Research Highlights

Horizontal Lines of Nodes in the Superconducting Gap of Sr₂RuO₄: Evidence against the Anticipated Chiral $p$-wave Scenario

Sakakibara Group

The layered-perovskite superconductor Sr₂RuO₄ has been a leading candidate of a spin-triplet chiral $p$-wave superconductor; the spin-triplet pairing (chiral state) was suggested by the invariant spin susceptibility across $T_c$ (time-reversal symmetry breaking in the superconducting state) [1]. However, the recently-discovered first-order superconducting transition, reminiscent of the Pauli-paramagnetic effect, under an in-plane magnetic field is likely to favor the spin-singlet scenario [2, 3]. Moreover, whereas symmetry-protected nodes are forbidden in the spin-triplet scenario, the presence of nodes has been suggested from various thermodynamic experiments. Thus, the order parameter of Sr₂RuO₄ has remained controversial.

Recently, we have developed field-angle-resolved measurements of the specific heat as a powerful technique to identify the superconducting gap structure [4]. Here, in order to provide hints for resolving the puzzling issues on Sr₂RuO₄, we have performed the field-angle-resolved measurements at low temperatures down to 0.06 K by using a high-quality single crystal ($T_c = 1.505$ K) [5]. By subtracting the Schottky-type anomaly originating from the addenda heat capacity very precisely, we have revealed that the low-field specific heat of our sample increases in proportion to $H^{1/2}$ with no multigap structure at 0.06 K. This behavior is in sharp contrast to the previous reports [6], and suggests that multiple gaps on the three bands ($\alpha$, $\beta$, and $\gamma$) equivalently survive up to high fields and possess nodes somewhere. In addition, the fourfold oscillation in the specific heat observed under an in-plane rotating field [6] does not change its sign even at a low temperature of 0.04$T_c$ in the low-field region (Figs. 1(a) and 1(b)).

The absence of a sign change in the fourfold specific-heat oscillation is incompatible with vertical line node scenario, such as the $d_{x^2-y^2}$- and $d_{xy}$-wave type; the present results are clearly different from the cases of vertical line node superconductors such as CeCoIn₅ [4]. Also, it is obvious that the present observations cannot be explained within the anticipated chiral-$p$-wave scenario. By contrast, the results favorably support the presence of horizontal line nodes; the specific-heat oscillation arises due to nodal quasiparticles that have anisotropic in-plane Fermi velocity of the cylindrical $\gamma$ band. On the basis of microscopic theoretical calculations, the observed field and temperature variations of the specific-heat oscillation can be reproduced by assuming the presence of horizontal line nodes on cylindrical bands whose Fermi velocity is highly anisotropic within the plane (Fig. 1(c)). The agreement between the experimental and the calculated results becomes even better by taking into account the Pauli-paramagnetic effect. Our findings, in particular the presence of horizontal line nodes in the gap, challenge the historical view of Sr₂RuO₄ and call for reconsideration of its order parameter.

References


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Fig. 1. (a) Field-angle dependence of the specific heat under a rotating magnetic field within the $ab$ plane of Sr₂RuO₄. (b) The $H$-$T$ phase diagram of the normalized amplitude $A_4$ of the fourfold specific-heat oscillation. (c) The calculated results of $A_4(T, H)$ obtained by assuming a horizontal line node gap (inset), anisotropic in-plane Fermi velocity, and the Pauli-paramagnetic effect.
Construction of Three-Dimensional Anionic Molecular Frameworks Based on Hydrogen-Bonded Metal Dithiolene Complexes and the Crystal Solvent Effect

Mori Group

Metal organic frameworks (MOFs) and covalent organic frameworks (COFs) are a class of crystalline materials with highly periodic structures formed through coordination or covalent bonds. Extensive synthetic studies of these materials have been carried out, because of the uniqueness of their structures and the resulting functionalities, such as gas adsorption/separation, catalytic, and sensing abilities and fuel cell properties. In addition, hydrogen-bonded (H-bonded) organic frameworks (HOFs) have recently emerged as a new class of such crystalline materials. By utilizing H-bonds instead of coordination or covalent bonds, HOFs have generally better crystallinity, solution processability, and flexibility than MOFs and COFs. Such ionic frameworks are expected to show unique features different from conventional neutral ones, due to their intrinsic ionic nature and the accompanying cation–anion interactions. However, the number of ionic frameworks reported so far is limited.

Recently, we have designed and synthesized a novel metal dithiolene complex with hydrogen-bonding (H-bonding) ability, [Au(catdt)₂]⁻ (catdt: catechol-4,5-dithiolate) and successfully constructed [Au(catdt)₂]⁻-based three dimensional (3D) anionic molecular frameworks in two kinds of salts, (Ph₄P)[Au(catdt)₂]·0.5H₂O (1a) and (Ph₄P)[Au(catdt)₂]Et₂O·n(solv) (1b; solv = Et₂O and/or acetone). To our knowledge, these are the first examples of the 3D molecular frameworks based on H-bonded metal dithiolene complexes. Importantly, these frameworks are constructed through 3D intermolecular H-bonds between [Au(catdt)₂]⁻ molecules, and have tubular channels occupied by large Ph₄P⁺ cations, where multiple cation–anion short contacts are formed to stabilize the 3D framework structures. Furthermore, in addition to 1a and 1b with 3D frameworks, we have obtained (Ph₄P)[Au(catdt)₂]·2THF (1c) having a 2D layered structure. A detailed comparison of the structures of these compounds reveals that the included solvent molecules play an important role in regulating the intermolecular interactions and assembled structures. Interestingly, we have found that, due to the differences in the H-bonding ability and molecular size of H₂O and Et₂O, the wall structures of the 3D framework in 1a without voids and 1b with voids are qualitatively different.[1]

Three kinds of 1:1 salts of Ph₄P⁺ and [Au(catdt)₂]⁻, that is, (Ph₄P)[Au(catdt)₂]·0.5H₂O (1a), (Ph₄P)[Au(catdt)₂]Et₂O·n(solv) (1b; solv = Et₂O and/or acetone), and (Ph₄P)[Au(catdt)₂]·2THF (1c), were synthesized, and their structures and chemical compositions were determined by single crystal X-ray analysis. Recrystallization of the obtained powder from acetone/hexane, acetone/Et₂O or THF/hexane provided the salt 1a (containing H₂O) as yellowish brown needle-like crystals, 1b (containing Et₂O and/or acetone) as yellow plate-like crystals or 1c (containing THF) as green plate-like crystals, respectively.

We first compare the structures of the three kinds of novel [Au(catdt)₂]⁻-based salts, (Ph₄P)[Au(catdt)₂]·0.5H₂O 1a, (Ph₄P)[Au(catdt)₂]Et₂O·n(solv) (1b; solv = Et₂O and/or acetone), and (Ph₄P)[Au(catdt)₂]·2THF (1c). All of them are 1:1 salts of Ph₄P⁺ and [Au(catdt)₂]⁻; however, their crystal structures are qualitatively different from each other, depending on the solvent molecules included in the crystal. The most prominent difference is the dimensionality of the assembled structures of [Au(catdt)₂]⁻; namely, in the water and ether-containing salts 1a and 1b, this planar anionic molecule forms a 3D assembled structure (i.e., 3D framework, Fig. 1), whereas in the THF-containing salt 1c, it forms not a 3D but a 2D structure (i.e., 2D layers). Furthermore, although both the 3D framework structures in 1a and 1b have tubular channels with a similar size, the structures of their walls are significantly different from each other; namely, the walls in 1a are densely packed with [Au(catdt)₂]⁻ whereas those in 1b are loosely packed to form voids, into which the cation and Et₂O molecules partially penetrate (Fig. 1). These differences should be caused by changing the intermolecular interactions between the component molecules upon the change of the crystal solvent.

We finally discuss how the crystal solvent makes differences in the intermolecular interactions and assembled structures. Here, we focus on the H-bonding ability, size, and shape of the crystal solvents. Et₂O, included in the 3D system 1b, and THF, included in the 2D system 1c, have proton-accepting ability due to the ether oxygen atom, which actually allows them to form the H-bonds with the catechol O–H protons of [Au(catdt)₂]⁻ molecules. On the other hand, the overall shapes of these solvent molecules are greatly different from each other [rod-shaped (Et₂O) vs. disk-shaped (THF)], which should contribute to the great structural difference in 1b and 1c (i.e., 3D vs. 2D). Namely, due to the disk shape, the THF molecules are positioned (orientationally) disordered, which leads to the formation of the THF–THF H-bonds and consequently the 2D layered structure. In contrast, the rod-shaped Et₂O molecules have no such structural disorder and additional intermolecular interactions; thus they seem to simply occupy the space.
between the large PhP\textsuperscript{+} and [Au(catdt)\textsubscript{2}]\textsuperscript{−} molecules without interrupting the intermolecular interactions between the PhP\textsuperscript{+} and [Au(catdt)\textsubscript{2}]\textsuperscript{−} molecules for constructing the 3D framework. Meanwhile, due to the steric bulkiness of the ethyl groups in Et\textsubscript{2}O, the walls of the 3D framework have the voids. In contrast, the water containing 3D system 1a has no such voids and thus the wall is densely packed with the lateral S⋯S interactions between [Au(catdt)\textsubscript{2}]\textsuperscript{−} molecules. This is probably because the solvent water molecules are involved in the wall structure, which should eliminate the above mentioned steric hindrance effect from the solvent molecules. Here, the water molecule has both proton-donating and -accepting abilities, in contrast to Et\textsubscript{2}O and THF having only proton-accepting ability. In addition, the size of water molecule is much smaller than that of the others. These features should allow the water molecules to exist between the catechol moieties of [Au(catdt)\textsubscript{2}]\textsuperscript{−} molecules and participate in the densely packed wall structure of the 3D framework. Therefore, we have successfully illustrated the role and effect of the crystal solvent molecules on the construction of these new 3D anionic molecular frameworks based on [Au(catdt)\textsubscript{2}]\textsuperscript{−} in terms of the molecular size and shape and H-bonding abilities. As for the next step, by taking advantage of this new type of metal dithiolene complex with H-bonding abilities, we are currently investigating cooperative properties and functionalities of H-bond dynamics (e.g., dielectric properties and proton conductivity) and π−/d-electrons (e.g., electronic conductivity and magnetic properties).

Reference

Authors
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Quantum Size Effects Associated with Ultra-Thinning of Layered Semimetals

Osada Group

We have investigated thickness dependence of the electronic properties of two layered semimetals, graphite and WTe\textsubscript{2}, under magnetic fields. Their monolayer limits are known as a 2D Dirac fermion system (graphene) and a 2D quantum spin Hall insulator, respectively. Therefore, it is significant to see how their electronic properties changes associated with thinning them.

Generally, under the normal magnetic field, the band structure of the layered conductor is quantized to a set of Landau subbands with interlayer dispersion. Here, as the sample thickness approaches the de Broglie wavelength, the interlayer electron wave number is quantized, so that the bulk Landau subbands separates to discrete levels as shown in Fig. 1. This causes various size effects on electronic properties.

Bulk graphite shows a unique field-induced electronic phase transition above 30 T. Although the density wave formation due to the \(2k_F\) instability of the Landau subband was proposed as a possible mechanism of the transition, it has never been confirmed yet. In order to identify the high field phase, we performed transport measurements of thin-film graphite samples under the magnetic field up to 40 T, which was generated by a home-made miniature pulse magnet system. The thin-film flake was prepared on a silicon substrate by the mechanical exfoliation technique, and the device structure was fabricated using the electron beam lithography (Fig. 2(b)). As seen in Fig. 2(a), the magnetoresistance shows a saturation around 10 T, above which there exist only a few occupied Landau subbands (quasi-quantum limit). The field-induced phase transition appears above 30 T as indicated by an arrow. On the phase diagram, the phase boundaries in thin films shift to higher fields, accompanied by a reduction in temperature dependence. These results are consistently explained by the density wave model with the quantum size effect, because the \(2k_F\) instability of the Landau subband is weakened by the discretization of the subband in thin films (Fig. 1(b)). The present finding strongly suggests the density wave state standing along the interlayer direction [1].

