DAC) with a 300 µm culet size. A CeNiC₂ single crystal (~100 µm) was loaded into the DAC with a ruby pressure manometer, and a 4:1 methanol-ethanol mixture served as the pressure transmitting medium.

Figure 1(b) shows the normalized unit-cell parameters and unit-cell volume of CeNiC₂ in the pressure range from 0 to 18.6 GPa. The normalized unit-cell parameters show anisotropic compressibility under pressure; the length of the a-axis decreases at a much faster rate compared to the b- and c-axes. The compressibility of the a-axis (k_a = $d(a/a_0)/dP = -3.70 \times 10^{-3}$) is the highest, whereas the b-axis is the lowest (k_b = $d(b/b_0)/dP = -1.39 \times 10^{-3}$ GPa⁻¹). The unit-cell parameters decrease linearly with pressure, showing no structural phase transition. Compressibility is anisotropic, with the a-axis compressing fastest. The bulk modulus B₀ is $\sim 134 \pm 3$ GPa with B₀' = 0.75 ± 0.05.

The anisotropic compressibility of CeNiC₂, with higher compressibility along the a-axis than along the b- and c-axes, likely causes this behavior. The stiffness of the NiC₂ layer, attributed to strong C-C bonds and Ni-C interactions in the bc plane, hinders compression along these axes. This results in different responses of interatomic distances under pressure. Similar effects on magnetic exchange interactions have been observed in other CeT₂X₂ compounds, like CeRh₂Ge₂ and CeCu₂Ge₂, where interatomic distances govern the c-f interaction strength.

Figures 2(a), (b) and (c) show the interatomic distances between Ce-Ce, Ni-Ni and Ni-Ce atoms. Atomic coordinates

Fig. 1. (a) The positions of C, Ni, and Ce atoms in the unit cell are illustrated with red, blue, and black dashed circles, respectively. (b) The pressure dependence of normalized lattice parameters and unit cell volume. The error bars are smaller than the symbols. The dashed lines are the linear fittings to the pressure dependence of the lattice parameters used for estimating the compressibility. The solid line represents a fit of the Birch-Murnaghan equation of state to the normalized unit cell volume [2].

Fig. 2. The pressure dependence of interatomic distances between the (a) Ce-Ce atom, (b) Ni-Ni atom, and (c) Ni-Ce atom is illustrated. The dashed lines in (c) represent the linear fitting results. The red and black dot-dashed lines in the inset illustrate the direction of interatomic distances 1 and 2 in the unit cell. The solid symbol shows the ambient condition data [2].

of Ce, Ni, and C, and interatomic distances were measured under pressure, revealing changes primarily in the y-coordinate of C and the C-C bond length, especially around 7 GPa. The interatomic distances between Ce-Ce, Ni-Ni, Ni-Ce, and C-C exhibit notable changes with pressure, indicating anisotropic compressibility and bond length variations, particularly highlighting the unique behavior of C-C and C-Ni bonds around 7 GPa.

Nonmonotonic pressure dependencies in C-C, C-Ni, and C-Ce distances, particularly around 7 GPa, indicate anomalies that may result from increased Ce-Ce interaction along the a-axis penetrating the NiC₂ layer. These findings highlight the intricate relationship between pressure, atomic distances, and magnetic properties in CeNiC₂, providing critical insights into the behavior of heavy fermion materials. As shown in Fig. 2 the first and second nearest neighbor directions of Ce-Ce and Ni-Ni atoms interchange around 7 GPa, with nonmonotonic pressure dependence observed for interatomic distances between C-Ce, C-Ni, and C-C atoms at this pressure. Increasing pressure causes these distances to decrease and become equal around 7 GPa. Above this pressure, the FNN and SNN directions interchange; the FNN aligns along the a-axis, and the SNN lies in the bc-plane. This interchange correlates with the weakening of incommensurate antiferromagnetic (ICAF) order and the emergence of the Kondo effect above 7 GPa, suggesting increased interplanar Ce-Ce interaction influences the spin structure of CeNiC₂ [2].

In summary, we investigated the crystal structure of CeNiC₂ from 0 to 18.6 GPa by using single crystal X-ray diffraction with a laboratory X-ray source. Our results reveal a large Bulk modulus ~ 134 GPa and anisotropic linear compressibility following the relationship |ka| > |kc| > |kb|. Although, we do not detect any signature of structural phase transition, the direction of FNN and SNN between the Ce-Ce and Ni-Ni atoms interchanges near the pressure where the antiferromagnetic ordering temperature reaches a maximum in the pressure temperature phase diagram of CeNiC₂. Our results suggest that the direction of nearest neighbors interexchange might play a key role in the suppression of magnetic order and the enhancement of the Kondo effect.

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Dynamics in Active Cyclic Potts Model

Noguchi Group

Spatiotemporal patterns, such as traveling waves, have been observed in nonequilibrium active systems. Many phenomena are well-captured by a description in terms of nonlinear but deterministic partial differential equations. However, noise effects are not understood so far. We focused on the effects of thermal fluctuations, since they are significant on a molecular scale.

We simulated the nonequilibrium dynamics of a Potts model with three cyclic states (s = 0, 1, and 2) [1]. The neighboring sites of the same states have an attraction to induce a phase separation between different states, and they have a cyclic state-energy-difference in the rock-paperscissors manner. Both forward and backward flips are considered by the Monte Carlo method. It is a model system for chemical reactions on a catalytic surface or molecular transport through a membrane. For the reaction case, the three states are reactant, product, and unoccupied sites. For the transport case, the molecule can bind to both surfaces and flip between these two states. For one cycle, a reaction proceeds in bulk in the former case, and a molecule is transported across the membrane in the latter case. In this study, we consider the cyclically symmetric condition, i.e., the self-energy difference of the successive states is constant as $\varepsilon_0 - \varepsilon_1 = \varepsilon_1 - \varepsilon_2 = \varepsilon_2 - \varepsilon_0' = h$. This model can be tuned from thermal-equilibrium to far-from-equilibrium conditions and corresponds to the standard Potts model at h = 0.

We found two dynamic modes: homogeneous cycling mode and spiral wave mode. At a low cycling energy h between two states, the homogeneous dominant states cyclically change as $s = 0 \rightarrow 1 \rightarrow 2 \rightarrow 0$ via nucleation and growth, as shown in Fig. 1(a). In contrast, spiral waves are formed at high energy h, as shown in Fig. 1(b). The waves are generated from the contacts of three states and rotate around them. The homogeneous cycling mode is newly found in this study, whereas the spiral waves have been

Fig. 1. Sequential snapshots of active cyclic Potts model. (a) Homogeneous cycling mode at h = 0.8. (b) Spiral wave mode at h = 1.1. The states, s = 0, 1 and 2, are displayed in gray, blue, and red colors, respectively.

reported in continuum models and other lattice models.

