Entangled Electromagnetic and Thermal Responses of Topological Insulators and Superconductors

We studied the nontrivial responses of topological insulators and superconductors to determine their electromagnetic and thermal potentials. Magnetization was generated by application of an electric field, which is known as the topological magnetoelectric (ME) effect. We investigated the stability of the ME effect and clarified its robustness with regard to randomness and a strong magnetic field. We generalized this cross-coupling to the case of thermal response and predicted that the temperature gradient generates orbital angular momentum.

In 2005, the theoretical prediction of a new class of materials known as topological insulators [1] promised novel physics and the potential for various applications. The key distinction from ordinary insulators lies in the fact that topological insulators support stable gapless boundary modes. Topological insulators owe their unique properties to time-reversal symmetry: if the flow of time is reversed, the material would behave in the same way. One of the most striking foundations is that the surface states are protected from any perturbation, which preserves the time-reversal symmetry when the bulk energy gap remains intact. Anderson localization is topologically forbidden on the surface of topological insulators even in the presence of disorders. On the other hand, magnetic impurities cause an effective mass gap in the Dirac spectrum on the surface. When the Fermi level resides in the surface gap, a quantized anomalous Hall effect is realized.

As depicted in Fig. 1 (a), applying an electric field produces a Hall current on the surface of the topological insulator, which generates a magnetic field, or magnetization in the bulk. This electrically induced magnetization without dissipation is referred to as the topological magnetoelectric (ME) effect [1, 2]. This type of cross-coupling is described by the energy density functional

\[ U_{EM} = -\int d^4x \left( \frac{e^2}{4\pi^2\hbar c} \right) |\mathbf{E} \cdot \mathbf{B}| \]

where \( \theta = \pi \) for a topological insulator and \( \theta = 0 \) for an ordinary insulator. The topological ME effect is not only a useful signature of a topological insulator but has a variety of potential applications. Therefore, the stability of this effect is of central interest to researchers in this community.

We studied the effect of magnetic disorder on the surface of a topological insulator and clarified that randomness unexpectedly enhances the surface quantized anomalous Hall effect that helps realize the topological ME effect [3]. Using scaling analysis, we clarified that all surface states are localized because of magnetic impurities, while the quantized Hall plateau width becomes enlarged.

Fig. 1 Illustration of a magnetically doped topological insulator with (a) a cylindrical geometry and (b) a slab geometry.
from the original surface gap to all energy regions. We recently studied the effect of bulk impurities [4] and electron–electron [5] interaction. The topological phase withstands such perturbations to some extent.

By using the quantized Hall surface states, surface magnetization can be controlled through the application of both electric and magnetic fields: to get the energy gain in Eq. (1), all surface spins tend to point out perpendicular to the surface. In the presence of only the magnetic field, on the other hand, all surface spins point in the same direction to the field because of Zeeman coupling.

We recently examined this topological ME effect in a thin-film topological insulator [6]. When the width of the film was not very thin, we found that the ME effect worked even beyond the linear response regime.

Topological superconductors are superconductor analogs of topological insulators [1]. The bulk has a finite superconducting gap, while there are gapless Andreev bound states on the surfaces. Topological superconductors intrigue physicists because they are expected to host exotic particles on the surface known as Majorana fermions that differ fundamentally from any other known particles in the sense that the particles are their own antiparticles [1]. Since Majorana fermions are expected to have applications in quantum computation, detecting and manipulating them are the great challenges in the field.

We predicted the existence of a unique and unexpected signature of topological superconductors: a temperature gradient applied to a topological superconductor generates mechanical rotation, i.e., orbital angular momentum[7].

The magnetoelectric coupling in topological insulators is because electrons moving along the surface of a sample under the influence of an electric field generates a magnetic field or magnetization in the bulk. Similarly, Majorana fermions on the surface of topological superconductors moving under the influence of a temperature gradient contribute to the orbital angular momentum. Simultaneously, the thermal Hall conductivity, which characterizes the heat transport of Majorana fermions on the surface, is quantized in terms of universal constants and the mean temperature. This feature indicates that the effect should be stable over extrinsic perturbations.

We obtained the free energy describing this nontrivial thermomechanical coupling as [7]

\[
U_m = -\int d^3x \left( \frac{k_f T^3}{12\hbar v} \right) \nabla T \cdot \Omega
\]

where \(v\) is the Fermi velocity and \(\Omega\) is the angular velocity. The Einstein–de Haas effect reveals the relationship between magnetism and angular momentum of the system and has been used for the study of ferromagnetic materials. We assumed a cylindrical three dimensional (3D) topological superconductor suspended by a thin string and applied a thermal gradient. This induced a surface energy current with angular momentum \(L_z\). By the conservation law of total angular momentum of the material, which can be directly measured in principle, the inverse effect is the generation of thermal polarization induced by rotating the material [7].

References
A magnetic field is a powerful and precise tuning knob for matter such as magnetic and semiconducting materials. It induces various new states with unexpected magnetic and electronic properties. Photospectroscopy is widely used as one of the most powerful means to investigate the states of materials. However, the combination of these two tools has mostly been limited to magnetic fields of less than 20 T at university laboratories. This is because a superconducting magnet is used in most cases; such magnets are easy to handle, and a continuous magnetic field is supplied, but the maximum field is limited. Resistive water-cooling magnets and pulsed magnets that generate magnetic fields of above 20 T are operational in dedicated high magnetic field laboratories. Pulsed magnets are running in smaller laboratories having specialists for high magnetic fields.

Besides the limited maximum magnetic field, there are some technical difficulties in combining a superconducting magnet with optical spectroscopy experiments. A large stray field has a strong influence on detectors and optical systems driven by motors. The optical pass can be as long as a few meters in 20-T magnets; in many cases, an optical fiber is used in such experiments. This is not compatible with techniques such as wide-band THz time domain spectroscopies, which need a direct optical pass.

Compact bench-top pulsed high magnetic field generators, which were developed by the magnetism division of IMR, are a new breakthrough in this field. The idea is very simple. The energy needed for a pulse magnet is known to scale with both the magnet volume and the square of the magnetic field intensity. When a magnet is reduced in scale, the energy can be reduced, and the power supply can be compacted[1]. Because of the compactness of the magnet, the system can easily be placed on the optical bench of the spectrometer. Even so, extremely strong magnetic fields of 30 T are easily obtained. The instrument and operational costs are quite small. For example, the full set including a magnet shown in Fig. 1 costs £50,000.