Fig. 1. Concept of the quantum size effect under magnetic fields. The Landau subbands in the bulk (red curves) are quantized into discrete levels (blue circles) due to the size effect in thin films. (a) In the low field region, several SdH oscillations with different frequencies appear in thin films, instead of the oscillation of the extremal orbit in the bulk. (b) At the high-field quantum limit, the field-induced density wave transition due to the \(2k_F\) instability of the lowest subband is suppressed by the discretization of the subband.

Fig. 2. Quantum size effect on the field-induced electronic phase transition in graphite. (a) Transverse magnetoresistance of a graphite thin film with the thickness of 80 nm. The arrow indicates the field-induced transition. (b) Microscope image of a Kish graphite thin film device. (c) Phase diagram of the field-induced transition in graphite thin films.
Spin Thermal Hall Conductivity in a Kagomé Antiferromagnet

Yamashita and Kawashima Groups

Searching for the ground state of a Kagomé Heisenberg antiferromagnet (KHA) has been one of the central issues of condensed-matter physics, because the KHA is expected to host spin-liquid phases with exotic elementary excitations.

To study the elementary excitations, we investigate the longitudinal (\(κ_{xx}\)) and transverse (\(κ_{xy}\)) thermal conductivities of a new candidate of \(S = 1/2\) KHA Ca kapellasite (CaCu₃(OH)₆Cl₂∙0.6H₂O) [1]. The magnetic Cu²⁺ ions in Ca kapellasite form an ideal Kagomé structure (Fig. 1 (a) and (b)). The fitting of the temperature dependence of the magnetic susceptibility shows that the spin Hamiltonian in Ca kapellasite is well approximated as an ideal KHA with the effective spin interaction energy \(JHKB ≈ 66\ K\) [1, 2]. Although the ground state is not a quantum spin liquid, the magnetic transition temperature \(T \sim 7\ K\) is much lower than \(JHKB\), providing a wide temperature range of the spin liquid phase \(T' < T < JHKB\) to study the elementary excitations.

Figure 1 (d) shows the field dependence of the transverse temperature difference \(ΔT_x = T_{L1} - T_{L2}\) (see Fig. 1 (c) for the experimental configuration). Remarkably, asymmetric field dependence is clearly observed, demonstrating a thermal Hall signal in this transparent insulator. By asymmetrizing \(ΔT_x\) with respect to the field direction, we obtain the field dependence of \(κ_{xy}\) (Fig. 1 (c)) which is found to be linear to the field in the spin liquid phase.

The temperature dependence of \(κ_{xy}/T\) shows an increase as lowering temperature below \(JHKB\), which is followed by a peak at \(T \sim J/3K_B\) (Fig. 2 (a)). Quite unexpectedly, the temperature dependence and the magnitude of \(κ_{xy}\) in Ca kapellasite is similar to that of another Kagomé antiferromagnet volborthite [4], whereas the \(κ_{xy}\) in Ca kapellasite is about one order of magnitude smaller than that of volborthite. Given that \(κ_{xy}\) is dominated by phonons in this temperature range, similar \(κ_{xy}\) in these Kagomé compounds rules out phonons as the origin of \(κ_{xy}\).

We find that \(κ_{xy}\) is well reproduced, both qualitatively and quantitatively, by spin excitations described by the Schwinger-boson mean-field theory [3] with the Dzyaloshinskii-Moriya interaction (D) shown by the symbols. \(J_1, J_2,\) and \(J_3\) (solid red lines) represent the nearest-neighbor, next nearest-neighbor, and diagonal magnetic interactions, respectively [2]. (c) An illustration of our experimental setup. Three thermometers \((T_{L1}, T_{L2}, T_{L3})\) and a heater were attached to the sample. A heat current \(Q\) was applied within the ab plane and a magnetic field was applied within the c || z axis. (d, e) The field dependence of the transverse temperature difference \(ΔT_x = T_{L1} - T_{L2}\) (d) and \(κ_{xy}\) (e). Solid lines in (e) represent linear fits.
ski-Moriya interaction of $D$. Most remarkably, both $\kappa_{xy}$ of Ca kapellasite and that of volborthite are found to converge to one single curve of our Schwinger-boson calculation only by choosing $J$ and $D$ as fitting parameters (Fig. 2 (b)). This excellent agreement demonstrates not only that the thermal Hall effect in these kagomé antiferromagnets is caused by spins in the spin liquid phase, but also that the elementary excitations of this spin liquid phase are well described by the bosonic spinons. Although whether our ansatz is the only successful state for describing $\kappa_{xy}$ or other spin liquid states – in particular spin liquids with fermionic spinons having a different $\kappa_{xy}$ – remains an open question, our results suggest that thermal Hall conductivity of a kagomé antiferromagnet has a common temperature dependence described by Schwinger bosons.

References

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Floquet-Theoretical Formulation and Analysis of High-Harmonic Generation in Solids

Tsunetsugu Group

High-harmonic generation (HHG) is a nonlinear optical phenomenon, and monochromatic input light irradiates a target medium to be converted to output with multiple high harmonics, which is an indispensable technology for the state-of-the-art ultrafast physical measurements. While atomic gases were traditionally used target media, recent experiments have achieved the high-harmonic generation in bulk solids [1]. However, it remains an open problem how the interaction of light with electrons in solids results in the conversion to higher frequencies.

In this study [2], we invoke the mathematical tool known as Floquet’s theorem to analyze the electron dynamics driven by light with single frequency $\Omega$, which induces HHG in output light. We have tailored this theoretical framework for a simple lattice electron model in one dimension. This model is a tight-binding Hamiltonian with two bands which are controlled by site-alternating potentials, and electrons acquire a time-oscillating phase in their hopping amplitude due to their coupling to input light. We have obtained an analytical solution for the time evolution of electron wave function in the limit of no potential scattering, and proceed to analyze the effects of the potential scattering by a perturbation approach. While the highest frequency of HHG in the no-scattering limit is too low to explain the related experimental data, we have found that it becomes large enough as the scattering amplitude increases.

Our result [2] also predicts that the highest order in HHG is inversely proportional to the square of the input frequency, $N_{\text{max}} \propto \Omega^{-2}$, in contrast to the conventional scaling $\propto \Omega^{-1}$ in atomic gases. This anomalous behavior deserves experimental confirmation. Besides, our Floquet-theoretical approach is general and thus applicable to various lattice systems. Therefore, for realizing effective HHG, it is useful to employ this approach and examine the effects of important characteristics of the model, such as dimensionality and symmetry of solids.

References

Authors
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Heat Transport via a Two-State System

Kato Group

Heat transport in macroscopic systems has been studied for long time. Recent technological progress has enabled us to measure heat transport carried by photons or phonons via a nanoscale object, for which quantum properties of the system are revealed [1]. Based on this development, we studied heat transport in the spin-boson model, in which a two-state system is coupled to two thermal reservoirs (see Fig. 1 (a)) [2]. Even though this spin-boson model is simple, it is known that there appear various physical phenomena such as the Kondo effect [3,4].

The properties of the thermal reservoirs are characterized by a spectral density function, \( I(\omega) \propto \omega^s \). In Ref. [2], we studied thermal conductance for heat transport via a two-state system for arbitrary exponent \( s \), comparing analytic approximations with numerical results based on the continuous-time quantum Monte Carlo method. By systematic comparison, we revealed that heat transport via a two-state system is described by one of three processes, i.e., (i) sequential tunneling, (ii) co-tunneling, and (iii) incoherent tunneling (see Fig. 1 (b)-(d)). We derived an asymptotically exact expression for the sufficiently low-temperature region (the co-tunneling regime). This formula predicts power-law temperature dependence at low temperatures. We also found that for the high-temperature or strong-coupling regions (the incoherent tunneling regime), the thermal conductance is well explained by the noninteracting-blip approximation (NIBA).

As an example, we show the temperature dependence of the thermal conductance for the ohmic reservoir (\( s = 1 \)) and \( \alpha = 0.1 \) (\( \alpha \) is a dimensionless system-reservoir coupling constant) in Fig. 2. At low temperatures, the numerical result (the legends) agrees well with the asymptotically exact formula for the cotunneling process (the blue dashed line). This regime, the thermal conductance is always proportional to \( T^3(= T^{2s+1}) \), which is consistent with the result of Ref. [4]. At moderate temperatures and high temperatures, the numerical result deviates from the cotunneling formula, and instead agrees well with the NIBA (the black solid line). We note that the thermal conductance obtained by the NIBA is proportional to \( T^{3-\alpha} \) at low temperatures as indicated in the figure, and deviates from the low-temperature numerical results. We also show the approximate formula for the sequential tunneling (the green dot-dashed line), and the

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References


Authors

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Realization of a Current-Controlled Superconducting Device

Katsumoto Group

Ultra-high speed, low-power consumption logic device action has been predicted for Josephson superconducting junctions, which dream, however, has not come true yet for more than three decades. The device action itself had been confirmed at the beginning of the 1980s [1]. Nevertheless,
the two-terminal nature of the junction has blocked the application to the real world of logic devices. The obstacle is explained as follows. The switching to normal state occurs when the junction is “fired” by applying a bias current larger than the critical current $J_c (J_{c1})$. Then to switch the next junction a current larger than its $J_c (J_{c2})$ is required while the current swing of the first junction is $J_{d1}$. Hence for the circuit action, condition $J_{d1} > J_{c2}$ should be fulfilled. The condition means that $J_c$ decreases monotonically over the chain of logic gates, thus sharply limits the scalability of the circuit. The finding of a gate-controllable supercurrent through the two-dimensional electrons (2DE) on the surfaces of InAs [2], this was thought to solve the problem. However, as a voltage-driven device, the Josephson junctions have too high off-conductance, and the obstacle was realized to exist stubbornly. Therefore a current-current three(or four)-terminal device is required for the practical use.

We here report pure current-control of supercurrent, which would solve the long-standing technical problem. We prepared a 2DE in an InAs quantum well grown on an InP substrate. Figure 1 shows the sample structure, in the center of which a Nb-InAs 2DE-Nb superconducting junction is formed. Besides, the sample has six normal terminals, through which local or non-local electric currents can flow. InAs 2DE is known to have a strong Rashba-type spin-orbit interaction (RSOI), and the layered structure is design to maximize the RSOI.

One of the expected device actions is described as follows. When a supercurrent is flowing between the two Nb electrodes, a normal current is applied transverse to the supercurrent. The normal current is associated with the spin Hall effect, which causes spin accumulation at the super-normal interfaces and breaks the time-reversal symmetry locally. The normal current can thus reduce the critical current of the superconducting junction. The other is a kind of “remote reduction,” in which the normal current is applied parallel to the supercurrent but at a different part of the sample (red arrow no.2). In this case, the normal current causes the spin current, which should have a significant disorder in electron spins through the Zitterbewegung [3] and crosses the supercurrent. The disordered spin current again should lead to the reduction of the critical current.

In the experiments, the care was taken to avoid heating by the normal currents and the application of voltages due to the imbalance of the potentials at the normal electrodes. Figure 2(a) is a color plot of the resistance of the superconducting junction against the junction current and the control current. The black region corresponds to the zero-resistance state, and an apparent reduction of the critical current is observed. The current gain (the derivative of the edge line on the zero-resistance region) is larger than unity (0 dB) below 100 nA of the transverse current. The result of the remote-reduction experiment is shown in Fig. 2(b). The remote current also reduces the critical current through the sensitivity is lower, and the region for positive current gain (above 0 dB) is limited to just around the zero parallel currents.

In conclusion, we have realized a current-controlled four terminal superconducting device with finite current gains.