For large systems, a discontinuous transition occurs from these cyclic homogeneous phases to spiral waves, while the opposite transition is absent. Conversely, these two modes can temporally coexist for small systems, and the ratio of the two modes continuously changes with increasing h. The transition from the homogeneous cycling to spiral wave modes occurs by the nucleation of the third state during the domain growth, i.e., it is determined by the competition of the nucleation and growth. The opposite transition from the spiral wave to homogeneous cycling modes occurs through the stochastic disappearance of three-state contacts. With increasing system size, the former transition rate increases, but the latter rate exponentially decreases. The transition character is changed by these size dependencies.

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A New Superconductor Family with Various Magnetic Elements

Okamoto Group

There is a complex relationship between superconductivity, where the electrical resistance of a material becomes completely zero at low temperatures, and magnetism, which is the property of a material as a magnet. Generally, superconductivity is destroyed by strong magnetism, so superconductivity does not often appear in materials containing magnetic elements such as iron. In rare cases, however, materials containing magnetic elements exhibit unconventional superconductivity with very high critical temperature or unusual properties that cannot be explained within the framework of existing theories. Uncovering the complex relationship between superconductivity and magnetism may be important for the realization of room-temperature superconductivity. The discovery of unique superconductors is essential for elucidating this relationship.

We discovered that the ternary telluride series Sc_6MTe_2 is a unique family of d-electron superconductors incorporating various magnetic elements [1]. Sc₆MTe₂ compounds with M = Mn, Fe, Co, Ni, Ru, Rh, Os, and Ir have been synthesized and reported to crystallize in the hexagonal Zr₆CoAl₂type structure, but their physical properties have not been reported thus far [2,3]. A characteristic point of this crystal structure is the fact that the M atoms are trigonal prismatically coordinated by six Sc atoms and form one-dimensional chains along the c axis, as shown in Fig. 1(a). Polycrystalline samples of Sc_6MTe_2 with various transition metal M were synthesized by the arc-melting method and the bulk superconducting transitions in seven M cases were confirmed based on the electrical resistivity, magnetization, and heat capacity measurements on the obtained polycrystalline samples. A Sc₆FeTe₂ sample is shown in the lower right panel of Fig. 1(a).

Figure 1(b) shows the electrical resistivity at low temperatures for various M cases. The seven M cases except for M = Mn, the resistivity shows a sharp drop to zero above 2 K. They also show large diamagnetic signal and clear heat

Fig. 1. (a) Crystal structure of Sc₆MTe₂. The lower right panel shows a polycrystalline sample of Sc₆FeTe₂ synthesized by the arc-melting method. (b) Temperature dependence of electrical resistivity of Sc₆MTe₂ polycrystalline samples.

capacity jump, indicating the bulk superconducting transition occurs in them. A characteristic feature of the superconductivity in Sc_6MTe_2 is the M dependence of the superconducting transition temperature T_c. Four compounds with M = 4d and 5d elements displayed almost the same T_c of approximately 2 K, but those with M = 3d elements displayed higher values and increased in the order of Ni, Co, and Fe. Therefore, Sc_6FeTe_2 showed the highest T_c of 4.7 K.

These results strongly suggest that the 3d electrons of Matoms play an important role in realizing the superconductivity in this system. First principles calculations indicate the presence of significant contribution of Fe 3d orbitals at the Fermi energy, which most likely enhance the T_c of Sc₆FeTe₂. The heat capacity data of Sc₆FeTe₂ indicate that the electronic specific heat in Sc₆FeTe₂ is strongly enhanced by some reason. At present, the origin of this enhancement is still unclear, but it might be interesting if the strong electron correlation of Fe 3d electron plays an important role in this enhancement

Another important point of this Sc₆*M*Te₂ family is that all of Sc, M, and Te sites can be replaced by various elements and physical properties of almost all of them have not been investigated thus far. In fact, following Sc₆MTe₂, we recently discovered superconductivity in a Zr analogues Zr₆MTe₂ [4]. The T_c values in Zr_6MTe_2 is much lower than those for Sc₆MTe₂, but the highest T_c was realized in Zr₆FeTe₂ as in the case of Sc₆MTe₂. Zr₆FeSb₂ is also found to show superconductivity at 1.3 K [5]. It is expected that more new superconductors will be found in this family and the future research on this family will contribute to a complete understanding of the relationship between superconductivity and magnetic elements.

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Dynamics of Acetonitrile Absorbed in a Metal–Organic Framework MIL-101 with Mg-Ion Conduction

Yamamuro Group

MIL-101 is a kind of Metal–Organic Framework (MOF), which contains numerous pores and attracts great attention for various applications, e.g., gas reservoirs, filters, reaction fields, ionic conductors, etc. Recently, the group of Prof. Sadakiyo (our collaborator and visiting professor of ISSP) discovered that MIL-101 containing Mg(TFSI)₂ (TFSI: Bis(trifluoromethanesulfonyl)imide) exhibits superionic conductivity of around 10⁻³ S cm⁻¹ after absorbing acetonitrile (AN) vapor [1]. This discovery may contribute to the development of Mg-ion batteries, which are promising candidates for non-lithium-ion solid-state batteries.

To clarify the effect of AN on Mg-ion conduction, we conducted a quasielastic neutron scattering (QENS) experiment using AGNES at JRR-3 and DNA at J-PARC for three samples: bulk AN, MIL-101 with absorbed AN (AN-MOF) and MIL-101 with absorbed AN and Mg(TFSI)₂ (AN-Mg-MOF). The QENS spectra observed by AGNES and DNA were Fourier transformed into intermediate scattering functions I(Q,t)s and smoothly joined as shown in Fig. 1. As shown in Fig. 2, the I(Q,t) of bulk AN is fitted well by a single Kohlrausch-Williams-Watts (KWW) function as ordinary α relaxations of molecular liquids, while those of AN-MOF and AN-Mg-MOF by the sum of a KWW function, a constant (elastic component) which corresponds to the stational hydrogen atoms in MIL-101, and an exponential function which may correspond to a methyl rotation decoupled from the α -relaxation.