Fig. 1(a) View of bench-top 30 T pulsed magnet installed in Rice University. The magnet is installed inside the tall cryostat (left panel). The capacitor bank is installed close to the optical table (right upper panel). The wave form is recorded by an oscilloscope (right middle panel). A sample is cooled by the micro-spectroscopy cryostat in the center. In this photo, the cryostat has been temporarily removed from the beam axis shown by arrows. An ultrafast laser, lens system, and detector are arranged on the optical bench for normal zero field experiments (bottom panel).
only a few million JPY, and cheap liquid nitrogen is used for magnet cooling instead of expensive liquid helium.

Fig. 1 shows the bench-top spectroscopy setup. The magnet is installed in the compact liquid nitrogen cryostat, and the magnet inner bore is 13 mm in diameter. The distance from the optical window to the magnet center is only 35 mm. The cryostat can be put on the optical bench, and no special probe is needed for 30 T experiments. The power supply stores an energy of 11.2 kJ and charged with 2 kV. The energy required for 30 T is about 9 kJ. The rise time and total pulse width are 2 ms and 10 ms, respectively. By combining this system with a compact cryostat used for micro-spectroscopy, a sample can be cooled down to 5–10 K. The experimental setup in Fig. 1 is at Rice University, Houston. The first results of fluorescence in a semiconductor superstructure have been reported elsewhere [2].

The system is quite versatile in terms of both generating magnetic fields and application to spectroscopies. The 16 kJ system designed for the Photon Science Institute of Manchester University, as shown in Fig. 2, can be upgraded to charging at 4 kV. The system will be used for THz spectroscopies [3].

In summary, the bench-top 30 T pulsed magnet system developed at IMR will extend the frontiers of magneto-spectroscopies and increase the opportunities for new findings in research on magnetic and semiconducting materials.

References


Fig. 2 16 kJ capacitor bank exported for the Photon Science Institute at Manchester University using the Material Transfer Agreement protocol of Tohoku University. The dimensions are 760 mm wide × 1000 mm long × 1400 mm high (upper panel). The capacitor, charge-discharge, and high-voltage power supply components are assembled as independent units; thus, a flexible upgrade is possible. The inside view of the charge-discharge unit. The high-voltage terminal is on the right front side. The matching filter is on the left front side (lower panel).
Relaxor Ferroelectricity Induced by Electron Correlation in Molecular Dimer Mott Insulator

The charge degrees of freedom in the molecular dimer Mott insulator $\beta'-(\text{BEDT-TTF})_2\text{ICl}_2$ were investigated. An anomalous peak structure with strong frequency dependence on the temperature dependence of the dielectric constant and corresponding glassy polarizations along the dimer direction were observed. These results suggest that the charge degrees of freedom in dimers fluctuate and survive even in a dimer Mott insulator.

The ferroelectricity induced by electrons [1], not conventional ionic displacements, is currently being explored in the field of strongly correlated electron systems, which is related to the charge-ordered state of Mott insulators. Molecular dimer Mott insulators are a good candidate for ferroelectricity and are constructed from dimers of organic molecules such as bis(ethylenedithio) tetrathiafulvalene (BEDT-TTF). When each dimer in a crystal possesses a charge carrier, particularly for the half-filled case of a dimer molecular orbital, the electron system often shows a Mott transition for relatively large (onsite) Coulomb interactions $U$ at the dimer site compared to the electron hopping energy $t$. An important physical insight is that a dimer can be viewed as the primitive constituent in a crystal rather than as a molecule, as shown in Figs. 1(a) and 1(c). In this manner, the understanding of strongly correlated electron systems based on the dimer picture within the Hubbard model has progressed [2].

However, recent reports on the dielectric properties of several dimer Mott insulators [3-5] have implied that the charge degrees of freedom in a dimer survive even in the dimer Mott insulating state [6,7]. If a charge disproportionation occurs in the dimers, electric dipole moments appear as shown in Figs. 1(b) and 1(d). The fluctuation of charges in dimers can be observed in the dielectric properties. This discovery will enable a deeper understanding of organic Mott insulators beyond the successful dimer lattice model.

$\beta'-(\text{BEDT-TTF})_2\text{ICl}_2$ is an anisotropic quasi two-dimensional molecular dimer Mott insulator with a one-hole carrier in the dimer of a BEDT-TTF molecule. The molecular dimer forms the square lattice shown in Figs. 1(c) and 1(d). The dimers are aligned along the $b$ axis, arrayed in a column on the $bc$ plane; the layers are stacked along the $a'$ axis ($L_{bc}$ plane) and are well separated by ICl$_2$ anion layers. Dimerization was supported by NMR [8] and calculation of the intradimer transfer integral. The long-range antiferromagnetic order [9] below $T_N = 22$ K, as shown in Fig. 2(c) indicated that this system is located inside the well-defined dimer Mott insulating region with a large $U/t$ value.

Fig. 2(a) shows the temperature dependence of the dielectric constant $\varepsilon$ for $\beta'-(\text{BEDT-TTF})_2\text{ICl}_2$ in $E||b$ parallel to the dimer array at each frequency [6]. An anomaly with a strong frequency dependence was discerned at around $80-150$ K. With decreasing frequency, the anomaly in the dielectric constant becomes large and forms a peak structure. A similar frequency-dependent dielectric constant was observed for $\kappa-(\text{BEDT-TTF})_2\text{Cu}_2(\text{CN})_3$ [3], which is typically seen in relaxor ferroelectric materials with randomness and frustration.

The dielectric constant obeys the Curie–Weiss law with a constant term: $\varepsilon / \varepsilon_0 = C(T - T_C) + \varepsilon_{\text{const.}} / \varepsilon_0$. Here, $\varepsilon_0$, $C$, and $T_C$ are the vacuum permittivity, Curie constant, and Curie temperature, respectively. The Curie constant $C$ was obtained according to the fit to the Curie–Weiss law. The dipole moment parallel to the $b$ axis was estimated to be $0.13ed$, where $e$ and $d$ are the electron charge and distance between the BEDT-TTF molecules in a dimer, respectively.

