Half-Magnetic Topological Insulator with Magnetization-Induced Dirac Gap at a Selected Surface

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The recent discovery of the intrinsic magnetic topological insulator (TI) $MnBi_2Te_4$ and $MnBi_2Te_4/(Bi_2Te_3)_n$ (n=1,2,3,...) have boosted exciting possibilities of producing exotic quantum phenomena by engineering topology and magnetism at the atomic scale [1-4]. Such magnetic TIs are promised to host two exotic quantum phenomena: the "quantum anomalous Hall effect" and the "axion insulating state" [5, 6]. The former has integer-quantized surface Hall resistivity, while the later might present Half-quantized surface resistivity. However, partially because of the lack of a suitable material, it is still not clear if the Half-quantized surface resistivity can be observed in transport measurement, lacking the direct proof of the "axion insulating state".

In this study, we performed a μ -Laser-angle-resolved photoemission spectroscopy (μ -Laser-ARPES) on an intrinsic ferromagnetic TI, MnBi₂Te₄-(Bi₂Te₃)₃ (MnBi₈Te₁₃), and demonstrated that MnBi₈Te₁₃ can be an ideal platform to explore and manipulate the exotic half-quantized surface resistivity. The energy bands show a Dirac gap at the magnetic MnBi₂Te₄ layer but gapless Dirac cone at its nonmagnetic Bi₂Te₃ layers in the opposite side. Remarkably, the magnetic Dirac gap (~ 28 meV) decreases monotonically with increasing temperature and closes right at the Curie temperature (as shown in Figure 1), smoking-gun evidence of magnetization-induced topological surface gap among all known magnetic topological materials.

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FIGURE 1. ARPES results of the Dirac gap evolution with temperature at the magnetic MnBi₂Te₄ layer of MnBi₈Te₁₃. Spectra

are shown in the form of original ARPES spectra (top row) and 2D curvature spectra (bottom row). Black dashed line indicates the position of gapless Dirac point.

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Observation of spin-momentum-layer locking in a centrosymmetric crystal

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The spin polarization in nonmagnetic materials is conventionally attributed to the outcome of spin-orbit coupling when the global inversion symmetry is broken. The recently discovered hidden spin polarization indicates that a specific atomic site asymmetry could also induce measurable spin polarization, leading to a paradigm shift in research on centrosymmetric crystals for potential spintronic applications. Here, combining spin- and angle-resolved photoemission spectroscopy and theoretical calculations, we report distinct spin-momentum-layer locking phenomena in a centrosymmetric, layered material, BiOI. The measured spin is highly polarized along the Brillouin zone boundary, while the same effect almost vanishes around the zone center due to its nonsymmorphic crystal structure. Our work not only demonstrates the existence of hidden spin polarization, but also uncovers the microscopic mechanism of spin, momentum, and layer locking to each other.

BiOI has a tetragonal crystal structure with a centrosymmetric space group P4/nmm containing nonsymmorphic operations of a glide mirror $\{M_z | (\frac{1}{2}, \frac{1}{2}, 0)\}$ and two screw axes $\{C_{2x} | (\frac{1}{2}, 0, 0)\}$, $\{C_{2y} | (0, \frac{1}{2}, 0)\}$. The inversion center is located in the middle of two inequivalent O atoms (site point group D_{2d}), while the Bi and I atoms occupy the noncentrosymmetric polar sites with the site point group C_{4v} . The polyhedrons coordinated by Bi and I atoms are intersected by the O plane. Hence, the quasi-2D unit cell is divided into two sectors α and β , respectively, as shown in Fig. 1(a).

The BZ and DFT-calculated electronic structures of BiOI with SOC are shown in Fig. 1(b) and 1(c). The valence band maximum (VBM) is close to the X point. It is noticeable that at the points X and M, the glide reflection symmetry $\{M_z | (\frac{1}{2}, \frac{1}{2}, 0)\}$ anticommutes with the inversion operator, leading to an extra two-fold degeneracy between two pairs of Kramer's degeneracy, i.e., four-fold degeneracy including the spin. Such a four-fold degeneracy is maintained along the entire X-M line in the absence of SOC. Thus, the band splitting along the X-M line shown in Fig. 1(c) is caused by SOC solely. In analogy to the conventional Rashba/Dresselhaus effect, such a splitting is composed of two sets of spin splitting bands originating from the sectors α and β , respectively [1]. In comparison, the splitting along the X-M line. The orbital projection analysis shows that in the vicinity of the points Γ and X, the top two valence bands (designated as VB1 and VB2) are mainly composed of the $p_x + p_y$ and s orbitals, while VB3-VB6 are dominated by the p_z and s orbitals.