To investigate the α -relaxation expressed by the KWW function, we examine the Q^2 -dependence of the inverse of

Fig. 1. Intermediate scattering functions of AN-MOF obtained from the Fourier transformation of the QENS data at T = 300 K and Q = 1 Å⁻¹ The I(Q,t) data from the standard (ST) and high-resolution (HR) modes of AGNES and the low-resolution (LR) and high-resolution (HR) modes of DNA are smoothly joined.

Fig. 2. Fitting of the intermediate scattering functions of bulk AN and AN-MOF at T = 300 K and Q = 1 Å⁻¹.

Fig. 3. Fitting of the Arrhenius plots of the diffusion constants of bulk AN, bulk AN/Mg(TFSI)₂, AN-MOF, and AN-Mg-MOF.

the average relaxation time $<\tau>^{-1}$. The plots for bulk AN and AN-MOF show continuous diffusion ($\langle \tau \rangle^{-1} = DQ^2$, D: diffusion constant), whereas that for AN-Mg-MOF is represented by the jump-diffusion model ($\langle \tau \rangle^{-1} = DQ^2/(1 + \tau_0 DQ^2)$), τ_0 : mean residence time). This jump may be related to the connection/disconnection process of AN molecules to Mg²⁺. Figure 3 displays the Arrhenius plots of D comparing the three samples. The plots for bulk AN and AN-MOF are classified to Arrhenius type, while that for AN-Mg-MOF is non-Arrhenius type. This may be because AN molecules coordinate to Mg²⁺ ions and the number of the coordinated AN molecules increases as temperature is lowered. The diffusion constants become smaller in order of bulk AN, AN-MOF and AN-Mg-MOF, indicating that the diffusion of AN is hindered by the pore walls of MIL-101 and further by Mg^{2+} ions. The mean jump distance $\langle l \rangle$ was calculated by $\langle l \rangle = (6D\tau_0)^{1/2}$ to be 1.6 Å. The results shown above should provide important information to clarify the mechanism of Mg²⁺ conduction.

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Field Control of Quasiparticle Decay in a Quantum Antiferromagnet

Masuda Group

The concept of a quasiparticle has been successful in explaining various types of low-energy excitations in manybody systems including charge, spin, and lattice. Using a spectroscopic approach, a weakly coupled quasiparticle with a long lifetime can be probed as a well-defined excitation, allowing identification of the effective Hamiltonian and basic understanding of the system. Momentum-resolved spectroscopy has permitted investigations into the intricate structure of spectra, revealing the effect of quasiparticle interactions that results in the renormalization of the dispersion and instability of the quasiparticle.

The microscopic phenomena in the spectra affect bulk properties of materials. In the thermoelectric material PbTe, the interaction between longitudinal acoustic and transverse optical modes (here, the quasiparticles are phonons) induces the decay and overdamping of the former phonon in the low energy region, leading to low conductivity of thermal current [1]. The instability of the quasiparticle is key for the current to exist in bulk property.

Two examples illustrate that the instability of the quasiparticle is changed by the interaction between the one-quasiparticle and two-quasiparticle continuum [2]. An example for a case of the strong interaction is found in the longitudinal sound wave, phonon, in superfluid ⁴He [3]. The spectrum in low energy exhibits a local minimum with energy Δ , called a roton, for which qualitative behavior is explained by Feynman and Cohen (FC) harmonic dispersion. However, the spectrum does not exceed a critical energy of 2Δ , which is the lower boundary of the two-phonon continuum. The strong interaction between the one-phonon and continuum pushes one-phonon energy downwards, and the one-phonon stays at 2Δ outside the continuum. On the FC dispersion beyond the critical energy, the bare one-phonon decays into a pair of rotons, and a remnant of one-phonon which is ascribed to the bound state of two-phonon was observed. The phenomenon is considered universal in bosonic systems and has also been observed in a spin-gap antiferromagnet BiCu₂PO₆ [4].

An example for the weak interaction is found in a two-dimensional quantum magnet, piperazinium hexachlorodicuprate (PHCC) [3]. This case is simple; the quasiparticle decays in the continuum, and a remnant one-magnon is probed as a broad excitation. The conjecture which this work tests is that if one tunes the interaction between a quasiparticle and the continuum in an identical material by applying external field, would the quasiparticle decay behavior change?

This study [5] examines magnon decay in a triangular lattice quantum antiferromagnet RbFeCl₃. Magnetism of Fe²⁺ ion surrounded by Cl⁻ octahedra with trigonal distortion is effectively described by an S = 1 spin with strong easy-plane anisotropy. Fe²⁺ ions form a one-dimensional ferromagnetic chain along the crystallographic *c*-axis, and the interchain interaction in the triangular lattice in the *ab*-plane is antiferromagnetic. At low temperatures the compound exhibits a non-collinear 120° structure due to the frustration. The spectrum was qualitatively similar to that of the pressure-induced ordered state in the isostructural compound CsFeCl₃ near the quantum critical point (QCP) [6], which cannot be explained by standard linear spin wave

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Fig. 1. False color map of inelastic neutron scattering (INS) spectra and calculated two-magnon density of state in RbFeCl₃. **a-l**: Magnetic field (H // c-axis) dependences of false color maps for observed (**a-f**) and calculated (**g-l**) INS spectra. Red arrows in **a-f** indicate broadening linewidth. White arrows in **e** and **f** indicate magnons avoiding decay. White and red solid curves in **g-l** are one-magnon dispersion relations of $\hbar\omega_1$ and $\hbar\omega_2$ modes calculated using linear extended spin wave theory (LESW) using the best fit parameters. The calculated spectra are convoluted by the instrumental resolution.

theory. Instead, the strong hybridization of the transverse and longitudinal fluctuations resulting from the non-collinear magnetic structure renormalizes the magnetic excitation, as explained by the linear extended spin wave theory (LESW) [3]. Because a non-colinear magnetic structure is realized near the QCP and the excitation is strongly hybridized with longitudinal fluctuation, the magnon decay is anticipated in wide four-dimensional momentum-energy space. Furthermore, gapless behavior and a large dispersion perpendicular to the triangular lattice yield a two-magnon continuum covering the whole region of one-magnon excitation.

In this study, we performed inelastic neutron scattering (INS) measurements in the magnetic field on RbFeCl₃ to study the magnon decay and the interaction between single magnons and the two-magnon continuum. We observed a simple magnon decay in a low field where the interaction is small and a magnon avoiding decay in high field where the interaction was large as shown in Fig. 1. Thus, we succeeded in controlling the magnon decay using the field. In contrast with the avoided phonon decay in superfluid ⁴He and magnons in magnetic materials previously reported [2,4], the phenomenon was observed in the presence of a two-quasiparticle continuum, indicating that the phenomenon is not limited to outside the continuum, but also occurs inside.