Fig. 1 Schematic crystal structure of $\kappa-(\text{BEDT-TTF})_2\text{Cu}_2(\text{CN})_3$ in (a) and (b) and $\beta'-(\text{BEDT-TTF})_2\text{ICl}_2$ in (c) and (d). The upper two panels represent the dimer lattice model, and the lower two represent the dipole dimer model. The circles in the dimer lattice model are the sites of the dimers where the molecules in the dimers are ignored. The ovals in the dipole dimer model represent the dimers. The circles in the oval are molecules where a dipole moment can emerge if a charge disproportionation occurs.
The inset of Fig. 2(b) shows the fit to the data for $E_{∥b}$ of $\beta’$-(BEDT-TTF)$_2$ICl$_2$ to the Vogel–Fulcher (VF) relation for $\epsilon$: $f = f_0 \exp(-E_{VF}/(T_{max} - T_{VF}))$, where $f_0$, $E_{VF}$, and $T_{max}$ are the representative flipping frequency of electric dipoles, average random energy barrier, and temperature at which $\epsilon$ takes a maximum, respectively. The empirical VF relation accurately represents the frequency dependence of the peak in $\epsilon$ with $T_{VF} = 23$ K, $E_{VF} = 804$ K, and $f_0 = 2.17 \times 10^7$ Hz. $T_{VF}$ is very close to the Neel temperature of 22 K. This implies a possible relation between the glassy dielectric behavior and the magnetic property.

Fig. 2(b) shows the electric polarization $P$ with $E_{∥b}$ obtained by pyrocurrent measurements, and (c) shows the temperature dependence of the magnetic susceptibility in a magnetic field with $H_{∥a}$, $b$, and $c$ for $\beta’$-(BEDT-TTF)$_2$ICl$_2$. A small but measurable polarization was observed below the temperature of $T_E = 62$ K, which is nearly identical to the estimated $T_C = 67$ K from the Curie–Weiss behavior. However, the experimentally obtained polarization of 6 nC/cm$^2$ at $E_{pol} = 1.2$ kV/cm was ~100 times smaller than the expected full polarization using the Curie constant. A fully polarized state has not yet been obtained under poling electric fields of 1.2 k V/cm. Thus, such a polarization indicates the formation of glassy polar domains, which is also consistent with the strong frequency dependence of $\epsilon$.

The temperature dependence of the magnetic susceptibility shown in Fig. 2 (c) is explained by a two-dimensional Heisenberg model with an antiferromagnetic interaction $J_{AF}$ of 59 K [9]. Around this temperature, the magnetic susceptibility significantly decreased, which indicates a short-range spin correlation in the low-dimensional system. This energy scale is comparable to $T_E$, which also implies a relation between the glassy nature of the dielectric and antiferromagnetic interaction. Several scenarios based on the spin-charge correlation in the dielectric anomalies have been proposed [3-7].

However, deepening understanding of the charge-spin correlation and the dielectric is a topic for future research.

References
Three-Dimensional Elemental Analysis in Semiconductor-Based Actual Devices with Atom Probe Tomography

Large-scale integration and high performance of metal-oxide-semiconductor field-effect transistors (MOSFETs) have supported advances in the contemporary information society. The large-scale integration and performance of these transistors have been developed rapidly. Controlled dopant position and density would gain prominence, as device scales decrease to less than 30 nm. Since the electrical properties of these devices are sensitive to the spatial distribution of dopants in them, an analytical technique for determining the exact location of each dopant is desired.

Atom probe tomography (APT) can be used for determining the three-dimensional (3D) distribution of individual dopants in materials with nearly atomic-scale resolution. In laser-assisted APT, a pulsed laser combined with high standing voltages is applied to a needle-shaped specimen, resulting in the ionization and extraction of the atoms on the apex, also known as field evaporation. The elemental distribution and mass-to-charge-state ratio of each atom are determined using spatially resolved time-of-flight analysis.

The development of sample preparation techniques using a focused ion beam (FIB) equipped with a high-resolution scanning electron microscope (SEM) has greatly improved sampling productivity for site-specific analysis. A combination of sophisticated FIB techniques and APT instruments has enabled us to obtain 3D dopant distribution in device structures (Figs. 1(a) and 1(b)) and contribute to broad areas of research in device physics [1-4].

The characteristic variability in MOSFETs has increased substantially owing to their continuously decreasing feature sizes. In particular, the variability in n-MOSFETs is larger than that in p-MOSFETs. Through statistical analysis using APT, we found that an anomalous redistribution of dopant (boron) occurs in n-MOSFETs owing to ion irradiation during source/drain extension (SDE) formation (Fig. 1(c)) [2]. To clarify the electrical variability, we directly obtained the channel dopant concentration of actual n-MOSFETs whose threshold voltage (Vt) widely ranging from ±4.0σ deviation from the median Vt in one million (1024 × 1024) transistors. We attempted to fabricate a needle-shaped specimen (Fig. 2(a)). Fig. 2(b) shows the elemental map of the main dopants (boron, phosphorus, and arsenic), nickel, and oxygen atoms. APT assessments revealed that Vt is positively correlated with the channel boron concentration (Fig. 2(c)) [3].

With respect to multi-gate (non-planar) device structures, dopant distribution analysis of FinFET, a potential future device structure, was carried out. Fig. 3(b) exhibits the elemental map of a prototype boron-doped fin array, tilted at ~45° [4]. The point is that near-surface dopant distribution in non-planar
devices can be obtained using APT after being filled with amorphous silicon by low-energy silicon beam deposition without a significant temperature rise. Oblique sample preparation is required for obtaining a uniform spatial resolution across the edge regions because the spatial resolution of APT in the lateral direction is lower than that in the depth direction [5]. We found that the boron concentrations in the top and bottom of the sample are higher than that in sidewall. Nevertheless, the amount of boron in the sidewall is higher than the amount of activated boron resulting from thermal annealing.

Thus, the combination of a sample preparation technique and APT enables us to characterize dopant distribution in devices having complicated structures.