References

Authors
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Magneto-Thermodynamic Properties in Submicron Wires of Pd-doped FeRh

Otani Group

An FeRh alloy with B2 order shows a first-order phase transition from antiferromagnetic (AFM) to ferromagnetic (FM) phases with raising temperature. As the transition temperature is tunable around room temperature, this is a candidate material for several applications such as heat-assisted magnetic recording, AFM memories and memristor devices. Recently, an asymmetric behavior around the AFM-FM phase transition has been reported on some tiny sample structures. Remarkably, a discontinuous and asymmetric resistance change around the phase transition was reported in submicron wires of FeRh, which is caused by suppression of the nucleation of AFM domains during the cooling process [1]. In this work, we performed resistivity measurements of submicron wires of Pd-doped FeRh as a function of temperature and external magnetic field. We further evaluated some thermal properties such as an energy loss around the temperature hysteresis in each wire to characterize those finite-size effect.

We used Pd-doped FeRh alloy in order to decrease the AFM-FM phase transition temperature. A 60-nm-thick epitaxial film of Pd-doped FeRh was prepared and fabricated into submicron wires. Detailed processes for film growth and patterning are shown in Ref. 2. As the resistivity in AFM phase is larger than that in FM phase, the electrical transport measurement can be a probe to detect the AFM-FM phase transition which is induced by sweeping temperature or external magnetic field. The resistance on 270-nm-wide wire against temperature and magnetic field is plotted in Fig. 1(a). We can see the temperature-driven and field-driven hysteresis
Fig. 1. (a) Fe L_{2,3} remanent XAS (upper) and XMCD (middle) of a 7-ML Fe film on Cu(001), and XMCD (lower) of a 5-ML Mn/7-ML Fe film in the normal incidence (NI) and grazing incidence (GI) geometries. Here, external magnetic field is parallel to the incident x-ray. (b) Iron magnetization curves in the heterostructures of Mn (x ML, x = 0, 1, 2, 3, and 5) overlayers on the 7-ML Fe film measured in the NI (left) and GI (right) geometries. The L_{2} XAS peak intensity normalized by the L_{3} one is plotted as a function of the magnetic field. In the GI geometry, the magnetic field is applied along the [100] direction of the Cu(001) substrate.

Dynamic Interface Formation in Magnetic Thin Film Heterostructures

Komori Group

In magnetic thin film heterostructures, interaction at the interface plays a dominant role in the development of novel electronic and magnetic properties. The interlayer coupling strength primarily relies on the interfacial structure at the atomic scale, including atomic roughness, steps, and intermixing. However, the impact of the atomic scale interfacial structure on the magnetic coupling in magnetic thin film heterostructures has not yet been elucidated well in relation to the macroscopic magnetic properties. We use scanning tunneling microscopy (STM) and x-ray absorption spectroscopy/x-ray magnetic circular dichroism (XAS/XMCD) as complementary tools for clarifying the correlation between the atomic structure at the interface and the magnetism. Successive atomically-resolved STM characterizations of not only structural but also electronic and magnetic properties during the growth of magnetic thin film heterostructures provide crucial information on the atomic-scale interfacial factors in the dynamical process of the interface formation. The element-specific, quantitative and macroscopic observations of electronic and magnetic properties by XAS/XMCD can be linked with the microscopic interface characteristics.

We have studied fcc Fe thin films grown on Cu(001) with Mn overlayers (Mn/Fe films) as a unique system for investigating the interface interaction. [1] The electronic and magnetic properties of the films depend on the atomic structure at the interface and the magnetism. Successive atomically-resolved STM characterizations of not only structural but also electronic and magnetic properties during the growth of magnetic thin film heterostructures have been conducted, and the atomic-scale interfacial factors in the dynamical process of the interface formation have been elucidated. The element-specific, quantitative and macroscopic observations of electronic and magnetic properties by XAS/XMCD have been linked with the microscopic interface characteristics.

Fig. 2. (a-c) STM images of 7-ML Fe films with 1.0-ML (a), 1.5-ML (b), 1.8-ML (c) Mn overlayers. (d-g) High-resolution surface STM images of 1.0-ML (d), 1.5-ML (e), 1.8-ML films (first (level-1) (f) and second (level-2) (g) levels). The disorder alloy can be seen in each image as bright protrusions. (h) Statistical plots of the fraction of the ordered alloy region with the (4 × 2) and (4 × 4) reconstructions in level-1 and level-2 as a function of the average thickness of the Mn overlayer. The dashed lines are linear extrapolations of the fractions of the ordered alloy.

References


Authors

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and magnetic properties of ferromagnetically-coupled top two layers in the fcc Fe thin film on Cu (001) [2] is susceptible to the structural changes on the atomic scale. At the interface, a collinear and homogeneous antiferromagnetic/ferromagnetic coupling is expected at the Mn/Fe interface as observed in the reference system of Mn thin films on the bulk bcc Fe(001) substrate. Thus, the fcc Fe thin film highlights the role of atomic-scale interfacial factors with the Mn overlayers.

The films were fabricated by successive deposition of Fe and Mn on Cu(001) at room temperature (RT) in an ultrahigh vacuum. The thickness of the fcc Fe layer was fixed to ~7 monolayer (ML). The Fe layer in the Mn/Fe film exhibits a two-step spin reorientation transition (SRT) from out-of-plane to in-plane direction with increasing the thickness of the Mn overlay as observed by XAS/XMCD measurements shown in Fig. 1. After 1 ML deposition of Mn, the coercive field in the magnetic field perpendicular to the film decreases to a value less than that in the in-plane magnetic field. Furthermore, the in-plane anisotropy gradually increases up to 3-ML Mn deposition. Corresponding atomically-resolved STM observations reveal the dynamic structure change from a disordered surface to an ordered one by the Mn deposition at RT as in Fig. 2. First, a disordered surface alloy with the Fe film is formed by the Mn deposition, which induces the first SRT. The ordered-alloy area of the surface gradually increases with increasing the amount of the deposited Mn atoms more than 1 ML on average. The ordering of the alloy completes around 3-ML Mn deposition, which corresponds to the completion of the second SRT.

The present complementary approach by XAS/XMCD and STM successfully disentangles the hidden functionality of the interface alloying, which changes and enhances the magnetic anisotropy in the Fe layer. The results will pave new ways to understand novel phenomena emerging at the interface on the atomic scale, and to improve the electronic and magnetic properties of the magnetic thin film heterostructure.

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Direct Visualization of Electrical Resistance at Single Surface Steps
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Atomically-thin two dimensional electron systems (2DES) have been one of the hot topics because of their unique properties originating from the low dimensionality and reduced symmetry. Among them 2DES by metallic surface states, which are formed by a few monolayer (ML) deposition of metallic elements on semiconducting substrates, have a unique status. Because of the thermal stability through the surface reconstruction, self-organized high-quality periodical structures can be formed in macroscopic dimensions. Basic properties such as atomic structure and electronic states can be well characterized by standard surface science techniques including scanning tunneling microscopy (STM). Recent discovery of superconductivity in surface 2DES attracted further attentions.

Net and local misorientations of the substrate from a nominal plane results in the formation of steps on it. Superstructure due to the surface reconstruction inherently forms boundaries that separate domains whose periodical phases are different from each other. Both of the one-dimensional line defects disrupt the periodicity of the surface atomic arrangement and therefore work as a barrier for the electrons across them. In order to investigate the role of the line defects in electrical transport, we measured the nanometer-scale spatial distribution of local electrochemical potential of an archetypical metallic surface states; the 7×7 structure of Si(111) substrates, using an STM-based technique called scanning tunneling potentiometry (STP) [1]. Using STP, we found potential drops clearly at step edges and phase boundaries of the 2D metallic surface, demonstrating the presence of significant electrical resistance there.

Figure 1 shows STM and electrochemical potential images taken simultaneously on the 7×7 surface under the net current flow from the lower left to the upper right in the topographic image (Fig. 1(a)). In the corresponding potential image (Fig. 1(b)), potential drops are found at the step edges, as more quantitatively presented in the inset cross-sectional plots, which was taken along the dashed A-B line in Fig. 1(a).

The steps are, however, not the only defects that disrupts the electron transport on the surface. In the potential mapping, which exhibits a ladder-like pattern, one notices several potential drops in narrow terraces separated by the steps. The potential drop due to the rungs of the ladders is more clearly displayed in a cross-sectional profile shown in the inset. The rungs correspond to boundaries that separate domains of the 7×7 reconstructed structures whose phases do not match. The potential images indicate that the phase boundaries also have electrical resistance.

From the obtained potential images and their cross-sectional plots, we can quantitatively analyze the conductivity through an individual step and phase boundary. Since the absolute value of the current density is unknown, we cannot measure the terrace, step, or phase boundary conductivity directly. But, their ratio can be estimated precisely. Since in our measurement we used low-doped substrates, the electrical conductance through the substrate is quite small. The poorly conductive substrate safely eliminates the problem of the bulk contributions in our measurements.

We estimated the conductivity ratio of the step to the

Fig. 1. STM (a) and electrochemical potential (b) images taken simultaneously on the Si(111)7×7 surface. (inset) cross-sectional plots of topographic height and potential taken along the dashed line drawn in (a).

Figure 1. STM (a) and electrochemical potential (b) images taken simultaneously on the Si(111)7×7 surface. (inset) cross-sectional plots of topographic height and potential taken along the dashed line drawn in (a).
Strain Relaxation at Doped Epitaxial Interfaces

Lippmaa Group

A quasi-two-dimensional quantum well is known to form by electron accumulation at an epitaxial heterointerface between SrTiO$_3$ and LaAlO$_3$. The accumulation of carriers at this interface is the result of a peculiar interplay between several effects, including the polar discontinuity between SrTiO$_3$ and LaAlO$_3$, tetragonal distortion of the interface layer due to the 3% epitaxial strain at the interface, field- and strain-dependent giant dielectric permittivity of SrTiO$_3$, and possibly due to Sr and La intermixing within the first unit cell of the interface. Although the carrier number is essentially fixed by the structure, it is possible to tune the depth distribution of the accumulated carriers by either top- or bottom-side gating, thereby changing the occupancy of the nearly degenerate $d_{xy}$, $d_{xz}$, and $d_{yz}$ orbitals. Due to the tetragonal distortion of the interface layer, the orbital degeneracy is partially lifted, lowering the energy of the $d_{xy}$ orbital. Gating can then be used to shift the Fermi level below or above the level crossing, leaving the $d_{xy}$ orbitals either empty or partly filled. One unique feature of this interface is the sharply asymmetric potential profile of the quantum well due to the wide bandgap of LaAlO$_3$. This asymmetry leads to a relatively strong Rashba-type spin-orbit coupling at the interface and this coupling strength can be tuned to some extent by gating, either because the asymmetry of the potential well is changed or due to a Lifshitz transition that occurs when the Fermi level is tuned across the $d_{xy} - d_{x^2-y^2}$ crossing.

Since this level crossing energy is determined by the tetragonal distortion of the interface layer, we have turned our attention to the possibility of tuning the interfacial strain by doping the interface. Additionally, by adding heavy elements, such as Ir to the interface, it may be possible to control the spin-orbit coupling experienced by the electrons in the quantum well.

SrTiO$_3$/LaAlO$_3$ heterostructures with interfaces doped either with Ir or Co were grown by pulsed laser deposition and the interfacial strain relaxation was studied by hard (7940 eV) x-ray photoelectron diffraction (XPD) at SPring-8 BL47XU. It was thus possible to estimate the strain state at the interface by comparing XPD forward focusing peak (FFP) positions between La and Sr (perovskite A-site) or Al and Ti (perovskite B-site) (Fig. 1) for different interface doping levels. A shift of the La and Al FFPs towards larger angles relative to Sr and Ti showed that in all cases the LaAlO$_3$ cap layer is under compressive strain in the out-of-plane direction due to epitaxial strain. However, the level of strain depends on interface doping, especially for Ir. One possible cause is the interdiffusion of Ir across the SrTiO$_3$/LaAlO$_3$ interface. The work suggests that the interfacial strain can be tuned by doping the first unit cell layer of LaAlO$_3$ at the interface with a larger ionic radius cation to reduce the epitaxial strain imposed on the first few unit cells of SrTiO$_3$. This technique may be effective for controlling the critical carrier density where the Lifshitz transition occurs and thus selecting the gate bias range where the spin-orbit coupling in the quantum well is tunable by gating.