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Single-q and Multi-q Magnetic Orders in the Collinear Commensurate Antiferromagnet CeRh₂Si₂

Nakajima Group

Since the discovery of magnetic skyrmion lattice (SkL) in MnSi[1], magnetic orders described by multiple magnetic modulation wave vectors (q-vectors), which are referred to as multi-q magnetic orders, have been attracting remarkable attention. In the early stage of the magnetic skyrmon studies, the Dzyaloshinskii-Moriya (DM) arising from the broken inversion symmetry of the crystal structure was considered to be one of the most important ingredients for realizing the SkL states. Thus, non-centrosymmetric magnets were intensively investigated. This trend has changed since the discovery of the SkL state with a large topological Hall effect in Gd₂PdSi₃ [2], which has the centrosymmetric crystal structure. It was also theoretically pointed out that the biquadratic interaction term derived from the perturbative expansion for the Kondo lattice Hamiltonian can stabilize a variety of multi-q states even in centrosymmetric systems [3]. In the present study, we applied this model to the centrosymmetric collinear-commensurate antiferromagnet CeRh₂Si₂ [4].

CeRh₂Si₂ has a ThCr₂Si₂-type centrosymmetric tetragonal crystal structure and is known to have two antiferromagnetic phases at low temperatures in zero magnetic field [5]. Both magnetic phases are characterized by commensurate q-vectors. Specifically, the high-temperature phase (AF1) has a single q-vector of q = (1/2, 1/2, 0). This q-vector breaks the fourfold rotational symmetry of the crystal structure, and thus results in two magnetic domains characterized by q = (1/2, 1/2, 0) and (1/2, -1/2, 0). On the other hand, the low-temperature phase (AF2) is characterized by four q-vectors of q = (1/2, 1/2, 0), (1/2, -1/2, 0), (1/2, 1/2, 1/2), and(1/2,-1/2,1/2). In contrast to the AF1 phase, AF2 phase was reported to be a multi-q phase, i.e., the magnetic structure is described by a superposition of the four magnetic modulations. This means that the AF2 phase retrieves the fourfold rotational symmetry of the crystal, although it was lost in the high-temperature AF1 phase. This distinct change in symmetry should be seen in bulk properties such as magnetization, resistivity etc. as well as the neutron diffraction intensities. However, they were not observed because the AF1 phase exhibits a multi-domain state, in which the two single-q magnetic domains coexist. The intrinsic anisotropy of the magnetic order and associated physical properties were not macroscopically observed.

We thus applied a weak uniaxial stress to a single crystal of CeRh₂Si₂, and performed magnetization, resistivity and neutron diffraction measurements. The direction of the

Fig. 1. (a) Temperature dependence of magnetization M at $\mu_0 H = 0.2$ T and $\sigma = 0$, 20 MPa. $M ||H| ||\sigma|| [1-10]$. M is normalized by M at 40 K. (b) Temperature dependence of the difference of magnetization ΔM . (c) Temperature dependence of resistivity ρ at $\mu_0 H = 0$ T and $\sigma = 0$, 20 MPa. Electric current I is applied along $\sigma ||$ [1-10]. (d) Temperature dependence of the difference of resistivity Λ_0 . The measurements were dependence of the difference of resistivity Δ_0 . The measurements were performed under cooling condition. A schematic of the geometry for each measurement are shown in inset. Black arrows indicate ordering temperature. This figure is taken from Ref. 4.

uniaxial stress was selected to be the [1-10] direction of the crystal to lift the degeneracy between the two magnetic domains. In Fig. 1, we show temperature variations of magnetization and resistivity measured at ambient pressure and under uniaxial stress of 20 MPa. In both the measurements, the applications of the uniaxial stress induced the difference in magnetization and resistivity only in the AF1 phase. We also performed neutron diffraction measurements with uniaxial stress. We measured temperature variations of the magnetic Bragg peaks at (1/2, 1/2, 0) and (1/2, 1/2, 1), which correspond to the two q-vectors of (1/2, 1/2, 0) and (1/2,-1/2,0) respectively. Similarly to the magnetization and resistivity measurements with the uniaxial stress, we observed significant uniaxial-stress dependence of the intensity only in the AF1 phase. Specifically, the magnetic scattering corresponding to the q-vector of (1/2, -1/2, 0)completely suppressed by the application of uniaxial stress, demonstrating that the system exhibits a single-domain AF1 phase under uniaxial stress. Interestingly, the magnetic Bragg peak at (1/2, 1/2, 1) reappeared in the AF2 phase even in the finite uniaxial stress. In addition, the temperature dependence of the magnetic peak at (1/2, 1/2, 1/2), which is characteristic of the AF2 phase, was not affected by the uniaxial stress. These observations mean that the AF2 phase indeed has the multi-q magnetic order with fourfold symmetry. This is also consistent with the fact that the bulk properties of the AF2 phase are insensitive to the uniaxial stress. We also performed neutron inelastic scattering experiments and determined the exchange interactions between the magnetic moments. We calculated the exchange energies for the AF1

Fig. 2. Temperature dependence of integrated intensity at $\sigma = 0$ and ~25 MPa at Q = (a) (1/2, 1/2, 0), (b) (1/2, 1/2, 1), and (c) (1/2, 1/2, 1/2), respectively. Open (closed) symbols are the data at $\sigma = 0$ Pa (~25 MPa). The experimental geometry is shown in inset of (c). k_i and k_f indicate the incident and reflection neutron, respectively.

and AF2 phases and found that they are equal. By introducing the biquadratic interaction term mentioned above, the degeneracy is lifted, and the multi-q state is stabilized as the ground state. The present results demonstrated that the biquadratic term, which was originally introduced to explain the SkLs in centrosymmetric magnets, is also applicable to collinear commensurate multi-q orders. We also emphasize here that an application of uniaxial stress is quite useful to investigate magnetic materials exhibiting both single-q and multi-q orders.