Fig. 2 (a) Cross-sectional TEM image of 65-nm-node MOSFET. (b) Elemental map of n-MOSFET ($V_T = 0.421$ V). Nickel, phosphorus, arsenic, oxygen, and boron atoms are shown. Silicon atoms are not shown. (c) Correlation between $V_T$ and channel boron concentrations in $25 \times 25 \times 30$ nm$^3$ box just below gate oxide.

Fig. 3 (a) Cross-sectional scanning TEM image of silicon fin arrays. Observed region is indicated by broken curve. (b) Elemental map of specimen tilted at ~45°. (c) One-dimensional concentration profiles of oxygen and boron across (i) top, (ii) sidewall, and (iii) bottom interfaces.

References

Further progress in InGaN-based light-emitting devices is required for their widespread use. However, overcoming the decrease in the radiative recombination rate due to the quantum-confined Stark effect is a serious challenge in the longer wavelength region, where In concentration and misfit strain increase. To this end, non-polar and semi-polar InGaN growth is an attractive alternative. Furthermore, these surfaces have in-plane anisotropy in atomic structures depending on the direction of the c-axis. The efficiency of In incorporation into an InGaN film grown on a miscut [1010] m-GaN substrate depends on the sign of the off-angle toward the [0001] (Ga-polar) or [000 1] (N-polar), as shown in Figs. 1 (a) and (c) [1].

Fig. 1 2θ-ω scan spectra of (1010)-symmetric X-ray diffraction using Cu Ka line from InGaN films grown on m-GaN substrate. The numerical values in the figure indicate the miscut angle of the substrate in the +c direction. Thickness of the InGaN films is about 150 nm for (a), (b), and (c), and 300 nm for (d).

Three InGaN films, each approximately 150-nm thick, were grown at 750 °C by metalorganic vapor phase epitaxy on +5°, 0°, and -5° miscut m-GaN substrates. The conventional 2θ-ω X-ray-diffraction spectra of these films are shown in Figs. 1(a), (b), and (c). Anomalous-dispersion x-ray diffraction measurements were performed at beamline 13XU in SPring-8. The c-polarity of the samples was determined such that agreement between the calculated and measured values was obtained for intensity variation along the 202 2, 202 1, 2021, and 2022 series of reflections. As a result, it was confirmed that the negative off-angles, where +c [0001]-direction sticks out of the miscut m-plane (Fig. 2(a)), is higher than that at the negative off-angles (Fig. 2(b)). Additionally, the anisotropy of the m-plane induces the characteristic elongated-island morphology and phase separation into different In-content regions. Fig 3(a) shows a differential-interference-contrast microscopy image of the islands elongated about 10 μm along the a-axis, observed after the partial strain relaxation of the InGaN film grown on a 0°-off m-plane GaN substrate.
The $2\theta-\omega$ X-ray diffraction spectrum of this film is shown in Fig. 1(d). In this case, an approximately 300-nm-thick InGaN film was grown under a triethylgallium flow rate that was 3x higher than that for the other three films shown in Fig. 1 for inducing the desired island morphology. The phase separation of two different In concentrations can be inferred from the two InGaN peaks seen in Fig. 1(d).

To clarify the phase-separation mechanism, the microscopic two-dimensional distribution of In concentration in the InGaN film was observed with microbeam X-ray diffraction. The X-ray beam was focused using a zone plate and slits to be 0.2 μm and 0.5 μm in the vertical and horizontal full-width half-maximum, respectively [2]. The In mole fraction, $x$, was estimated from the peak position in the reciprocal-space map by considering strain relaxation due to misfit dislocations [1,3]. Fig 3(b) shows the real space mapping of $x$, where the incident position of the microbeam X-ray is scanned in 0.2-μm steps along the c-axis and in 1.0-μm steps along the a-axis by moving the sample. The size and shape of the high-$x$ region near the center of Fig. 3(b) is comparable to that of the [0001]-side slope (dark contrast area) of the elongated islands in Fig. 3(a). Therefore, it is considered that the In incorporation efficiency is high on the [0001] side of the island surface. Lymperakis et al. calculated the Ga adatom diffusion barrier of $m$-GaN as 0.93 eV in the c-direction and 0.21 eV in the a-direction [4]. These anisotropic diffusion barriers are consistent with the elongated-island morphology along the a-direction. Furthermore, the small diffusion length in the c-direction induces the nucleation of islands on the m-plane terraces, thus increasing the step density along the c-axis. The In incorporation efficiency increases on the resulting slope toward [0001] owing to the nitrogen-terminated step structure on this side (Fig. 2(a)).

In summary, the in-plane c-polarity of $m$-GaN was determined using ADXRD. The In incorporation efficiency increases when the +c-direction sticks out of the miscut m-surface. In addition, it was found that the In mole fraction is high on the slope toward [0001] of the islands extended along the a-axis. The formation of these islands is induced by the anisotropic features of m-plane growth and is expected to be applicable for fabricating micro-sized structures.

References

Keywords: nitride, vapor phase epitaxy (vpe), x-ray diffraction (xrd)
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Low Field Magnetization Switching of Hard Magnetic L1₀-FePt Triggered by Spin Wave Excitation

Recent rapid progress in spintronic and magnetic storage devices has required nanomagnets to balance competing goals for high coercive field and low switching field. In this study, we experimentally demonstrated extremely low field magnetization switching in a highly coercive L1₀-FePt using a spin wave excited in a soft magnetic Permalloy (Ni₈₁Fe₁₉; Py), where Py was exchange-coupled to L1₀-FePt through the interface. Because a significant decrease of one order of magnitude was achieved in the switching field when the spin wave was excited, this spin wave-assisted magnetization switching is a promising technique for manipulating the magnetization direction with ultralow energy.

Spintronic and magnetic storage devices store information using the magnetization directions of magnetic bits. For maintaining its magnetization along a certain direction, a nanometer-sized magnet should possess high magnetic anisotropy energy that can overcome thermal energy. However, high magnetic anisotropy leads to a large external energy for writing information onto a bit, i.e., for switching the magnetization direction. Thus, in a magnet, the high thermal stability of magnetization, namely, high coercive field ($H_c$), and the low switching field ($H_{sw}$) are competing properties, both of which are crucial for the advancement of spintronic and magnetic storage devices. Therefore, we need to find a solution for this dilemma.