References

Authors

ISSP Activity Report 2018
CO₂ Activation and Reaction on Zn-Deposited Cu Surfaces Studied by Ambient-Pressure X-Ray Photoelectron Spectroscopy

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It is important to understand the mechanisms of activation and hydrogenation of carbon dioxide (CO₂) in order to utilize the abundant CO₂ effectively as a chemical feedstock. One way of utilizing CO₂ is methanol synthesis on Cu-based catalysts. Metallic copper in the catalysts is considered to be an active site for methanol synthesis. So far, the adsorption and reaction of CO₂ on Cu surfaces have been widely investigated under ultrahigh vacuum (UHV) and under ambient pressure conditions.

In this study [1], the reaction of CO₂ on Zn-Cu(111) and Zn-Cu(997) was systematically studied using ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) at SPring-8 BL07LSU (2015B7496 and 2016A7401). AP-XPS allows adsorbate and substrate electronic states to be elucidated under reaction conditions. The aim of this study is to reveal the roles of Zn and water in the CO₂ reaction, and elementary steps of methanol synthesis by a series of systematic experiments performed under well-defined conditions at temperature between 299–473 K. We used Zn-deposited Cu(111) and Cu(997) single crystals as model catalytic systems. Stepped Cu surfaces are more reactive for dissociation of CO₂ compared to flat Cu surfaces. Recently, we have investigated adsorption states of CO₂ on Cu(997) surfaces under UHV, and near-ambient condition. In this study, we have focused on hydrogenation of CO₂ under near-ambient pressure conditions to clarify the effect of the step sites. The oxidation state of Zn-deposited Cu surfaces and the stability of reaction products depend strongly on the gas composition and sample temperature. The effect of water on the CO₂ activation was also examined by a set of control experiments.

In the presence of 0.8 mbar CO₂ and 0.4 mbar H₂ gases, hydrogenation products are not observed; only carbonate is formed on Zn-deposited Cu(111) and Cu(997) surfaces (not shown here). We found that the formation rate of carbonate at 299 K is significantly faster on Zn/Cu(997) than that on Zn/Cu(111), indicating that step sites are more reactive for CO₂ activation than terrace sites. On the other hand, the addition of water (D₂O) in the feed gas leads to hydrogenation of CO₂ to formate at sample temperatures around 400 K (Fig. 1). This suggests that hydroxyl produced from dissociative adsorption of water is a reactant in the CO₂ hydrogenation observed under the present reaction conditions. Figure 2 schematically shows the proposed reactions on the Zn-deposited Cu surface in the presence of CO₂, H₂ and H₂O. We also found that the reaction products such as carbonate and formate on the Zn/Cu(997) surface are more stable than those on the bare Cu(997) surface. In particular, formate remains on Zn-deposited Cu surfaces up to 473 K, which is close to the operation temperature of industrial Cu-ZnO catalysts. We conclude that an important role of Zn on Cu surfaces is the stabilization of reaction intermediates originated from CO₂.

Reference

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Biophysical Study on the Function and Molecular Mechanism of Rhodopsins

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Rhodopsin is photo-receptive heptahelical transmembrane proteins in which retinal chromophore is covalently bound to a conserved lysine residue in the seventh helix, and animal and microbial rhodopsin families are known so far. Animal rhodopsins present in animal retina transfer visual signal to brain and are also related to non-visual light sensing. Microbial rhodopsins show diverse functions: light-driven ion pump, light-gated ion channels, light-regulated enzyme and so on. Both types of rhodopsins are being widely used in optogenetics to control various cellular events, such as neural activity, gene expression and so on, by light. Recently, we reported third class of rhodopsin, heliorhodopsin (HeR), which is evolutionally isolated from both of microbial and animal rhodopsins [1]. The biochemical study revealed its inverted structure compared with other class of rhodopsins, and N- and C-termini of HeR faces extracellular and cytoplasmic milieus, respectively (Fig. 1). HeRs are diversely distributed from bacteria, archaea, eukaryotic algae and giant viruses. Although the function of HeR has not been clarified yet, we observed a long photo-reaction cycle up to seconds to minutes by laser flash photolysis suggesting HeR works as a signaling protein which transfers light signal to unidentified intracel-
The retinal chromophore in HeR isomerizes from all-trans to 13-cis form upon light illumination, and we dominantly observed K, M and O-intermediates in the photocycle. While the K and O intermediates show red-shifted absorption compared with that of the dark state, the absorption of M-intermediate is highly blue-shifted to 400 nm and a proton is released from retinylidene Schiff-base. A mutational study suggested that the proton is not transferred to a specific residue and it is trapped in a hydrogen bonding network, called proton accepting group (PAG), constituted from several amino-acid residues including conserved histidines and internal water molecules on the extracellular side of the protein.

Rhodopsins show wide range of absorption wavelength and the color regulation of retinal chromophore in rhodopsins to achieve longer-wavelength absorption is one of critical elemental technique to develop new types of optogenetics tools which can avoid strong light-scattering by biological tissues and phototoxicity. We reported that the mutation of the conserved proline and serine residues in sodium pump rhodopsin (KR2) induces 40-nm red-shift of the absorption without impairing sodium-transport activity [2]. Also, FTIR spectroscopy and quantum mechanical calculation revealed that the change in dipole moments of these residues lowered energy gap of \( \pi \)-electron of retinal chromophore by electrostatic interaction. Furthermore, we identified a new type of sodium pump rhodopsin from \( \alpha \)-proteobacterium, Jannaschia seosinensis, in which the proline residue was naturally altered to glycine and it shows 20-nm longer absorption than that of KR2. Since J. seosinensis is derived from solar saltern, the natural mutation of the proline occurred to use longer wavelength light in turbid environment. Since sodium pump rhodopsin can suppress the neural spiking without alterations of intracellular pH and Cl\(^{-}\) concentration, this red-shifted KR2 would be expected to be applied as a new type of optogenetic tool.

References

Emergent SU(4) Symmetry and Quantum Spin-Orbital Liquid in \( \alpha \)-ZrCl\(_3\)

Oshikawa Group

As materials are cooled down towards the absolute zero temperature, generally they become a solid with a long-range order in location of atoms. Likewise, magnetic materials develop a magnetic long-range order at sufficiently low temperatures. However, we may expect a “quantum spin liquid” as a ground state of a magnetic material, if strong quantum fluctuations destroy the magnetic order even at zero temperature. Theoretical studies have revealed that quantum spin liquids exhibit various exotic phenomena such as fractionalization. Its realization has been one of the central topics in quantum magnetism and condensed matter physics. After intensive studies over several decades, several materials have been found to be strong candidates of quantum spin liquids. However, such candidate materials are still limited, and it is desirable to find new class of quantum spin liquid materials.

Quantum magnets often possess the (approximate) spin rotation symmetry. Mathematically it corresponds to the group of “rotations” of two-component complex vectors, SU(2). Here the two components of the vector correspond to the amplitudes of the spin pointing up and down. It is then natural to consider an extended symmetry of “rotations” of N-component complex vectors, SU(N). For a larger N, the symmetry is larger, and the quantum fluctuations would be stronger. In fact, there have been numerous theoretical studies of SU(N) “spin” systems, many of which are found to be quantum spin liquids. Experimentally, the SU(N) symmetry has been realized using nuclear spin degrees of freedom in cold atoms. However, it is still difficult to observe the SU(N) quantum spin liquid behavior in cold atoms, it is desirable to realize it in a magnetic material.

In principle, the SU(N) symmetry can appear if there are degenerate orbitals which can be occupied by electrons. For example, there are two degenerate orbitals in each atom, an electron can take 2 orbital states and 2 spin states, namely 4 states in each atom. If the system is symmetric with respect to the “rotation” of these 4 states, it is SU(4) symmetric.
In the field of condensed matter physics, there has been an intense search for topological nontrivial electronic phases in strongly correlated materials. To date, most research on topological electronic systems has been limited to weakly correlated materials where electronic correlations play a minor role. Among newly-found topological phases, the Weyl semimetal phase has attracted the most significant attention because the Weyl fermions exhibit extremely high electrical and thermal conductivities, which may find use in ultrahigh-speed and low-power consumption devices. While the Weyl semimetal phase was experimentally discovered in the inversion symmetry broken TaAs system in 2015 [1,2], only a few candidates of the magnetic version have been found in systems with broken time reversal symmetry. Historically, a magnetic Weyl system is the first Weyl semimetal predicted for condensed matter in 2012 in the seminal paper by Wan et al. [3]. Notably, this prediction was specifically made for the pyrochlore iridates.

Here, we focus on a pyrochlore iridate Pr2Ir2O7. This material is known as a Luttinger semimetal where electronic correlations are strong [4]. According to theoretical predictions, the electronic state can be tuned into a Weyl semimetal state by perturbations such as lattice strain and external magnetic field [5,6]. However, experimental proof of the existence of the Weyl semimetal remains elusive because it is difficult to apply uniaxial strain on bulk single crystals. One possible solution to this problem is to use Pr2Ir2O7 thin films where lattice strain can be introduced through epitaxy. To that end, more than 10 groups around the world have been working on fabricating Pr2Ir2O7 thin films, but there have been no reports of success.

What makes the fabrication of the thin films difficult is the high volatility of iridium, especially at high temperatures. We therefore turned to solid-state epitaxy, namely, the deposition of precursors at room temperature by pulsed laser deposition followed by annealing in air. This synthesis route mimics bulk crystal growth and allowed us to successfully fabricate high-quality epitaxial thin films of pyrochlore Pr2Ir2O7 on yttria-stabilized zirconia substrates [7]. Detailed crystal structure analysis revealed that strained and relaxed grains coexisted in the films. When Hall measurements were performed using the Pr2Ir2O7 films, spontaneous Hall effect was found below 50 K even though the material shows no spontaneous magnetization nor was an external magnetic field applied to the film. This temperature of 50 K is very high, considering that bulk single crystals show spontaneous Hall effect only below 1.5 K [8]. The spontaneous Hall effect appears due to the all-in-all-out structure of the iridium 5d moments and the associated time reversal symmetry breaking. In this case, the theoretically predicted condition that the Weyl semimetal state appears when both the cubic symmetry and the time reversal

tuning. Indeed, no material has been known to possess the SU(4) symmetry, even approximately.

In this work [1], we demonstrate theoretically that the SU(4) symmetry emerges in α-ZrCl3 (Fig.1). In the limit of strong spin-orbit coupling, the effective model of electrons in this material has strongly orbital-dependent hoppings (Fig. 2). As a result, the model looks far from SU(4) symmetric. However, the electron hopping between neighboring Zr ions can be identified with an SU(4) gauge field on the lattice. We find that, with an appropriate SU(4) gauge transformation on the lattice, the model is mapped to a manifestly SU(4)-symmetric one (Kugel-Khomskii model at the SU(4) point). This means that α-ZrCl3 has an emergent SU(4) symmetry, despite the strong spin-orbit coupling which seems to destroy even the spin SU(2) symmetry. In the strong electron repulsion limit, the effective model is reduced to the SU(4) “antiferromagnetic Heisenberg” model, which has a gapless spin liquid ground state according to a preceding theoretical study. Therefore, we expect that α-ZrCl3 realizes an SU(4)-symmetric quantum spin liquid. In fact, the SU(4) symmetry means that the spin and orbital degrees of freedom are intertwined and fluctuating together. In this sense, the ground state should be better called a quantum spin-orbital liquid.
In summary, we have successfully fabricated epitaxial thin films of Pr$_2$Ir$_2$O$_7$ and experimentally demonstrated that the Weyl semimetal state can be induced either by lattice strain or by applying an external magnetic field. Based on the results with the Weyl semimetal, the research for the topological phases in strongly correlated systems, which has not been done so far, will proceed. It is expected to lead to the development of ultrahigh-speed and low-power devices utilizing the Weyl fermions having high electric and thermal conductivities.