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Stiff and Tough Ion Gels for Electrolyte **Membranes of Flexible Batteries**

Mayumi Group

Gel electrolytes consist of polymer network and ion-conductive liquids as solvent. Due to their flexibility, they have been applied for electrolyte membranes of flexible Li ion batteries that can be attached to our skin or clothing. Electrolyte membranes require a high elastic modulus to prevent Li metal crystals from growing at the electrode surface during charging and discharging, causing a short circuit in the batteries. Previous research has reported that the formation of lithium metal crystal is suppressed for electrolyte membranes with an elastic modulus of 10 MPa or more. In addition, to prevent crack growth during repeated deformation of flexible batteries, gel electrolyte membranes need to exhibit high fracture toughness. For conventional gel electrolytes, polymer crystallization was used to increase stiffness. However, hard gel electrolytes tend to become

Fig. 1. Phase-separation and strain-induced crystallization of stiff and tough gel electrolyte

Fig. 2. Schematic illustration of flexible battery containing a stiff and tough gel electrolyte membrane.

brittle, and it has been difficult to achieve both stiffness and toughness. Although various high-strength gel electrolytes have been developed, no gel electrolytes achieved high elastic modulus (over 10 MPa) and fracture toughness. In our laboratory, by combining phase separation and straininduced crystallization, we have succeeded in developing a gel electrolyte that exhibit a high elastic modulus of over 10 MPa and high toughness of about 100 MJ/m³ (Fig. 1) [1]. When our gel electrolyte is deformed, stretched polymer chains form crystals, which improvs the mechanical toughness [2]. To homogenize chain deformation in the gel electrolytes, we used slide-ring (SR) network in which polymer chains are connected by ring molecules. The ring molecules of the SR network are aggregated to form a hard continuous phase, which resulted in a high elastic modulus (70 MPa). Our gel electrolytes are sufficiently stiff to prevent short circuits during charging and discharging of the batteries, and are also tough enough to withstand repeated deformation, which leads to improved durability of flexible batteries (Fig. 2).

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Hyperoctagon Cobalt Oxalate MOF as a **Platform for Kitaev Spin Liquid Physics**

Kindo, Yamashita, and Yamaura Groups

Water becomes vapor or ice when the temperature changes. In the same way, spins change the state and exhibit various magnetic properties when the environment such as temperature and magnetic field changes. Generally, at sufficiently low temperatures, the orientation of the spins aligns like a solid. On the other hand, a state where the spins are not ordered down to the lowest temperatures, despite the presence of sizable interactions between the spins to order their orientations, can be viewed as a liquid state that does not solidify. Such a state is called a quantum spin liquid and has attracted condensed matter physicists as a new state of matter. The most promising theoretical model for realizing a quantum spin liquid state is the honeycomb lattice model proposed by Kitaev [1]. A worldwide research competition involving both physics and chemistry communities is underway to create a material that realizes the Kitaev's honeycomb model. Thus far, simple inorganic compounds with a two-dimensional honeycomb lattice and their derivatives have been studied exhaustively. On the other hand, it has been pointed out that there are small number of variations of materials and the effect of disorder can be problematic in the layered compounds. Therefore, the development of materials from a new perspective has been desired.

We focus on a three-dimensional honeycomb lattice called a hyperoctagonal lattice realized in a Metal Organic Framework (MOF), which has been studied as an ionic conductor previously. In this MOF, metal ions are linked by the oxalic acid molecules to form a three-dimensional network. A similar situation was theoretically studied in 2017 by M. Yamada, H. Fujita, and M. Oshikawa in the Institute for Solid State Physics at the University of Tokyo, who proposed the realization of a quantum spin liquid [2]. However, no experimental studies have been conducted to date. We selected cobalt as the magnetic element because the effect of the spin-orbit coupling is prominent. We synthesized the crystals of the MOF and investigated the magnetic properties down to low temperatures and in the strong magnetic fields [3].

Our experiments revealed that the MOF with a hyperoctagonal lattice exhibits various spin states as the temperature and magnetic field change. In particular, as the temperature is lowered, a peculiar intermediate temperature state where the spins are not ordered appears, despite the fact that interactions between spins are active. Interestingly, the entropy of the spin is released by about a half around the intermediate temperature region, which is similar to the behavior expected in the theory. This interesting magnetic property should be attributed to the unique cobalt network connected

Fig. 1. (Left) Hyperoctagon lattice in the cobalt oxalate MOF. (Right) Image of the quantum spin liquid state.

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by the oxalic acid molecules, which generates the magnetic interactions to align the spins in different directions for each bonding direction of the hyperoctagon lattice.

It has been proposed that the properties of the quantum spin liquids can be used to perform quantum computation. Our results represent a totally new direction in the development of materials that can be the platform for the quantum computation. The development of MOFs is expected to accelerate the development of materials of the research area.

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Quantum Liquid-Quantum Liquid Transition in a Strong Magnetic Field

Kindo and Tokunaga Groups

In recent years, quantum liquids of quasiparticles, which are disordered states by quantum fluctuations, has attracted much attention. The similarities and differences between quantum and classical liquids are an interesting topic. In the case of classical liquids, the absence of order typically suggests the existence of only a single liquid phase. However, some anomalous molecules, such as H₂O, which have locally stable structures, exhibit multiple liquid phases, and liquid-liquid phase transitions have been observed. Due to the involvement of various degrees of freedom in liquidliquid transitions, its complete understanding is still elusive. For quantum liquids, it has not even been clear whether a quantum liquid state can exhibit athermal transition to a distinctly different quantum liquid state.

We have investigated the organic charge-transfer complex, TTF-QBr₃I (tetrathiafulvalene-2-iodo-3,5,6 -tri-bromo-*p*-benzoquinone) that simultaneously exhibits ferroelectric and spin-Peierls (FSP) transition at 5.6 K. As the one-dimensional alternate stack of ionic TTF (cation) and QBr₃I (anion) molecules, spin solitons are excited as topological defects in the FSP ordered state, as shown in Fig. 1. Our earlier research in zero magnetic field [1] demonstrated that spin solitons traverse potential barriers by quantum tunneling even at extremely low temperatures. In this study [2], we performed magnetization, dielectric property, and ultrasound measurements of this salt in pulsed high magnetic fields. Given the density and dynamics of spin

1 Schematic illustration of one-dimensional chain of TTF and OBr3I molecules and creation of spin solitons at the domain walls in the ferroelectric spin-Peierls (FSP) state. Green arrows represent spins, while the site colors indicate the ion type (red: cation, blue: anion). Thick arrows show the electric polarization of the dimers.

solitons, we demonstrated that these solitons can be regarded as a quantum liquid at zero field. TTF-QBr₃I positions near the quantum critical point in its electronic phase diagram, and the FSP state is strongly influenced by strong quantum fluctuations. We revealed that the quantum liquidity originates from the developed quantum fluctuations.