An energy-assisted switching method using external microwave power, which is called microwave-assisted magnetization reversal (MAMR) [1], is considered as a promising method for reducing the switching field of a highly coercive magnet. It applies a radio-frequency magnetic field ($H_{rf}$) to a magnet for inducing uniform magnetization precession, thus resulting in decreased $H_{sw}$. However, MAMR utilizes the ferromagnetic resonance (FMR) mode, and its frequency ($f_{FMR}$) is of the order of 100 GHz for a highly coercive magnet. This high $f_{FMR}$ is a serious obstacle for practical applications. Thus, another method for reducing $H_{sw}$ while maintaining high $H_c$ is eagerly desired. The concept of magnetization switching we propose here is based on the use of spin wave modes in a soft magnet for switching the magnetization in a hard magnet [2].

We prepared exchange-coupled bilayer films consisting of a hard magnetic L1₀-FePt layer and a soft magnetic Permalloy (Fe₈₁Ni₁₉; Py) layer by employing sputtering systems. In this L1₀-FePt/Py bilayer, the L1₀-FePt (110) layer was epitaxially grown on a MgO (110) substrate, resulting in a uniaxial easy magnetization axis along the in-plane [001] direction. Py was exchange-coupled with L1₀-FePt through the interface. The magnetic moments in Py are spatially twisted when the magnetic field ($H$) is applied in the direction opposite to that of the magnetic moments in L1₀-FePt, which is schematically shown in Fig. 1a. [3] The Py layer thickness ($t_{Py}$) was varied from 40 nm to 120 nm, while the FePt layer thickness was fixed at 10 nm. Fig. 1b shows the FMR spectrum of L1₀-FePt/Py for $t_{Py} = 100$ nm. We observed three resonance peaks at the frequencies ($f$) of 8.0 GHz, 9.5 GHz, and 13.5 GHz, as indicated by the red, blue, and green triangles, respectively. This experimental FMR spectrum is well reproduced by numerical simulation. From the numerical simulation, we found that perpendicular standing spin wave (PSSW) modes with $n$ nodes were excited in the L1₀-FePt/Py bilayer.

![Fig. 1a](image1.png)  
**Fig. 1a** Magnetic structures in L1₀-FePt/Py bilayer. The left (right) panel depicts the direction of magnetic moments in the saturated (twisted) state. A magnetic field ($H$) was applied along the in-plane [001] direction of the MgO (110) substrate, which corresponds to the easy magnetization direction of FePt.  
![Fig. 1b](image2.png)  
**Fig. 1b** FMR spectra of L1₀-FePt/Py at $H = -700$ Oe. The triangles indicate the resonant frequencies of the PSSW modes with $n = 0$ (red), $n = 1$ (blue), and $n = 2$ (green).
bilateral.

We measured the anisotropic magnetoresistance (AMR) curves of the microfabricated L10-FePt/Py element to examine magnetization switching under PSSW-mode excitation. Fig. 2a shows the AMR curve for \( t_{Py} = 100 \text{ nm} \) without the application of \( H_rf \). When \( H \) was swept from positive to negative (denoted by red circles), the device resistance change (\( \Delta R \)) showed an abrupt decrease at \( H = -175 \text{ Oe} \), reflecting the formation of a twisted structure of magnetic moments in Py, as shown schematically. \( R \) returned to the baseline of \( \Delta R = 0 \text{ \Omega} \) at \( H = H_{sw} = -2050 \text{ Oe} \), where all magnetic moments of the bilayer were switched. Fig. 2b shows the AMR curve under the application of \( H_rf = 145 \text{ Oe} \) with \( f = 8.0 \text{ GHz} \). This \( f \) corresponds to the resonance frequency of the PSSW mode with \( n = 0 \). A decrease in \( H_{sw} \) down to \(-325 \text{ Oe} \) was obtained, indicating that magnetization switching was induced by the PSSW-mode excitation.

We achieved the desired large reduction in \( H_{sw} \) for \( t_{Py} = 120 \text{ nm} \). \( H_{sw} \) was reduced from 2000 Oe to 250 Oe at \( f = 7 \text{ GHz} \) and \( H_rf = 134 \text{ Oe} \). This \( H_{sw} \) reduction is significant compared to that achieved by conventional MAMR techniques, and the excitation frequency remained less than 10 GHz, even for switching in the highly coercive L10-FePt. Because we simultaneously achieved the competing goals of high \( H_c \) and low \( H_{sw} \), spin wave-assisted magnetization switching can be a new technology for information writing across a wide range of spintronic and magnetic storage applications.

References
Lithium-containing Oxide Film for All-solid-state Lithium-ion Battery by Chemical Vapor Deposition

For the development of all-solid-state thin-film lithium-ion battery, the oriented textures and chemical compositions of the electrolytes and active materials should be controlled precisely for fast transportation of lithium ions. Furthermore, the deposition rate is required to be high for practical processes. Our group has been developing a process for the chemical vapor deposition (CVD) of the oxide-based cathode and electrolyte film. LiCoO2 cathode films with off-c-axis orientation and garnet-type, cubic Li7La3Zr2O12 electrolyte films were successfully fabricated at high deposition rates by metalorganic and laser CVD.

The development of all-solid-state thin-film lithium-ion batteries is required for reducing battery size, mitigating safety issues associated with them, and fulfilling the power requirements of recent electronic devices such as cellphones, electric vehicles, and energy storage modules. Oxide-based electrolytes and active materials have great advantages because of their chemical stability in air, and the thin-film processing of these materials is necessary for assembling all-solid-state lithium-ion batteries.