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Authors
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Fig. 1. Schematic of thermal spin injection from a ferromagnetic insulator into an attached metal layer.

Fig. 2. Temperature dependence of the dielectric constant. The low-temperature value is several tens of times larger than that of known zero-gap semiconductors (e.g. α-Sn and HgTe). The dielectric constant becomes larger when the Fermi level approaches the band touching.

We have thus demonstrated that electronic correlations are indeed very strong in a Luttinger semimetal with quadratic band touching. In the future, it is expected that further understanding of the role of electronic correlations in determining the physical properties of zero-gap semiconductors will lead to the creation of novel metallic states and new functional materials.

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Large Spin Hall Effect in Amorphous Mn-Sn Alloy Thin Film
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Pure spin current contains only angular momentum without net charge flow, which greatly reduces the Joule heating. This feature makes spin current beneficial for low power spintronic devices. The spin Hall effect (SHE) converts charge current to transverse spin current, serving as an effective way to generate pure spin current. Meanwhile, as the reciprocal effect of the SHE, the inverse spin Hall effect (ISHE) converts pure spin current to transverse charge current, and plays an important role in pure spin current detection and conversion.

Although manipulation of pure spin current in heavy transition metals, ferromagnetic metals, and their alloys have been extensively explored in the past decade, antiferromagnets have become a new central stage due to its prominent advantages such as high frequency magnetic dynamics, negligible stray field, and perturbation insensitivity. Among these materials, the non-collinear Kagome lattice antiferromagnets Mn3X (X = Sn, Ge, Ga) stand out because of their large transverse electrical [1-4] and optical [5] responses to the external magnetic field as well as their negligible magnetic moment.

In our work, we used the thermally generated pure spin current from the spin Seebeck effect (SSE) in the ferrimagnetic insulator yttrium iron garnet (YIG) to study the inverse spin Hall effect in Mn and the Mn-Sn alloys (Fig. 1). A series of samples with different thicknesses are sputtering deposited onto YIG substrates. By measuring the ISHE voltage, we obtained a sizable spin Hall angle $\theta_{SH}$ of -0.23% (which measures the conversion efficiency between charge current and spin current), and a long spin diffusion length $\lambda_{sd}$ = 11.5 nm for the single element material Mn, as shown in Fig. 2 (a). Most importantly, by doping Sn in Mn, we found that the $\theta_{SH}$ of the Mn-Sn alloy, even in its amorphous form, is increased by 20 times to -4.4%, while the resistivity ($\rho$) is reduced by about 10 times, as shown in Fig. 2 (b). Therefore, the energy consumption ($-\rho\theta_{SH}$) of the Mn-Sn alloy is reduced by 4000 times compared to Mn. A spin pumping measurement further corroborates the enhancement of the $\theta_{SH}$ in the Mn-Sn alloy. These results not only serve as essential references in studying the pure spin current phenomena in Mn-based alloys, but also offer a promising method for exploring future energy efficient spin Hall materials with high spin Hall angle but low resistivity and thus low energy consumptions [6].

References

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Large Anomalous Hall Effect in Thin Films of a Weyl Magnet Mn₃Sn

Nakatsuji and Otani Groups

Recently, there has been a surge of interest in antiferromagnets (AFMs) as prospective spintronic materials for high-density and ultrafast memory devices because of their vanishingly small stray field and orders of magnitude faster spin dynamics compared to their ferromagnetic counterparts. In particular, the recently discovered functional antiferromagnet D0₁₉ Mn₃Sn has attracted broad attention as the first example of a magnetic Weyl material/Weyl magnet [1-5]. This material exhibits a variety of useful functions that have never been observed before in antiferromagnets at zero magnetic field, including the anomalous Hall effect [1], the anomalous Nernst effect [2], and the magneto-optical Kerr effect [5] at room temperature. All these properties are controllable by a magnetic field and thus can be used for designing antiferromagnetic spintronic devices.

For the thin film fabrication, we employ DC magnetron sputtering. The films (40-400 nm) are deposited at room temperature from the Mn₃Sn target. After the deposition at room temperature, we anneal the film at 500°C for one hour, and thereby crystallizes the as-deposited amorphous film in a polycrystalline form of the Mn₃Sn film. XRD measurements reveal that the films are the single amorphous film in a polycrystalline form of the Mn₃Sn phase of Mn₃Sn film. XRD measurements reveal that the films are the single phase of Mn₃SnSn and are in a randomly oriented polycrystalline form of the Mn₃Sn film. All these peaks can be indexed by the hexagonal P6₃mmc symmetry of D0₁₉ Mn₃Sn, with no additional peaks due to plausible impurity phases (Fig. 1(a)).

Figure 1(b) shows the temperature dependence of the longitudinal resistivity $\rho$ and the spontaneous Hall resistivity $\rho_H$ of the Mn₃Sn thin film under zero field. The behavior of longitudinal resistivity $\rho$ confirms the metallic transport consistent with the previous work on bulk single crystals [2]. The zero-field Hall resistivity $\rho_H$ was obtained from $(\rho_H(H = +0) - \rho_H(H = -0))/2$. (Here, we use +0 and -0 to indicate zero magnetic field approached, respectively, from +5 T and -5 T in the Hall resistivity measurement at each temperature.) We have observed a sharp decrease in $\rho_H$ at $H = 0$ below $T = 260$ K on cooling; this behavior agrees with the magnetic symmetry consideration in Mn₃Sn that the inverse triangular spin structure breaks the global time-reversal symmetry, whereas time-reversal symmetry is restored in the low temperature helical phase. Figure 1(c) displays the field dependence of the Hall resistivity $\rho_H$ at 300 K as a function of the magnetic field applied perpendicular to the film surface. The anomalous Hall effect of the Mn₃Sn films exhibit a significant change in $\rho_H$ (H) from 1.5 $\mu$Ωcm to -1.5 $\mu$Ωcm with increasing field despite the vanishingly small magnetization; this feature is generated by the switching of the antiferromagnetic domain in real space and the large fictitious field in momentum space [6]. Notably, this is the first report on the thin film of the antiferromagnetic Mn₃Sn film exhibiting the large anomalous Hall effect of the same order of magnitude as the value reported for bulk. Our fabrication of the high-quality thin film of the Weyl magnet Mn₃Sn and the observation of its large anomalous Hall effect provide an important step to further develop devices useful for antiferromagnetic spintronics, such as for high-speed and high-density information storage.

References


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Giant Anomalous Nernst Effect at Room Temperature in a Weyl Ferromagnet

Nakatsuji Group

The anomalous Nernst effect (ANE) is a well-known thermoelectric effect for ferromagnets, namely the generation of an electric voltage perpendicular to both magnetization and an applied temperature gradient. This transverse geometry of ANE leads to various advantages for thermoelectric modules compared to the conventional one based on Seebeck effect, such as simpler structure to efficiently cover a heat source, higher flexibility, lower production cost, and larger conversion efficiency for the same figure of merit [1]. However, the size of ANE is generally very small (on the order of ~0.1 $\mu$V/K), which hinders its practical applications. Recent theoretical and experimental investigations on topological materials indicate that the intense Berry curvature of Weyl points near the Fermi energy can enhance the intrinsic ANE, rendering ANE an powerful probe to
clarify the topological electronic structure in magnetic Weyl semimetals [2–4]. In other words, a ferromagnet exhibiting a giant ANE may serve as an ideal ground for magnetic Weyl semimetall state.

In this work, we report the giant ANE in a full-Heusler ferromagnet Co$_2$MnGa, reaching a record high value of $S_{yx} \sim$6 μV/K at room temperature [5] (Fig. 1). The crossover from Mott relation $\alpha_{yx} \sim T$ to $-\ln T$ dependence is observed on warming, where $\alpha_{yx}$ is the transverse thermoelectric conductivity, indicating the proximity to the quantum Lifshitz transition between type-I and type-II magnetic Weyl fermion states. Our study provides a new guideline for searching new topological magnets which are useful for energy harvesting and spintronics.

References

Authors

Magnetic Spin Hall Effect in a Non-Collinear Antiferromagnet
Otani and Nakatsuji Groups

The conventional spin Halle effect (SHE) converts electrical currents to transverse spin currents in non-magnetic conductors in response to an electric field. The SHE has thus drawn much attention as a means to switch the magnetization of the adjacent ferromagnetic layer via spin orbit torque. New functions have been further explored in various materials in terms of spin-charge currents interconversion. The magnetic contribution to the SHE has therefore been studied intensively in these days. Here we show that antiferromagnets have richer spin Hall properties than that of non-magnetic materials. The material focused on here is Mn$_3$Sn, which shows non-collinear antiferromagnetic order of Mn magnetic moments that have an inverse triangular spin configuration on stacked kagome lattices [1]. We find non-trivial time reversal-symmetry-breaking counterparts of the conventional SHE, which is called magnetic spin Hall effect [2].

To study the SHE in a non-collinear antiferromagnet, we fabricated a device consisting of ferromagnetic NiFe and non-magnetic Cu electrodes formed on the top surface of a microfabricated 100-nm-thick Mn$_3$Sn single crystal (see Fig. 1). An electric current was applied along the [2110] axis and the voltage was measured between electrodes aligned along the [0110] axis, perpendicular to the current. If current inside Mn$_3$Sn generated spin accumulation with a component parallel to the NiFe magnetization, it would shift the electrochemical potential across the Mn$_3$Sn/NiFe interface and can therefore be detected as a voltage between NiFe and the Cu electrodes. A rectangular resistance–magnetic field (R–B) hysteresis loop corresponding to the switching of NiFe magnetization is expected for a fixed polarization direction of the accumulated spins. Such a rectangular R–B hysteresis loop was observed in the magnetic-field dependence of the transverse voltage between NiFe and the Cu electrodes. The results in a and b were obtained after saturation of Mn$_3$Sn with a sufficiently large magnetic field B of $-0.75$ T.
and +0.75 T, respectively, which provide evidence that the rectangular loops originate from spin accumulation at the Mn$_3$Sn surface. The key observation in this work is that the spin accumulation signal changes indicate when the Mn$_3$Sn sub lattice moments are reversed, as illustrated in the inset. This unexpected sign change demonstrates that the dominant contribution to the SHE in Mn$_3$Sn is odd under time reversal. We find that in the non-collinear antiferromagnet Mn$_3$Sn, the SHE has an anomalous sign change when its triangularly ordered moments switch orientation. This discovery expands the horizons of antiferromagnet spintronics and spin–charge coupling mechanisms.

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Lithium-Ion Conductivity in Single Crystals of Li$_{10}$GeP$_2$S$_{12}$

Hiroi Group

The all-solid-state lithium-ion battery has been studied extensively as a next-generation secondary battery. It uses a solid instead of a liquid electrolyte, which enables to achieve greater safety, higher energy density, wider temperature range of operation, and larger output power compared with the conventional battery. To realize this, an efficient Li-ion conductor is required, which exhibits conductivity which is either comparable to or larger than that of commercially used organic liquid electrolytes. Li$_{10}$GeP$_2$S$_{12}$ (LGPS) is a promising candidate for the super ionic conductor; compared to other candidates, it has the highest conductivity of 12 mS cm$^{-1}$ at room temperature and an outstanding electrochemical performance in Li batteries [1,2]. Thus, LGPS is a key compound in the materialization of the all-solid-state battery.

The high Li-ion conductivity of LGPS has been ascribed to its specific crystal structure shown in Fig. 1a. There are four partially occupied Li sites inside the rigid framework composed of the tetrahedral units of Ge$_{0.5}$P$_{0.5}$S$_4$ and PS$_4$. Among them, the Li$_1$, Li$_3$, and Li$_4$ sites are located in the distorted tetrahedra of S, while the Li$_2$ site is in the distorted octahedron of S. It has been shown that the Li diffusion between the former sites is crucial for the high conductivity, while the Li$_2$ ions are almost immobile.