When a strong magnetic field of 40 T is applied, an anomaly was observed in all measured physical quantities, indicating the emergence of an additional FSP state. In the case of a conventional spin-Peierls state, the strong Zeeman effect leads to a transition to an incommensurate state with an emergent distortion wave vector, known as the solitonlattice state. Given this analogy, the solidification of solitons due to the lattice formation would be expected. Nevertheless, our results suggested that the presence of the strong quantum fluctuations in TTF-QBr₃I preclude the formation of such a soliton lattice, causing the dense solitons to remain in a quantum-mechanically melted state even in high magnetic fields. Namely, the observed transition indicates the realization of a quantum liquid-quantum liquid transition of topological particles by the application of a strong magnetic field.

Even in classical liquids, since liquid-liquid phase transitions appear only in anomalous systems, their origins are still mysterious. In this study, we have for the first time discovered the phenomenon where quasiparticles drifting quantum mechanically undergo a phase transition from one quantum liquid state to another under the influence of a magnetic field. This discovery not only represents a novel phenomenon but also holds potential to contribute to the understanding of classical liquids.

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Discovery of superconductivity in La₂IOs₂ with 5d Honeycomb Lattice

Kindo Group

5d transition metal compounds have gained considerable interest in the condensed matter community in the last decade. The combination of strong spin-orbit coupling and Coulomb interactions may stabilize a Mott insulating state with nontrivial ground states such as a quantum spin liquid on the honeycomb lattice. In metallic compounds, the spinorbit coupling and electron-electron interactions may cause a Fermi surface instability that gives rise to various electronic orders and exotic superconductivity.

We focus on the intermetallic compound La₂IOs₂ with Gd₂IFe₂-type, which is known as the intermediate between cluster compounds and intermetallic phases. The crystal structure (Fig. 1) features a two-dimensional slab made of a transition-metal-centered trigonal prism of lanthanum, where

Fig. 1. Crystal structure of La_2IOs_2 (left) and the honeycomb lattice of Os (right).

the Os form the honeycomb network. We have prepared the pure polycrystalline and $\sim 100 \ \mu m$ size single crystal samples of La₂IOs₂ and investigate its physical properties by the resistivity, torque, and specific heat measurements.

We have demonstrated the bulk superconductivity at $T_{\rm c} = 12$ K in La₂IOs₂ by the physical property measurements. Despite the heavy constituent elements, which are generally unfavorable for a phonon mediated mechanism, T_c is the highest among lanthanoid iodides made of lighter elements such as La_2IRu_2 with $T_c = 4.8$ K. Moreover, electronic anomalies are observed at 60 K and 30 K, which are similar to those observed in isostructural La2IRu2 at 140 K and 85 K, pointing to the presence of the common electronic instability inherent to the Gd₂IFe₂-type crystal structure. We consider the fluctuations relevant to the electronic instability enhances the superconductivity in La₂IOs₂, while this point should be clarified in the future work. Furthermore, we observed that the superconductivity is robust against the magnetic field especially when the magnetic field is applied parallel to the honeycomb layer. We observed zero resistivity at least up to 12 T and the estimated upper critical field is around 40 T.

Our discovery indicates that La₂IOs₂ is a layered 5d electron system providing a platform to investigate the interplay between the electronic anomaly, superconductivity, and strong magnetic field. Further investigations to understand the superconducting pairing mechanism and the origin of the unusual properties are ongoing. Besides the interest from the physical perspective, our first-principles electronic structure calculations reveal the effective valence of Os is -1, indicating the Os is anionic. Examples of transition metal anions in solids are limited to a few intermetallic compounds including platinum or gold. Exploring the *d*-electron physical properties of relative compounds with anionic transition metals are also of interest.

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H. Ishikawa, T. Yajima, D. Nishio-Hamane, S. Imajo, K. Kindo, M. Kawamura^a ^aInformation Technology Center, University of Tokyo Possible Intermediate Quantum Spin Liquid Phase in α-RuCl₃ under High Magnetic Fields up to 100 T

Y. Matsuda and Kindo Group

Quantum spin liquid (QSL) constitutes a topological state of matter in frustrated magnets, where the constituent spins remain disordered even down to absolute zero temperature and share long-range quantum entanglement. Due to the lack of rigorous QSL ground states, such ultra quantum spin states are less well-understood in systems in more than one spatial dimension before Alexei Kitaev introduced the renowned honeycomb model with bond-dependent exchange.

The 4*d* spin-orbit magnet α -RuCl₃ has been widely accepted as a prime candidate for Kitaev material. This compound is now believed to be described by the *K*-*J*- Γ - Γ ' effective model that includes the Heisenberg *J*(1, 3), Kitaev exchange *K*, and the symmetric off-diagonal exchange terms. The Kitaev interaction originates from chlorine-mediated exchange through edge-shared octahedra arranged on a honeycomb lattice. Similar to most of Kitaev candidate, additional non-Kitaev terms, unfortunately, stabilize a zigzag antiferromagnetic order below $T_N \approx 7$ K in the compound. Given that, a natural approach to realizing the Kitaev QSL is to suppress the zigzag order by applying magnetic fields to the compound.

Recently, the theoretical studies point out an interesting two-transition scenario with a field-induced intermediate QSL phase under the out-of-plane magnetic field [1], which is later confirmed by a large Kitaev-term spin Hamiltonian also based on the *K-J*- Γ ⁻ Γ ^{*} model [2]. With the precise model parameters determined from fitting the experimental thermodynamics data, they theoretically reproduced the suppression of zigzag order under the 7-T in-plane field, and find a gapless QSL phase located between two out-ofplane transition fields that are about 35 T and of 100-T class, respectively. However, because theoretical studies predict very high critical fields—where $H_C^1 \approx 32.5$ T and H_C^h is in 100-T range—they are challenging to observe experimentally.

In this work, we report the magnetization (M) process of α -RuCl₃ by applying magnetic fields (H) in various

Fig. 1. The field-angle phase diagram that summarizes the values of transition fields determined from both the experimental (black solid markers) and the calculated (grey open ones) H_C , H_C^l and H_C^h . We also plot the low-field results (blue stars) taken from ref. [3] as a supplement. The zigzag antiferromagnetic, quantum paramagnetic (QPM), and the quantum spin liquid (QSL) phases are indicated. Here, H_c denotes the critical field from zigzag order to the QSL phase, and H_C^h represents the critical field from the QSL to the QPM state.

directions within the honeycomb plane and along the c^{*} axis (out-of-plane) up to 100 T, and find clear experimental evidence supporting the two-transition scenario. Here, the c^{*} axis is the axis perpendicular to the honeycomb plane. Under fields applied along and close to the c^{*} axis, an intermediate phase is found bounded by two transition fields H_C^l and H_C^h . In particular, besides the previously reported $H_C^{\gamma} \approx 32.5 \text{ T}$ [3], remarkably we find a second phase transition at a higher field H_C^h (higher than 83 T) [4]. Below H_C^h and above H_C^l there exists an intermediate phase, i.e. the predicted field-induced QSL phase. When the field tilts an angle from the c^* axis by 9°, only the transition field H_C , is observed, indicating the intermediate QSL phase disappears. Accordingly, we also perform the density-matrix renormalization group (DMRG) calculations based on the previously proposed K-J- Γ - Γ ' model of α -RuCl₃, and find the simulated phase transitions and extended QSL phase are in agreement with experiments. Therefore, we propose a complete fieldangle phase diagram (as shown in Fig. 1) and provide the experimental evidence for the field-induced QSL phase in the prominent Kitaev compound α-RuCl₃ [4].