Lithium cobaltate (LiCoO2) is widely used as a cathode material in commercially available lithium-ion secondary batteries. In all solid-state batteries, optimization of the solid/solid interface between an electrode and an electrolyte with high intercalation/deintercalation of lithium ions in the cell is an important issue. The lithium ion migrates in two dimensions along a layer of lithium atoms within the layered LiCoO2 structure (Fig. 1(a)). Therefore, the orientation and morphology of the LiCoO2 films should be controlled for ensuring good transportation of lithium ions at a cathode–electrolyte interface. The development of an electrolyte with high Li-ion conductivity is another important issue. Garnet-type cubic Li7La3Zr2O12 is a promising electrolyte material because of its high lithium conductivity, wide potential window, and chemical stability in air. Solid-state reaction mainly involved in the synthesis of Li7La3Zr2O12, in which precise control over chemical composition and temperatures above 1500 K are required. The film fabrication of these active and electrolyte materials has been studied by employing physical vapor deposition (PVD) techniques such as pulsed laser deposition (PLD) and sputtering. To date, only a few research groups have reported control over oriented texture under low deposition rates, and the fabrication of well-formed Li7La3Zr2O12 films with good crystallinity has not been reported.

Chemical vapor deposition (CVD) allows the preparation of films under high deposition rates, while affording control over their morphology and chemical composition.
We have developed a laser CVD process that could be an effective approach to preparing highly oriented LiCoO₂ cathode films and Li₇La₃Zr₂O₁₂ electrolyte films under high deposition rates.

**Preparation of LiCoO₂ and Li₇La₃Zr₂O₁₂ films**

A highly (003)-oriented LiCoO₂ film was grown on polycrystalline Al₂O₃ substrate at a deposition temperature of 923 K by CVD (Fig. 1(b)) [2]. Hexagonally faceted flat surface reflected c-planes in the rhombohedral LiCoO₂ lattice. Rounded platelet grains were grown in the (104)-oriented LiCoO₂ at 1123 K (Fig. 1(c)); the platelet facets in these were (003) LiCoO₂ planes tilted 55° relative to the (104) planes. Fig.1(c) depicts the LiCoO₂ films by laser CVD under laser power of 150 W. This film showed (101)-orientation, and the deposition rate was 30 μm h⁻¹, which is 100 times greater than that reported in the literature.

Fig 1(g) and (h) shows Li₇La₃Zr₂O₁₂ films prepared by CVD. A film comprising tetragonal Li₇La₃Zr₂O₁₂ having polygonal facets was deposited at 1073 K (Fig.1 (g)), while a cubic Li₇La₃Zr₂O₁₂ film with fine granular surface morphology was formed at a relatively high temperature of 1223 K. The deposition rates of the tetragonal and cubic Li₇La₃Zr₂O₁₂ films were higher than 20 μm h⁻¹. In addition to the Li₇La₃Zr₂O₁₂ crystalline film, amorphous Li-La-Zr-O films with smooth morphology were deposited using laser CVD. The deposition rates of these Li₇La₃Zr₂O₁₂ films were more than 100 μm h⁻¹.

**Oriented growth of LiCoO₂ films**

Hetero-epitaxial growth is a powerful method for fabricating films oriented along a specific plane and direction on single crystals. LiCoO₂ films oriented along (104) and (018) were hetero-epitaxially grown on (100) and (110) MgO substrates by CVD [3, 4]. Fig. 1 shows the surface and cross-sectional morphologies of the (104)- and (018)-LiCoO₂ epitaxial films. The surface morphology of the (104) LiCoO₂ film contained diagonally arrayed rectangular facets (Fig.1 (a)), whereas the (018) LiCoO₂ film exhibited a roof-like structure extended unidirectionally (Fig.1 (b)) toward [110] MgO. Twin structures were formed with in-plane relationships of [010] LiCoO₂//[010] LiCoO₂ and [421] LiCoO₂//[010] LiCoO₂ in the (104) LiCoO₂ film and with in-plane relationships of [100] LiCoO₂//[100] LiCoO₂ in the (018) LiCoO₂ film, thus reflecting the striations on cross-sectional textures. The deposition rates of the (104)- and (018)-oriented LiCoO₂ films were about 10 μm h⁻¹, almost 100 times greater than those reported for LiCoO₂ epitaxial films fabricated by pulsed laser deposition.

**References**


Keywords: chemical vapor deposition (cvd), microstructure, electronic material
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Unveiled Fermi surfaces in hidden order state of URu$_2$Si$_2$

Actinide compounds are attracting interest in condensed matter physics because of their unique properties. The 5f electrons are intermediate between itinerant and localized electrons, and show strong spin–orbit interaction. URu$_2$Si$_2$ is a well-known uranium-based heavy fermion compound with a “hidden-order” transition, the origin of which remains unknown. Herein, we present our recent results on quantum oscillation measurements under extreme conditions with ultra-clean single crystals of URu$_2$Si$_2$. The properties of Fermi surfaces and their instabilities under strong magnetic fields are clarified, thus providing a clue to the origin of the hidden order state.

URu$_2$Si$_2$ is one of the most attractive actinide compounds in the heavy fermion system. It shows a second-order transition at 17.5 K; this is accompanied by a large jump in specific heat. However, more than 25 years since the discovery of this transition, the order parameter is remains unknown. Thus, this ordered state is called the “hidden order.” Unconventional superconductivity appears at low temperatures (<1.5 K) as well, coexisting with the hidden-order state.

Recently, we clarified the Fermi surface properties of URu$_2$Si$_2$ in the hidden-order state through quantum oscillation measurements under extreme conditions such as at temperatures as low as 30 mK and under magnetic fields as high as 35 T [1].

The Fermi surface is one of the most fundamental physical quantities that characterize the metal. Thus, it is important task for researchers to elucidate Fermi surfaces experimentally. We have developed a high-sensitivity quantum oscillation technique for the de Haas-van Alphen (dHvA) and Shubnikov-de Haas (SdH) effect, according to which the magnetic susceptibility or resistivity oscillates periodically as a function of the inverse of magnetic field.

A high-quality single crystal is essential for these measurements. Using the Czochralski method in a tetra-arc furnace, as shown in Fig.1, we grew ultra-pure single crystals of URu$_2$Si$_2$ with a residual resistivity ratio (RRR) > 500, which is the best possible quality of URu$_2$Si$_2$.

Fig 2 shows the angular dependence of the dHvA/SdH frequencies in the hidden order state of URu$_2$Si$_2$.