A highly anisotropic ion diffusion has been proposed based on neutron diffraction (ND) measurements and molecular dynamics calculations: a one-dimensional (1D) channel via the Li$_1$–Li$_3$ path along the c axis is dominant, and a two-dimensional (2D) hopping via the Li$_1$–Li$_4$ path in the <110> direction is secondary [3]. The activation energies of the local hopping processes for the 1D and 2D paths are determined as 0.16 (0.17) and 0.26 (0.28) eV from the NMR experiments (the molecular dynamics calculations), respectively. Thus, considerable anisotropy can be expected in the atomic-scale diffusion process. In contrast, pulsed-field gradient NMR measurements, which may be sensitive to long-range Li diffusion at the micrometer scale, suggests a nearly isotropic Li diffusion.

An impedance measurement using a single crystal provides important information with which to clarify the origin of this difference and the mechanism of ion diffusion in LGPS. However, because of the lack of a sufficiently large single crystal, the Li diffusion in the bulk had not been measured thus far. Previous impedance measurements using polycrystalline samples yielded an average conductivity of ~10 mS cm$^{-1}$ and activation energy of 0.22–0.28 eV. Understanding of the true conduction mechanism in LGPS is crucial for the improvement of LGPS and for further development of a better solid electrolyte for the all-solid-state battery. In the present study, we obtain large single crystals of LGPS, a few millimeters in size, using the self-flux method (Fig. 1b), and carry out impedance measurements in the [001] and [110] directions [4]. The conductivity is, in fact, higher along [001] than along [110]; however, the difference is only a factor of 4. In addition, the activation energies are nearly equal for the two directions, suggesting a weak anisotropic 3D diffusion in LGPS, as schematically illustrated in Fig. 1c.

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From Gapless Kitaev Spin Liquid to Classical String Gas through Tensor Networks

Kawashima Group

Quantum spin liquids (QSLs) represent a state of quantum matter which is not characterized by any local order parameters even at zero temperature. These novel states are expected to exhibit long-range entanglement leading to the topological order and fractionalized excitations. For example, the Haldane phase, which is known as a symmetry-protected topological phase, is a fascinating phase one can find in the...
S=1 quantum spin chain. The novel character that discriminates the Haldane phase from trivial gapped states was most clearly revealed by the discovery of Affleck-Kennedy-Lieb-Tasaki (AKLT) model and its exact ground state or the AKLT state. Its compact representation in the form of a matrix-product state provided a new insight into the Haldane phase. As a two-dimensional system with spin-liquid state, the Kitaev model on honeycomb lattice (KHM) is now a subject of active research, due to recent successful realizations of Kitaev materials. The model is exactly solvable and exhibits gapless and gapped Kitaev spin liquid (KSL) ground states with fractionalized excitations.

In the present work, we propose a "loop-gas" state, i.e., an exactly-solvable quantum state that has a compact and exact tensor-network representation, and a series of ansatze that starts from the loop-gas state and converges rapidly to the KHM ground-state. The loop gas state is defined by the loop-gas projector applied to a product state in which all spins are aligned in the (111) direction. The loop-gas projector is defined as tensor-network operator with bond-dimension 2, which is represented by a sum of all loop configurations each corresponding to a product of Pauli operators on all lattice points. (Fig. 1) We find that the norm of the loop gas state is exactly the same as the classical loop gas model at the critical fugacity on honeycomb lattice. The classical loop gas model appears in the low-temperature expansion of the Ising model, and therefore shares the same critical properties as the latter. These observations establishes that the correlation function of the loop-gas state is exactly the same as the correlation function of the critical Ising model. Furthermore, by defining the dimer-gas operator in an analogous way to the loop-gas operator, and applying it to the loop-gas state, we can improve the loop-gas state as an approximate to the KHM ground-state. (Fig. 2) For example, the second order approximation, which is obtained by applying the dimer-gas operator twice, achieves more than 4-digits accuracy in the energy. This is better than any other previous variational wave function. Also, note that there are only two adjustable parameters in the ansatz.

From these results, we conclude that the series of ansatze starting from the loop-gas state correctly reflects the essential properties of the family of KSLs, which is known to belong to the Ising universality class. Since the present description of KSLs does not rely on the mapping to fermions, it provides us with an alternative view point to discuss KSLs.

Reference

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Evolution of Magnetic Double Helix and Quantum Criticality Near a Dome of Superconductivity in CrAs
Uwatoko Group

The study of unconventional superconductivity (SC) is one of the most vigorous research fields in condensed matter physics. Although the underlying mechanisms for the unconventional SC in cuprate, iron-based, and heavy-fermion superconductors remains elusive, extensive investigations over the last decades have evidenced quantum criticality as a candidate mechanism for these diverse classes of superconductors. The phase diagrams of these materials often feature a superconducting dome situated adjacent to a magnetically ordered state, with the optimal superconducting transition temperature (Tc) located near a quantum critical point. The close proximity of SC to magnetic order makes it important to elucidate the nature of magnetism.

Recently, we found CrAs as the first superconductor among Cr-based compounds. The transport measurements indicated that the development of SC is accompanied by the suppression of double-helical magnetic order that is coupled with a first-order isostructural transition at ambient pressure. These observations make CrAs an ideal platform for in-depth studies on how the coupled structural and helimagnetic orders are tuned to the critical point and how the magnetism is coupled to the unconventional SC developed nearby. In combinations of elastic and inelastic neutron scattering, resistivity, and specific-heat measurements on undoped CrAs...
and P-doped CrAs1-xPx single crystals and powders, we have studied systematically the evolutions of static helical order and dynamic spin correlations as well as the electronic properties of CrAs when its coupled structural/helical order is suppressed by either external pressure or the chemical substitutions.

Neutron diffraction on the single-crystal CrAs under hydrostatic pressure (P) shows that the combined order is suppressed at \( P_c = 10 \) kbar, near which bulk superconductivity develops with a maximal transition temperature \( T_c \approx 2 \) K. We further show that the coupled order is also completely suppressed by phosphorus doping in CrAs1-xPx at a critical \( x_c \approx 0.05 \), above which inelastic neutron scattering evidenced persistent antiferromagnetic correlations, providing a possible link between magnetism and superconductivity. In line with the presence of antiferromagnetic fluctuations near \( P_c \) (\( x_c \)), the \( T_c \) of the quadratic temperature dependence of resistivity exhibits a dramatic enhancement as \( P(\frac{d\rho}{dT}) \) approaches \( P_c \) (\( x_c \)), around which \( r(T) \) has a non-Fermi-liquid form. Accordingly, the electronic specific-heat coefficient of CrAs1-xPx peaks out around \( x_c \). These properties provide clear evidences for quantum criticality, which we interpret as originating from a nearly second-order helimagnetic quantum phase transition that is concomitant with a first-order structural transition.

We propose that these results can be understood in terms of a proximity to a magnetic quantum critical point tuned by the degree of the incipient localization of the Cr-3d states, possibly via an orbital-selective Mottness mechanism. Our findings in CrAs highlight the distinct characteristics of quantum criticality in bad metals, thereby bringing out new findings in CrAs.

References


Authors


High-\( T_c \) Superconductivity up to 55 K under High Pressure in a Heavily Electron-Doped Li0.36(NH3)yFe2Se2 Single Crystal

Uwatoko Group

To find out the approaches to raise the critical temperature \( T_c \) of unconventional superconductors is one of the most enduring problems in contemporary condensed matter physics. The principal route to raise the \( T_c \) of FeSe is to dope electron, which has been successfully achieved via the interlayer intercalations \([\text{FeSe}_2]_n\) \((A = \text{K, Rb})\), \(A_y(\text{NH}_3)_z\text{FeSe}_2\), and \((\text{Li,Fe})\text{OHFeSe}\), interface charge transfer, surface K dosing, and gate-voltage regulation. Further enhancement of \( T_c \) via adding more electrons seems to be plagued by the observed insulating state in the over doped regime. Given the limitations of electron doping, it is imperative to explore other routes to enhance \( T_c \) of these heavily electron doped (HED) FeSe materials further. In contrast to electron-doping approaches, the application of high pressure can provide an alternative means.

In this work [1], we had performed high-pressure measurement on Li0.36(NH3)yFe2Se2 single crystal, which can reach an optimal \( T_c^{\text{onset}} \approx 44.3 \) K at ambient pressure. From high-pressure resistivity and AC-susceptibility measurement, we can conclude that superconducting transition temperature \( T_c \approx 44 \) K at ambient pressure is first suppressed to below 20 K upon increasing pressure to \( P_c = 2 \) GPa above which the pressure dependence of \( T_c(P) \) reverses and \( T_c \) increases steadily to 55 K at 11 GPa. These results thus evidence a pressure-induced second high-\( T_c \) superconducting (SC-II) phase in Li0.36(NH3)yFe2Se2 with the highest \( T_c^{\text{max}} \approx 55 \) K among the FeSe-based bulk materials. Also it is evident that the SC-II phase is bulk in nature for 6 GPa, whereas the sample contains two superconducting phases with different \( T_c \) above 6 GPa: The high-\( T_c \) phase has a small but nearly constant volume fraction-30% to 11 GPa, whereas the low-(33K) phase shrinks and vanishes completely \( T_c \) above 11 GPa.

Figure 1 summarizes the pressure dependences of \( T_c^{\text{onset}} \) and \( T_c^{\text{zero}} \) for Li0.36(NH3)yFe2Se2 together with the \( T_c^{\text{zero}} \) of FeSe for comparison. The temperature-pressure phase diagram depicts explicitly the evolution of the superconducting phase of Li0.36(NH3)yFe2Se2 under pressure. The high-\( T_c \) SC-I phase, intitially achived at ambient pressure via doping electron through inserting lithium Li+ and ammonia in between the FeSe layers, is quickly suppressed by pressure, and the superconducting phase emerges above \( P_c \) = 2 GPa and exists in a broad pressure range.

To further characterize the SC-II phase, we tentatively probe the information about Fermi surface under pressure by measuring the Hall effect in the normal state just above \( T_c \). Hall data confirms that in the emergent SC-II phase the dominant electron-type carrier density undergoes a fourfold enhancement and tracks the same trend as \( T_c(P) \). Interestingly, we find a nearly parallel scaling behavior between \( T_c \) and the inverse Hall coefficient for the SC-II phases of FeSe.

Fig. 1. The \( T-P \) phase diagram of the Li0.36(NH3)yFe2Se2 single crystal. The pressure dependence of the superconducting transition temperatures \( T_c \) up to 12 GPa.
Our present study thus demonstrates a way for high pressure to raise $T_c$ of these HED FeSe-based materials by increasing the effective charge-carrier concentration via a possible Fermi-surface reconstruction at $P_c$.

Reference

Authors
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Thermodynamic and Structural Studies on Super High Entropy Liquids, Alkylated Tetra-phenyl Porphyrins

Yamamuro Group

The fusion (melting) temperature $T_{\text{fus}}$ of molecules usually depend on molecular mass $M$; the larger $M$ is, the higher $T_{\text{fus}}$ becomes. For example, $T_{\text{fus}}$ of benzene (C$_6$H$_6$, $M = 78$) is 279 K while that of biphenyl (C$_6$H$_5$-C$_6$H$_5$, $M = 154$) is 342 K. This is because the intermolecular van der Waals interaction is larger in the crystalline phase with better molecular packing than that in the liquid phase with worse packing.

Recently, Nakanishi group in NIMS found a series of large molecules which exist in liquid states at room temperature. These molecules have π-conjugated cores such as pyrene, naphthalene, anthracene, fullerene, phthalo cyanine and long alkyl chains bonded to the cores [1]. We consider that these alkylated molecules are stabilized by the large entropy effect which is caused by the conformational disorder of alkyl chains. This situation is similar to that of ionic liquids which are in liquid states in spite of their strong inter-ionic interactions. We collectively call this type of liquids “super-high entropy liquids (SHEL)”. The physico-

chemical properties of SHEL have not been studied well. As the first target we have taken 2,5-C$_6$C$_{10}$-tetrphenylporphyrin (2,5-C$_6$C$_{10}$-TPP) and 3,5-C$_6$C$_{10}$-tetraphenylporphyrin (3,5-C$_6$C$_{10}$-TPP). The molecular structure of 2,5-C$_6$C$_{10}$-TPP is shown by the inset of Fig. 1; two -O-C$_6$C$_{10}$ groups are bonded symmetrically to a benzene ring in 3,5-C$_6$C$_{10}$-TPP. It is quite interesting that $T_{\text{fus}}$ of the alkylated molecules (2,5-C$_6$C$_{10}$-TPP, $M = 2538$) is lower than $T_{\text{fus}}$ of non-alkylated molecules (TPP, $M = 615$, $T_{\text{fus}} = 723$ K).