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Double-Peak Specific Heat Anomaly in Quantum Oscillation

Kohama Group

Quantum oscillation phenomenon is an essential tool for understanding the electronic structure of a metal. The origin of the quantum oscillation is the Landau quantization of the carrier motion, which gives rise to a series of quantized singularities in the density of states (DOS) that cross the Fermi level. The Lifshitz-Kosevich (LK) theory has been widely used to describe the behavior of the quantum oscillation, notably to extract parameters such as the effective mass and Landé g-factor. Although the theory is remarkably successful in the most of metals over a wide range of magnetic fields and temperatures, there is growing evidence to suggest that experiment often deviates from the predicted LK behavior [1]. Although the oscillatory magnetoresistance, magnetization, and thermopower exhibit a clear departure from LK theory at the high-magnetic field limit called the quantum limit, the oscillatory behavior of the specific heat (C_p) in the quantum limit has yet to be fully explored. In this research, we have measured C_p of graphite as a function of the magnetic field and demonstrated that the crossing of a single spin Landau level and the Fermi energy gives rise to a double-peak structure in C_p , in striking contrast to the singlepeak expected from LK theory.

When a Landau level crosses the Fermi energy, the occupation of the Landau level changes rapidly, inducing large changes in the entropy of the system, which can be probed using thermodynamic measurements, such as magnetocaloric effect (MCE) and C_p . To follow the evolution of the entropy in a metal sample, we show the MCE trace (1/T) of the natural graphite as a function of the magnetic field taken at an initial temperature of 0.7 K (Fig. 1a). The entropy is proportional to the logarithm of the number of states within the Fermi edge, and therefore shows a maximum when a Landau level is located at the Fermi level, resulting in a series of well-defined single peaks labeled as $N^{\pm}_{e=h}$ (see Fig. 1a). Here, N is the Landau index, e/h indicates if the Landau level originates from the electron or hole pocket, and \pm indicate the spin up/down levels. For better comparison, Fig. 1b shows background removed magnetoresistance ΔR_{xx} at 0.5 K. These results are in stark contrast to the electronic specific heat divided by temperature C_{el}/T which is proportional to the temperature derivative of entropy (Fig. 1c). Crucially, when low-index Landau levels ($N_{e/h} < 3$) cross the Fermi energy, $C_{\rm el}/T$ exhibits a series of double-peak structure, as indicated by the double arrows in Fig. 1c.

In order to elucidate the origin of the doublepeak structure, it is necessary to consider the exact expression for the specific heat. For electronic quasiparticles, C_{el}/T is given by, $C_{el}/T = k_B^2 \int_{-\infty}^{\infty} D(E) \left(-x^2 \frac{dF(x)}{dx}\right) dx$, where $F(x) = 1/(1 + e^x)$, $x = E/k_BT$ and k_B is the Boltzmann constant. The specific heat depends on the convolution of the Landau level DOS D(E) and a kernel term $-x^2 dF(x)/dx$, which involves the first derivative of the Fermi-Dirac distribution function. Importantly, the double-peak structure in C_{el}/T originates from the temperature-dependent splitting of the double maxima in the kernel term $-x^2 dF(x)/dx$. In Ref. 2, we show that there is a quantitative agreement between the observed double-peak structure and calculated C_{el}/T curve.

In summary, we demonstrate that, as the quantum limit is approached in high-quality graphite, Landau levels crossing the Fermi energy give rise to single features in MCE and magnetoresistance, while simultaneously a novel doublepeak structure is observed in the specific heat C_{el}/T . The

Fig. 1. Comparison of quantum oscillations in MCE, resistivity and specific heat. (a) Reciprocal temperature (1/T) of graphite as a function of applied magnetic field in a quasi-adiabatic condition. (b) Background removed resistance as a function of magnetic field. (c) Field sweep electronic specific heat divided by temperature.

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calculation based on the exact form of the free electron expression successfully reproduces the double-peak structure in specific heat. The specific heat, which depends on an integral involving the kernel term, represents a spectroscopic tuning fork of width 4.8 $k_{\rm B}T$ that can be tuned at will to resonance.

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Quasi-Periodic Growth of One-Dimensional Copper Boride on Cu(110)

I. Matsuda, Hasegawa, and Oshikawa Groups

A surface, located between a vacuum and a crystal substrate, forms a unique two-dimensional (2-D) lattice. By depositing atoms on the surfaces, adsorbate overlayers grow commensurately or incommensurately with respect to the substrate 2-D lattice, depending on a balance between adsorbate-adsorbate and adsorbate-substrate interactions. Such a degree of freedom, being specific to the surface system, results in formation of exotic long-range ordered phases, so-called surface superstructures or Moirè patterns. The unique environment has recently developed new research fields, such as twistronics, and has provided a space to examine interface materials that cannot be explored in a pure 2-D system. One of the notable findings is a longrange ordered layer of copper boride (Cu-Boride) that was grown incommensurately on the (111) surface of a *fcc* copper crystal. This was unexpected since it has been known that the bulk boron hardly forms compounds with the Group-11 elements. Structural analysis by diffraction unveiled that the 2-D copper boride on Cu(111) was composed of an alternating array of atomic boron and copper chains. This has indicated an intriguing relationship between the 2-D and 1-D atomic structures at the surface. Since the (110) surface of a fcc copper crystal is the well-known 1-D template in surface science, one can expect formation of a unique 1-D system at the B/Cu(110) surface.