With regards to the low carrier numbers of URu$_2$Si$_2$, all detected Fermi surfaces have low volume, and the topology of the main Fermi surfaces is of the closed-type with a nearly spherical shape. However, the cyclotron effective masses are extremely large, indicating a heavy fermion system. An anomalous split of the main branch, $\alpha$, is observed in the basal plane in the tetragonal structure, and the split immediately disappears when the field is tilted to the c-axis, implying a fingerprint of the hidden-order state. High-magnetic-field experiments reveal the Fermi surface instabilities with the field-dependent effective mass. Near 30 T, just below the critical field of the hidden-order state, a new Fermi surface with heavy quasi-particles was found. The interplay between the Fermi surface instabilities due to the Zeeman spin-split leading to the so-called Lifshitz transition and the field-dependent characteristic gap energy plays an important role in the collapse of the hidden-order state. Similar Fermi surface reconstructions under high fields have been detected in our thermopower measurements as well [2]. The polarized neutron experiments reveal the redistribution of magnetization below and above the
hidden-order transition, implying a fingerprint of rank 5 multipoles [3]. In addition, a key experiment on thermal expansion under uniaxial stress was performed [4].

This work was done in collaboration with members of CEA-Grenoble (Commissariat à l’énergie atomique et aux énergies alternatives), LNCMI (Laboratoire National des Champs Magnétiques Intenses), ILL (Institut Laue-Langevin), and JAEA (Japan Atomic Energy Agency).

References

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High-energy Neutron Scattering Study of Spin Excitations in New Frustrated Spin Ladder System

Quantum spin systems have been studied extensively owing to their exotic ground states and non-trivial phenomena. A spin-ladder system is one of ideal systems for testing a theory that bridges a one-dimensional spin chain and a two-dimensional square lattice. To characterize the ground state and magnetic excitations of the newly found two-leg spin ladder BiCu$_2$PO$_6$, we performed a time-of-flight inelastic neutron scattering measurement on its single crystal. Our result indicates triplon excitation with the minimum energy of 2 meV at the incommensurate momentum position. This indicates the formation of a rang-singlet at the ground state and the existence of strong competing interactions along the ladder.

The physics of low-dimension quantum antiferromagnets (AF) is fascinating because non-trivial behaviors emerge at low temperatures. The spin-ladder system is a characteristic system that bridges a one-dimensional (1D) spin chain and a two-dimensional (2D) CuO$_2$ layer. A two-leg spin-ladder system is indeed realized with the copper oxide families SrCuO$_3$ [1] and Sr$_{14−x}$(La,Ca)$_x$Cu$_{24}$O$_{41}$ [2]. Because superconductivity emerges in the latter system [3], the nature of antiferromagnetic (AF) spin correlation in a spin-ladder system has been investigated in connection with the mechanism of high-\(T_c\) superconductivity [4]. However, the quite large nearest-neighbor AF exchange interaction (\(J \approx 2000\) K) of these compounds prevents observation of the entire spin excitation spectrum [5]. No experimental evidence of two-triplon (coupled triplets on the lungs of ladder) continuum excitation, which is similar to two-spinon continuum excitation in one-dimensional quantum magnets [6], has been detected thus far. To make progress on this issue, we have started an experimental as well as a theoretical study on BiCu$_2$PO$_6$, a new model system, in which the \(S = 1/2\) quantum spins of Cu$^{2+}$ ions constitute two-leg spin ladders with relatively smaller \(J\) (\(<100\) K) [7]. Recently, we grew a high-quality large single BiCu$_2$PO$_6$ crystal (Fig. 1). This progress has enabled us to elucidate the full excitation spectrum of the spin-ladder system through neutron scattering measurements.

Sample preparation and characterization
A single crystal of BiCu$_2$PO$_6$ with a diameter of 8 mm and length of 100 mm was grown using the floating-zone method. The phase purity and sample mosaic of the grown crystal were confirmed through powder X-ray measurements and the X-ray back Laue method (Fig. 1), respectively. Our sample shows a spin-gap behavior in magnetic susceptibility. Two 35-mm-long samples were co-aligned for the inelastic neutron scattering measurement. To study the overall spin excitation spectrum of BiCu$_2$PO$_6$, in which \(S = 1/2\) quantum spins from Cu$^{2+}$ ions form a two-leg spin-ladder, we performed the first high-energy neutron scattering measurement at the chopper spectrometer 4SEASONS [7] installed at J-PARC.

Magnetic excitation spectrum in BiCu$_2$PO$_6$
As shown in Fig. 2, the magnetic excitation of BiCu$_2$PO$_6$ was successfully observed in wide momentum and energy spaces. The excitation along the crystallographic b-axis shows clear dispersion with the energy band between 2 meV and 28 meV, while that along c-axis and a-axis (not shown) is non-dispersive. Therefore, the spin correlation is one-dimensional, which is consistent with the result of the antiferromagnetic two-leg spin-ladder model, and a rung singlet is formed at the ground state. Importantly, the spin gap opens at the incommensurate (0, 1 ± 0.45, 0.75) momentum position along the leg direction. This result suggests the existence of a large next-nearest-neighbor interaction, namely, spin frustration along the leg. Thus, the BiCu$_2$PO$_6$ [8] system was confirmed to be...
a frustrated spin-ladder system, which affords a unique opportunity to study the novel nature of quantum spin systems. Furthermore, we investigated the temperature dependence of the entire spin excitation for characterizing the thermal evolution of spin correlation in this frustrated spin-ladder system. It was found that the intensity at 28 meV decreases with increasing temperature, and the peak disappears around 70 K. This temperature is consistent with the temperature at which the magnetic susceptibility shows a broad maximum. Therefore, the thermal evolution of the magnetic branch extending at 28 meV closely correlates with the change in magnetic ground state and the degradation of spin-singlet formation at high temperatures.

References

Fig. 2 Excitation spectrum of BiCu2PO6 along leg direction at \( l = 0 \) (upper left figure), \( l = 0.75 \) (upper right figure), and along rung direction at \( k = 0 \) (lower left figure) and \( k = 1 \) (lower right figure). Clear dispersion was observed along the b-direction with the maximum energy of \(~28\) meV. The minimum energy of \(~1\) meV was observed at the \((0, 1 \pm 0.45, 0.75)\) incommensurate position, suggesting the existence of frustration between the antiferromagnetic nearest and next-nearest neighbor interactions.