We have measured the heat capacities of 2,5-C$_6$C$_{10}$-TPP and 3,5-C$_6$C$_{10}$-TPP by use of an adiabatic calorimeter in our lab. The $C_p$ plot shown in Fig. 1 revealed that both molecules have a broad glass transition at around $T_g = 210$ K and the $C_p$ of 2,5-C$_6$C$_{10}$-TPP is 2-3 % larger than that of 3,5-C$_6$C$_{10}$-TPP at above $T_g$. The configurational entropies calculated from the $C_p$ data are more than 1000 JK$^{-1}$mol$^{-1}$ at high temperature limit, which is more than 10 times larger than those of usual molecular liquids. We have also measured the X-ray diffraction of 2,5-C$_6$C$_{10}$-TPP and 3,5-C$_6$C$_{10}$-TPP using a diffractometer at BL04B2, SPring-8. Figure 2 shows the reduced pair-correlation function $G(r)$ calculated from the diffraction data; a similar result is obtained in 3,5-C$_6$C$_{10}$-TPP. Most of the $G(r)$ peaks are attributed to the C-C correlations in alkyl chains. The broad peak at 9 Å, maybe also at 4.5 Å, is considered to be the correlation between porphyrin rings. The present data suggest that the configurations of alkyl chains and porphyrin rings of 2,5-C$_6$C$_{10}$-TPP and 3,5-C$_6$C$_{10}$-TPP are highly disordered at higher temperatures and becomes ordered at lower temperatures. Now we are measuring the quasielastic neutron scattering of both samples to investigate the dynamics of both alkyl chains and porphyrin cores.

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Authors
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Fig. 1. Heat capacities of 2,5-C$_6$C$_{10}$-TPP and 3,5-C$_6$C$_{10}$-TPP. The inset shows the molecular structure of 2,5-C$_6$C$_{10}$-TPP.

Fig. 2. Temperature dependence of the reduced pair distribution functions of 2,5-C$_6$C$_{10}$-TPP calculated from the X-ray diffraction data. The distances corresponding to the intra and intermolecular correlations are given in the figure.

Li$_{0.36}$(NH$_3$)$_2$Fe$_2$Se$_2$.

Our present study thus demonstrates a way for high pressure to raise $T_c$ of these HED FeSe-based materials by increasing the effective charge-carrier concentration via a possible Fermi-surface reconstruction at $P_c$. 

Reference

Authors
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Thermodynamic and Structural Studies on Super High Entropy Liquids, Alkylated Tetra-phenyl Porphyrins

Yamamuro Group

The fusion (melting) temperature $T_{\text{fus}}$ of molecules usually depend on molecular mass $M$; the larger $M$ is, the higher $T_{\text{fus}}$ becomes. For example, $T_{\text{fus}}$ of benzene (C$_6$H$_6$, $M = 78$) is 279 K while that of biphenyl (C$_6$H$_5$-C$_6$H$_5$, $M = 154$) is 342 K. This is because the intermolecular van der Waals interaction is larger in the crystalline phase with better molecular packing than that in the liquid phase with worse packing.

Recently, Nakanishi group in NIMS found a series of large molecules which exist in liquid states at room temperature. These molecules have π-conjugated cores such as pyrene, naphthalene, anthracene, fullerene, phthalo cyanine and long alkyl chains bonded to the cores [1]. We consider that these alkylated molecules are stabilized by the large entropy effect which is caused by the conformational disorder of alkyl chains. This situation is similar to that of ionic liquids which are in liquid states in spite of their strong inter-ionic interactions. We collectively call this type of liquids “super-high entropy liquids (SHEL)”. The physico-
Magnetic States of Coupled Spin Tubes with Frustrated Geometry in CsCrF₄

Masuda Group

When a theoretical model is realized in nature, small perturbation terms play important roles in the selection of the ground state in geometrically frustrated magnets. In case of a triangular spin tube, the two-dimensional network of the inter-tube interaction forms characteristic lattices. Among them Kagome-Triangular (KT) lattice in Fig. 1(a) is known to exhibit an enriched phase diagram [1] including various types of non-trivial structures: non-coplanar cuboc structure, coplanar 120° structure with the two-dimensional propagation vector of \( k_{2D} = 0, \sqrt{3} \times \sqrt{3} \) structure with \( k_{2D} = (1/3, 1/3) \), and incommensurate structure as shown in Fig. 1(b). We investigate the magnetic state in the model material CsCrF₄ in Fig. 1(c) and 1(d) by using neutron diffraction technique. Temperature evolution of the diffraction profile was collected as shown in Fig. 2(a). Combination of representation analysis and Rietveld refinement reveals that a very rare structure, i.e., a quasi-120° structure with \( k_{2D} = (1/2, 0) \) in Fig. 2(b), is realized at the base temperature. The classical calculation of the phase diagram elucidates that CsCrF₄ is the first experimental realization of the KT lattice having ferromagnetic Kagome bond. A single-ion anisotropy and Dzyaloshinskii-Moriya interaction play key roles in the selection of the ground state. Furthermore, a successive phase transition having an intermediate state represented by \( k_{2D} = (1/3, 1/3) \) is observed. The intermediate state is a partially ordered 120° structure in Fig. 2(c) [2].

This study was originally initiated for the neutron study of the Tomonaga-Luttinger liquid predicted in a spin tube using JRR-3 research reactor before east Japan earthquake in 2010. Since the magnetic state is sensitive to impurity in the titled compound, we need to check the reproducibility of the data carefully. As a result, the quality of some samples used at JRR-3 were not good, and we needed to redo the experiment on selected high-quality sample using foreign neutron facilities after 2010. All of the published data in Ref. [2] were, thus, collected at ECHIDNA spectrometer in ANSTO Australia. Furthermore, the difficulty of the transportation of radioactive material such as Cs after the earthquake made the situation complicated. Thanks to many people including scientists, technicians, and office staff, we completed the project.

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Authors
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Magnetic State Selected by Magnetic Dipole Interaction in Kagome Antiferromagnet NaBa₂Mn₃F₁₁

Masuda and Hiroi Groups

Long-range magnetic dipole-dipole (MDD) interaction is ubiquitous in nature. In most bulk magnets, the MDD interaction is not necessarily a primary interaction because its energy scale is much smaller than an exchange interaction. The MDD interaction, however, plays a key role in geometrically frustrated magnets, where the geometry causes macroscopic degeneracy of the magnetic state. For instance, the origin of an exotic monopole state in pyrochlore oxides is explained by the MDD interaction [1]. The frustrated geometry and the MDD interaction are, thus, a good combination for search of a new magnetic state.

In a classical Heisenberg kagome antiferromagnet, the ground state is known to be 120° structure with an infinite...
degeneracy. A small perturbation lifts the degeneracy and selects a unique structure, e.g., an all-in-all-out structure in case of Dzyaloshinskii-Moriya interaction [2]. The MDD is theoretically predicted to select a tail-chase structure (Fig. 1(a)) [3]. Such a structure, however, has not been experimentally identified yet to date. NaBa$_2$Mn$_3$F$_{11}$ having a unique kagome-triangular lattice was synthesized by Hiroi group in ISSP [4]. It exhibits an antiferromagnetic transition at $T_N = 2$ K. The estimated Curie-Weiss temperature of -32 K is smaller than those of many kagome magnets, indicating that the exchange spin interaction is small. The MDD interaction may be important for the determination of the magnetic state.

Recently we carried out neutron powder diffraction experiment to identify the magnetic structure of NaBa$_2$Mn$_3$F$_{11}$ [5]. We observed magnetic Bragg peaks at 0.25 K as shown in Fig. 1(b). They were indexed by a commensurate magnetic propagation vector $k_0 = (0,0,0)$, and two incommensurate vectors $k_1 = (0.3209,0.3209,0)$ and $k_2 = (0.3338,0.3338,0)$. The magnetic structure analysis by combination of Rietveld refinement and the representation analysis reveals that the tail-chase 120° structure modulated by the incommensurate vectors gives a satisfactory agreement with the experiment. Furthermore, we calculated the phase diagram with the parameters of the nearest- and second-neighbor exchange interaction, and MDD interaction. We identified that the MDD interaction solves the infinite degeneracy and selects the tail-chase 120° structure in NaBa$_2$Mn$_3$F$_{11}$. For the future perspective, the study of magnetic dynamics is beneficial for the search for exotic sates such as zero-energy mode induced by the MDD interaction.

References

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\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig1.png}
\caption{Overall view of the CL coil and the measurement probe setting. The liner vacuum chamber (made of the Bakelite cylinder and the acrylic resin plastic plates) with the measurement probe is firmly furnished to the CL primary coil with high precision.}
\end{figure}
50-mm length) undergoes high-speed implosion (above 5 km/s) accelerated by the magnetic force induced by a huge electric current injected to the primary coil (3–4 mega-Ampere) about its circumference, and the magnetic flux (3.2 T) initially generated in a large volume (diameter 120 mm, length 50 mm) is compressed finally into a small space (3 mm diameter, 20–30 mm length), and reaches a megagauss magnetic field of up to 1200 T. The CL coil was designed to improve the energy transfer efficiency of the imploding liner. The copper lining part bears the current, whereas the massive outer steel coil holds the inertia for the liner acceleration. A liner vacuum chamber with measurement probes are attached to the steel outer coil as shown in Fig. 1. Thus, measurement probes are set precisely at the liner implosion center with respect to the CL coil.

The signals obtained in this work are plotted in Fig. 2. Details are provided in our recent paper [4]. The dotted line is a signal taken from the pickup coil (BP), measured up to 600 T, and the green solid line measures the fields up to 1200 T by FR (BF). The liner imploding images are shown by black circles. The estimated liner inner diameter at each magnetic field intensity is given in axis of abscissa.

Fig. 2. Magnetic field intensity recorded up to 1200 T with an evolution of time. Upper panel: Faraday rotation signal (VFR) synchronized with the magnetic field intensity. The dotted line taken from the pickup coil (BP), measured up to 600 T, and the green solid line measures the fields up to 1200 T by FR (BF). The liner imploding images are shown by black circles. The estimated liner inner diameter at each magnetic field intensity is given in axis of abscissa.

Fig. 2. (a) Transverse magnetoresistance and (b) ultrasound attenuation in single crystals of PbTe. Quantum oscillations are clearly resolved in both experiments.

References


Authors


Determination of “Diracness” in PbTe
Tokunaga Group

One of the hottest research subjects in condensed matter physics is so-called topological materials, in which dynamics of charge carriers are expressed by the relativistic equations of motion that are utilized in research field of high energy physics. Since the relativistic Dirac/Weyl equations show characteristic linear dispersion relation, a great number of experimental and theoretical studies have been devoted to explore the linear dispersion as schematically shown in Fig. 1(a), which is distinguished from the parabolic one shown in Fig. 1(b). This parabolic dispersion, however, is merely the expanded view of the trace in Fig. 1(a) at around the origin. Therefore, argument based only on the appearance of the dispersion is sensuous and insufficient to quantitatively distinguish the Dirac/Weyl system from the others. As the

Fig. 1. (a) Schematic dispersion relation of kinetic motion of particles that is expressed by relativistic Dirac equation, which shows characteristic linear dispersion in wide range of the k-space. (b) Expanded view the same dispersion relation with that in (a), which appears as parabolic in this region.