In the present research, we experimentally examined a Cu(110) surface after boron deposition and discovered a new ordered phase, 3x'1' by low-energy electron diffraction[1]. In the following observation by scanning tunneling microscope, we found that the 3x'1'-B/Cu(110) surface has a 1-D atomic structure of Cu-Boride [1,2]. As shown in an STM image of the 3x'1' phase (Fig. 1(a)), the 1-D structures grow along the $[1\overline{1}0]$ axis, separated by trenches. The 1.1-nm trench interval corresponded to $3a_{[001]}$, where $a_{[001]}$ is a size of the Cu(110) unit cell along the [001] axis. This indicates the origin of the three-fold periodicity of the 3x'1'-B phase. The 1-D structure is composed of two types of unit lengths along the 1-D direction, one commensurate and the other incommensurate with respect to the substrate lattice. A Fourier transform spectrum shows apparent signals that are ascribed to the two wavenumber units, a and b, along the 1-D direction. In the regular crystal, the number of a rank is mathematically equal to the number of dimensions of the

Fig. 1. Quasi-periodic 1-D structure in the B/Cu(110) system. (a) A scanning tunneling microscopy image $(20 \times 20 \text{ nm}^2, \text{tunneling current} : 100 \text{ pA}, \text{ Bias} : 1.5 \text{ V}.)$. (b) The 2-D power spectrum obtained by fast Fourier transform with line profiles crossing the origin in [001] and [110] direction.

structure due to its translational symmetry. When the rank is higher than the dimension of the structure, the structure is called quasi-periodic. The two vectors, given in Fig.1(b), cannot be described by one another. The existence, thus, verifies the quasi-periodicity of the 1-D system. Namely, we can designate that the B/Cu(110) surface as an array of quasiperiodic chains[2]. Such a long-range 1-D quasi-periodic surface structure has been modeled as a 1-D quasi-crystal and the structural parameters, obtained experimentally, satisfied formation conditions predicted by the theory [2]. This system provides an actual interface material to examine 1-D quasicrystals.

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Nondestructive Visualization of Breakdown Process in Ferroelectric Capacitors Using in situ Laser-Based Photoemission Electron Microscope

Okazaki and Kobayashi Groups

HfO₂-based ferroelectrics are one of the most actively developed functional materials for memory devices because of its high scalability and compatibility with complementary metal-oxide-semiconductor (CMOS) technology and with back-end-of-line (BEOL) process [1]. In HfO₂-based ferroelectric devices, dielectric breakdown is a main failure origin during repeated polarization switching. Elucidation of the breakdown process may broaden the scope of applications for the ferroelectric HfO₂.

In situ laser-based photoemission electron microscope (laser-PEEM) has emerged as a powerful technique for studying dynamic processes in materials and devices at the nanoscale. By a laser with an energy comparable to the typical work function of materials, we can observe a bulk electronic structure over the depth of 50 nm [2]. This allows to reveal the chemical-state distribution in a dielectric embedded through a top electrode, nondestructively.

This report presents nondestructive analyses of HfO₂-based ferroelectric capacitors using a laser-PEEM system with an *in situ* voltage application and characterization system.

We fabricated crossbar-type HfO_2 -based metal-ferroelectric-metal (MFM) capacitors on an N⁺ Si substrate as shown in Fig. 1. We used $Hf_{0.5}Zr_{0.5}O_2$ with 10-nm thickness as a ferroelectric layer which is sandwiched by TiN with 30-nm thickness.

Figure 2(a) shows cycling characteristics of leakage current measured in our *in situ* laser-PEEM system. The leakage current began to increase above the detection limit from 1×10^6 cycles. Then, the leakage current reached a local maximum at 4×10^6 cycles, which corresponds to a soft dielectric breakdown (SDB). After that, the MFM capacitor was completely metalized at 7.4×10^6 cycles, which corresponds to hard dielectric breakdown (HDB). This leakage current behavior during the application of cycling stress has been reported as that of typical of MFM capacitors with HZO [3]. This indicates that the waveform was applied

Fig. 1. Structure of the sample used for in situ laser-PEEM measurements. The values in brackets indicate the thick- ness of each film. DUT and Ref. indicate device under test and reference capacitor, respectively.

Fig. 2. Breakdown process visualized by in situ laser-PEEM. (a) Leakage current at 2.4 V on return of voltage sweep as a function of stress cycle. (b–e) Dependence of detailed PEEM images focused on the device under test on the number of cycling stresses.

to the MFM capacitor as designed in the source measure unit implemented in our PEEM system and also suggests that damages caused by laser irradiation during the image acquisitions can be regarded as negligible.

Figures 2(b)–(e) show PEEM images taken after 1×10^{0} cycle, 1×10^6 cycles, 4×10^6 cycles, and 7.4×10^6 cycles, respectively. We found no significant difference between the PEEM image after 1 cycle of the square wave application and that after 1×10^6 cycles, except for an increase in intensity from the bottom electrode (BE). However, after applying 4×10^6 cycles, the PEEM image shows a slight increase in intensity at the corner of the MFM capacitor. From the PEEM image after HDB (Fig. 2(e)), a low- intensity spot was clearly observed near the center of the capacitor. The appearance of this spot just after the occurrence of HDB indicates that this spot is the conduction filament responsible for HDB. The result that the HDB spot was observed in the flat region is reproducible for the samples with the same dimension. This is because the electric field concentration near the edge of BE is suppressed by the voids incidentally formed at both ends of BE.

Figures 3(a) and 3(b) demonstrate that the HDB spot clearly observed by laser-PEEM is not found in the scanning electron microscope (SEM) image. This indicates that significant structural changes, such as a hillhock formation due to dielectric breakdown induced epitaxy (DBIE) of the top electrode, did not occur. It is also shown that laser-PEEM can observe changes in electronic states deeper than the probing depth of SEM. Furthermore, laser-PEEM can even investigate the electronic states in the regions where HDB and SDB have occurred. The ability to nondestructively observe not only the device topography but also the DOS distribution that dominates the functionality of materials will be indispensable for the research and development and mass

Fig. 3. Comparison of micrographs acquired by laser-PEEM and SEM. (a) PEEM micrograph after HDB, which is a magnified image of Fig.
 2(e). TE and BE indicate the top and bottom electrode, respectively. (b) SEM micrograph after HDB of the sample from the in situ laser-PEEM experiment. The acceleration voltage was set to 4 kV.

production of devices that implement functional materials.

In summary, we have proposed in situ laser-PEEM as a tool for observing the breakdown process of HfO2-based MFM capacitors. We observed an increase in photoelectron intensity in a region of the MFM capacitor with the onset of SDB. This corresponds to a precursory defect enhancement of HDB, which has not been clearly observed in previous TEM studies. Furthermore, we have clearly visualized the post-HDB breakdown spot. Ability of laser-PEEM to visualize the DOS distribution will be a key technology for accelerating the control of properties of functional materials and their implementation in CMOS circuits, thereby shortening time to market.

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