Fig. 3 Excitation spectrum of BiCu2PO6 along leg-direction measured at 45 K (upper figure) and at 125 K (lower figure). The intensity of excitation at \(~28\) meV decreases at high temperatures, suggesting rung-singlet formation degradation.

Keywords: neutron scattering, spin dynamics, quantum spin system
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Electrical Transport Properties of Ni-Nb-Zr-H Amorphous Alloy Ribbons

Ni-Nb-Zr ternary alloys have been known to form an amorphous phase in wide concentration regions [1]. The hydrogen permeability of Ni-Nb-Zr amorphous alloy ribbons was investigated by Yamaura et al., and an excellent permeability value of about $1.59 \times 10^{-8} \text{ mol/m-s-(Pa)}^{1/2}$ was reported for melt-spun amorphous (Ni$_{0.6}$Nb$_{0.4}$)$_{50}$Zr$_{50}$ alloy [2,3]. In addition, the mechanical properties of hydrogen-absorbed amorphous alloy ribbons were investigated by Kawashima et al. [4]. Recently, peculiar behaviors of the electrical transport properties such as superconductivity, electron avalanche behaviors, and Coulomb-blockade oscillations of hydrogen-absorbed [(Ni$_{0.6}$Nb$_{0.4}$)$_{1-x}$Zr$_x$]$_{100}$ amorphous alloy ribbons were elucidated by Fukuhara et al. [5,6]. They pointed out that the localization effect of hydrogen in outside and inside spaces of the distorted icosahedral Zr$_{5}$Ni$_{5}$Nb$_3$ clusters plays important roles in their various electrical transport properties. In other words, the state of hydrogen absorption is thought to be sensitive to the difference in the local structure of the glassy state [3]. Therefore, a systematic study of the effects of hydrogen absorption on the electrical transport properties of the Ni-Nb-Zr amorphous alloy is important for clarifying the mechanisms underlying such peculiar behaviors.

We made amorphous alloy ribbons of Ni$_{36}$Nb$_{24}$Zr$_{40}$, and controlled the amount of the absorbed hydrogen by changing the current density of electrochemical charging. The amorphous alloy ribbons were fabricated by the single roller melt-spinning technique, where the surface velocity of the copper wheel was about 50 m/s. The thickness and width of the fabricated ribbon were about 25 μm and 1 mm, respectively. Hydrogen-absorbed specimens were prepared by electrochemical charging in 0.5 M H$_2$SO$_4$ + 1.4 g/L thiourea (H$_2$NCSNH$_2$) at room temperature with a current density of about 25 A/m$^2$ for 2 h. The amount of absorbed hydrogen was measured using the inert gas carrier melting-thermal conductivity method several times under each condition. Thermal analyses were performed with a differential scanning calorimetry under a heating rate of 0.33 K/s. Phase state was identified using x-ray diffraction with Cu-K$_\alpha$ radiation. The electrical resistivity was measured using a conventional four-probe method in the 6–300 K temperature range with cooling and heating rates of about 0.017 K/s.

**Hydrogen absorption effects on electrical resistivity**

Fig. 1 shows mass concentration of the hydrogen absorbed by the electrochemical method as a function of current density. Here, the charging time was fixed to 2 h. The amount of absorbed hydrogen in the ribbon specimens was found to increase with increasing current density and to have a tendency to saturate. The maximum value of hydrogen absorption was thought to be limited to a maximum of 0.25 mass% (15 at.%), because the specimens turn very brittle if they are charged with the higher current density of 120 A/m$^2$.

![Fig. 1 Mass concentration of absorbed hydrogen as a function of the current density in the electrochemical charging of Ni$_{36}$Nb$_{24}$Zr$_{40}$ amorphous alloy ribbons. The dashed curve is a visual guide.](image)
to be about 9.2 and 14.7 at.%, respectively. The x-ray diffraction patterns show typical halo-type patterns, indicating an amorphous structure. In Fig. 2, it can be seen that the main peak around 40° shifts to a slightly smaller angle with increasing hydrogen absorption, thus indicating volume expansion.

Fig. 3 shows the temperature dependence of normalized electrical resistivity, $\rho/\rho_{300K}$, for $y = 0.0, 2.0, 3.3, 9.2$ and $14.7$ in $(\text{Ni}_{0.36}\text{Nb}_{0.24}\text{Zr}_{0.40})_{100-y}\text{H}_y$. All resistivity exhibits negative temperature dependence, according to the Baym-Meisel-Cote theory based on the Boltzmann transport equation for amorphous alloys with non-periodic crystal structure, as follows [7]:

$$\rho = \rho_0\exp[-2W(T)] + \rho_{ph}(1 - \frac{2\pi}{\Lambda q})$$

where $\rho_0$ is the residual resistivity, $\exp[-2W(T)]$ is the Debye-Waller factor, $\rho_{ph}$ is the phonon term, $\Lambda$ is the mean free path, and $q$ is the wave vector. For the amorphous and quasi-crystals with non-periodic structures, $\Lambda$ is small, and, consequently, the second term in Eq. (1) becomes negligible. Therefore, the electrical resistivity is governed by the temperature dependence of the Debye-Waller factor and not by the electron-phonon scattering. In such a case, the electrical resistivity shows $T^2$-dependence in the low-temperature range and $T$-linear dependence close to room temperature [8,9]. As shown in Fig. 3, the absolute value of temperature coefficient of resistivity, TCR, increases with increasing absorbed hydrogen, $y$, clearly indicating the effect of hydrogen absorption on electrical resistivity. With regards the origins of this effect, there are many possibilities, e.g., the change in the mean free path associated to volume expansion, change in the Debye temperature and electronic state, and the existence of scattering related to absorbed hydrogen. Clarifying this mechanism is the next objective of our study.

References

Fig. 2. X-ray diffraction patterns of Ni36Nb24Zr40 melt-spun amorphous alloy ribbon and hydrogen-absorbed specimens.

Fig. 3. Temperature dependence of normalized electrical resistivity, $\rho/\rho_{300K}$, for $(\text{Ni}_{0.36}\text{Nb}_{0.24}\text{Zr}_{0.40})_{100-y}\text{H}_y$ with $y = 0.0, 2.0, 3.3, 9.2$ and $14.7$.  

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