Fig. 2. (a) Schematic dispersion relation of kinetic motion of particles that is expressed by relativistic Dirac equation, which shows characteristic linear dispersion in wide range of the k-space. (b) Expanded view the same dispersion relation with that in (a), which appears as parabolic in this region.

Fig. 1. (a) Schematic dispersion relation of kinetic motion of particles that is expressed by relativistic Dirac equation, which shows characteristic linear dispersion in wide range of the k-space. (b) Expanded view the same dispersion relation with that in (a), which appears as parabolic in this region.
quantitative indicator that characterizes similarity of a system with the ideal Dirac system, which is called as “Diracness” in the following, we focus on the ratio between Zeeman and cyclotron energies (ZC ratio). Recent theoretical studies revealed that this ZC ratio becomes unity for the ideal Dirac system [1,2]. Relative magnitude of the ZC ratio and unity is predicted to invert when topology of a material changes from trivial to non-trivial.

To experimentally determine the ZC ratio, we studied quantum oscillations in single crystals of PbTe through measurements of magnetoresistance (Fig. 2(a)), magnetization, and ultrasound attenuations (Fig. 2(b)) in DC and pulsed high magnetic fields [3]. By measuring quantum oscillations up to the quantum limit state and comparing the results with the standard Lifshitz-Kosevich formula [4], we determined the ZC ratio of PbTe as 0.52. In this analysis, we clarified that when the ZC ratio becomes larger than one half, peak-dip relation in the quantum oscillation will be reversed, which will appear as the phase shift in the Landau level fan diagram. The results demonstrate that observation of spin-split quantum oscillations is crucially important to discuss the origin of the phase shift.

References

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Short-Range Spin Correlations in a Quantum Magnet Detected Through Magnetoelastic Couplings in a Kagome Quantum Spin Lattice

Y. H. Matsuda, Takeyama, and Hiroi Groups

In case of quantum magnets, magnetostriction can be a unique measure of short-range spin correlations. The spin components perpendicular to the external magnetic field is inherent in the local spin correlation. In quantum magnets, magnetostriction measurement is a direct measure of the local spin correlation.

We have recently developed a high-speed 100 MHz magnetostriction measurement system utilizing the fiber Bragg grating techniques [1] for the use in the µ-seconds pulsed magnetic fields beyond 100 T (megagauss region) and 1000 T (kilo-Tesla region) [2]. We found later that the system can also be used in the milli-seconds pulsed magnetic fields below 100 T with an appreciable high-resolution of $\Delta L / L \sim 10^{-6}$ [3]. Using the developed instrument, we have conducted the magnetostriction measurement for the two-dimensional quantum magnet of volborthite [4].

Volborthite ($\text{Cu}_3\text{V}_2\text{O}_7\text{(OH)}_2 \cdot 2\text{H}_2\text{O}$) is a fascinating example of a highly frustrated quantum magnet. In its magnetic layer, Cu ions possessing spin-1/2 moments form a deformed kagome lattice as schematically shown in Fig. 1(a).

![Fig. 1. (a) The lattice model of volborthite (b) Coupled trimer model for volborthite (c) A schematic drawing of the pantograph-like lattice modification of the magnetostriction in the crystallographic b axis.](image)

Owing to the lattice deformation, the anisotropic microscopic spin model based on coupled trimers as shown in Fig. 1(b) has recently been proposed, that now attracts attention as it provides a mechanism for a field-induced spin nematic phase adjacent to the 1/3 magnetization plateau. In the spin nematic phase, spin directors that break the in-plane rotational symmetry are formed as a result of the Bose-Einstein condensation of bimagnon excitations. The rotational symmetry breakings take place in the lateral direction of the spin space, which thus implies that the measurement of the lateral spin-correlation in this magnet is quite important.

Figures 2(a)-(c) shows the result of the magnetostriction

![Fig. 2. (a) Magnetostriction curves of volborthite (b) Magnetization curves of volborthite (c) A comparison of the curves of magnetostriction and magnetization indicating a peculiar dependence of $\Delta L - M^3$](image)
measurement. A negative magnetostriction and a peculiar dependence of the magnetostriction on the magnetization as $\Delta L \sim M^{1.3}$ are observed. The negative magnetostriction in the crystallographic $b$ axis is understandable with a pantograph-like lattice modification. As shown in Fig. 1(c), the Cu-O-Cu chain in the $b$ axis is responsible for the ferromagnetic superexchange interaction in the coupled trimer model. The closer the bond angles to 90 degree, the stronger the ferromagnetic exchange couplings due to the Kanamori-Goodenough rule, where, as a result, the bond length in the $b$ axis is elongated. The story is supported by a tentative DFT+$U$ calculations [4]. On the other hand, the peculiar dependence of the magnetostriction on the magnetization can also qualitatively understood as a manifestation of the short-range spin correlation within the exchange striction model. In the exact-diagonalization approach, it becomes clear that the spin-correlation is indeed in between the $M^{1.0}$ and $M^{2.0}$ and close to $M^{1.3}$. For further studies in the future, the spin-nematicity may show abnormal magnetoelastic response at even lower magnetic fields at around 28 T. Another possible study is the measurement beyond 100 T. The end of the 1/3 magnetization plateau may be detected in the magnetostriction measurement.

References

Authors
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Semi-Metallicity of Free-Standing Hydrogenated Monolayer Boron from MgB$_2$
I. Matsuda Group

Two-dimensional monatomic layers in van der Waals crystals or on solid surfaces have wide attention because of their unique physical properties and potential applications in quantum devices. There has been growing interests in layers of Xenes. Recently, borophene layers were discovered and found to have Dirac fermions. However, in contrast to graphene, these Xene layers form only on solid surfaces. It is, thus, necessary to develop technique to passivate it chemically so it can be placed on any substrate under ambient conditions.

In the present research, we synthesized a free-standing hydrogenated monolayer boron (HB) sheet and studied the electronic states via soft X-ray spectroscopy at the B K-shell absorption edge and the first-principles calculations [1]. As shown in Fig. 1, the HB sheet is semi-metallic with electron and hole pockets at symmetry points of $\Gamma$ and $Y$, respectively. The electron band results from the B-H-B bonds formed during synthesis from a MgB$_2$ crystal, while the hole band is kept through the process and originates from a honeycomb lattice boron layer or borophene in MgB$_2$. Figure 2 shows a summary of the calculation for a MgB$_2$ crystal. One can find the one-to-one correspondence between wave-functions of the $\alpha_1$-state in HB and the $\delta_2$-state in MgB$_2$. The present research reveals a relation between the surface treatment of monatomic layer and evolutions of the two-dimensional states, giving clues to design novel functional layers.

Reference
Interfacial Carrier Dynamics of Graphene on SiC, Traced by the Full-Range Time-Resolved Core-Level Photoemission Spectroscopy at SPring-8 BL07LSU

I. Matsuda Group

Time evolutions of the Dirac Fermions in graphene layers have attracted both academic and technological interests due to observations of the various intriguing opto-electric phenomena, such as carrier multiplications and generation of a terahertz laser. Nowadays, graphene layers can be epitaxially grown on a SiC substrate in wide area and such non-equilibrium carriers in the Dirac bands have been directly probed by time-resolved photoemission spectroscopy. On the other hand, the previous studies focused only on electronic evolutions within a graphene layer and little examination was made on carrier dynamics through the graphene/substrate interfaces. Unveiling dynamic roles of the graphene/SiC interface is necessary to understanding the opto-electric properties in SiC based detectors, for example.

In the present research, we conducted measurements of time-resolved core-level photoemission spectroscopy by a combination of laser and synchrotron radiation [1]. The experiment was performed at SPring-8 soft X-ray beamline BL07LSU with the beamline laser station, BL07LASER. Figure 1 shows temporal variations of peak positions of C 1s and Si 2p during relaxation of the surface photovoltage effect, induced by the optical pumping with a laser pulse. Two C 1s components are assigned to a graphene layer (G) and a SiC substrate (SiC), while one Si 2p component originates from a SiC substrate. Thus, the high-resolution core-level spectra selectively distinguish dynamical information between overlayer and substrate. While the whole relaxation of the electron-hole recombination process takes 100 nanoseconds, one can also find difference in temporal variation between C and SiC in the subnanosecond region. This is because carrier lifetime in the graphene layers take longer than that of the typical interface-state of SiC by the bottleneck effect of Dirac cones. When there is a buffer layer between graphene and SiC, electron-hole recombination is dominantly held at the interface and the lifetime shortens one-order of the magnitude [1]. The selective evaluations of carrier dynamics in non-uniform samples, such as heterojunctions, allow one to design and develop novel optoelectric devices.

Reference

Polarization Resolved High Harmonic Generation in Semiconducting Gallium Selenide

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Recent progress in ultrafast laser technology has realized to produce strong optical fields in the mid-infrared to terahertz spectral regions. Emergence of such intense long-wavelength light sources triggers ultrafast strong-field physics for condensed matters. When crystalline materials are irradiated by intense mid-infrared pulses, for example, extreme ballistic oscillation of electrons in a conduction band with terahertz to petahertz frequencies occurs, and high-order harmonics are often produced beyond a typical bandgap of solids. So far, most of the experiments employ one-dimensional study along a specific direction. However, we show that a one-dimensional model is not suitable to investigate...
polarization property of HHG in solids.

In this study, we investigate polarization properties of high harmonics produced in a 30-µm-thick gallium selenide (GaSe, ε-type, [001] z-cut, hexagonal structure, non-coat). The crystal is exposed to linearly polarized femtosecond mid-infrared pulses with a field amplitudes of ~10 MV/cm that are produced from a dual-wavelength optical parametric amplifier (wavelength: 5 µm, maximum pulse energy: 15 µJ, pulse duration: 200 fs, repetition rate: 1 kHz) [1]. The crystallographic orientation dependence of high harmonic spectra is measured after a set of wire-grid polarizers in the either parallel (Fig. 1(a), (c), (e), and (g)) or perpendicular (Fig. 1(b), (d), (f), and (h)) to the mid-infrared field. The observed high harmonics are extended up to the 11th order (2.70 eV, 460 nm) beyond the bandgap (1.98 eV, 625 nm). All even harmonics for both polarizations show modulations with 60° periodicities, which is consistent with the hexagonal structure of a GaSe crystal. In contrast to the even harmonics, the parallel and odd harmonics show 60° modulation on top of a constant offset as in Figs. 1 (e) and (g) for the third and fifth harmonics, respectively. More surprisingly, the perpendicular odd harmonics appear with 30° periodicity as can be seen in Figs. 1(f) and (h). This 30° periodicity cannot be intuitively understood from the hexagonal structure of the crystal.

To explain these results, a two-dimensional single-band model described by the Bloch theorem is used [2]. This model assumes that (i) the intraband current dominates odd harmonics and (ii) the electron wavepacket is launched around the Γ point. Detailed explanation of the model and a verification of these assumptions can be found in Ref. [3]. We found that the band curvature (Figs. 2 (b) and (c)) of the lowest conduction band (Fig. 2(a)) along the electron trajectory is responsible for the source of odd-order harmonics. Based on the two-dimensional single-band model, the parallel and perpendicular odd harmonics are calculated to show 60° and 30° periodicities as can be seen in Figs. 2(d) and (e), respectively. These results well reproduce the experimental observations of the orientation dependences and the polarization property for all odd harmonics.

In summary, we have investigated a polarization property of high harmonics from a bulk GaSe crystal using femtosecond MIR pulses and their dependence on crystallographic orientation. With the 10 MV/cm electric field, the perpendicular odd harmonic emerges with a periodic modulation of 30°, which cannot be explained by the perturbative nonlinear optics. The underpinned physics of the perpendicular component of the odd harmonics is attributed to anisotropic momentum dependence of the band curvature along the electron trajectory, which is equivalent to the inverse effective mass. Our demonstration establishes a direct link between the band structure and HHG in a crystalline solid. Multi-dimensional analysis combined with time-resolved measurement allows to investigate electron dynamics and field-dressed structure of energy bands in future.

References

Authors
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