The ARPES results measured at a photon energy of 65 eV are shown in Fig. 1(d) [constant energy contours (CECs)], Fig. 1(e), 1(f) (band dispersions) and Fig. 1(g), 1(h) [energy-distribution curves (EDCs)]. A square-like CEC exists at -1.3 eV, with corners located at X points. As the energy decreases, the CEC features at the X point expand and eventually form contours surrounding the M point, merging with those centered at the Γ point. This hole-like behavior is presented in the ARPES spectra along the M-X-M line in Fig. 1(e). From the CECs and spectra results, we have found that the VBM is located around the bulk X point, ~1.4 eV below the experimental Fermi level.

By directly comparing the calculated bulk band structure with the ARPES data shown in Fig. 1(e) and 1(f), a good agreement is found, indicating that the surface effect that breaks the global inversion symmetry is relatively weak. The predicted four-fold degeneracy at the X and M points and the splitting two-fold

degenerate branches (VB1 to VB6) away from X and M are all supported by the ARPES measured dispersion. Furthermore, Fig. 1(g) and 1(h) show the EDCs measured along the M-X-M and X- Γ -X directions. At the X point, the degenerate peaks, *i.e.*, $X_{1,2}$, $X_{3,4}$ and $X_{5,6}$ are unambiguously present, while at the Γ point, each of the degenerate peak splits into two individual peaks, *i.e.*, Γ_1 to Γ_6 . Consequently, three pairs of Rashbalike hole-type valence bands are formed at the X and M points, with the band crossing points located around -1.4 eV, -2.1 eV, and -3.0 eV for the X point, respectively (Fig. 1(e)). These results agree well with our calculation, thus confirming the nonsymmorphic feature of the material.



FIGURE 1. (a) The crystal structure of BiOI. The unit cell consists of two BiI layers as inversion partners, labelled as a sector α and β . (b) The bulk Brillouin zone. (c) DFT-calculated bulk band dispersion with orbital projection. (d) ARPES-measured CECs of the valence bands at different energies. (e, f) ARPES-measured spectra along the X-M, and Γ -X high symmetry lines, overlaid by DFT calculated dispersions (solid black lines). (g, h) EDCs corresponding to the spectra shown in (e) and (f), respectively. The lower parts are the EDCs at X and Γ points, respectively, from which one can resolve the spectral peaks corresponding to the top six valence bands.

Figure 2 presents the in-plane spin polarization of BiOI measured by spin-ARPES using photon energies of 65 eV for panels (a, b) and 30 eV for panels (c, d). The wide-ranging measurements involving different photon energies and geometries verified that we have essentially observed the spin polarization and spin textures derived from the initial state. The representative spin EDCs for the three pairs of two-fold degenerate bands VB1-VB6 are shown in Fig. 2(b) and 2(d), with the upper (lower) row showing the spin-resolved EDCs and the corresponding S_y (S_x) spin component. At three time-reversal invariant points M, X and Γ (momentum points (1), (3) and (8)), the spin-resolved EDCs overlap, indicating negligible spin polarization; this is consistent with the spin degeneracy originating from Kramer's pairs.

When the momenta moved away from the X point, we have observed significant spin polarization (up to 80%) along both k_x and k_y directions (momentum points (2), (4), (5) and (6)). For momenta (5) and (6), nearly all the six VBs were resolved as the individual polarizations peaked with opposing polarization signs in each pair. This is because the band splitting along Γ -X direction was more significant compared to the splitting along the X-M direction (Fig. 1(c), 1(e), 1(f)). In sharp contrast, the spin polarization surrounding the Γ point was very weak (<30% for momentum point (7), along both k_x and k_y directions.

The detected photoemission signal mainly arises from the topmost sector (α) of the cleaved BiOI single crystal, which is favourable to detect the spin polarization from a local sector. Compared with the previous measurements of HSP materials such as WSe₂[3], PtSe₂[4], LaO_{0.55} F_{0.45}BiS₂[5] and Bi2212 [6] that focus on the spin-momentum locking around a single high-symmetry point, our work revealed the distinct polarization features surrounding different high-symmetry points, i.e., BZ center (Γ) and BZ boundary (X), and observed a sharp contrast between them. Such observations suggest that momentum-dependent spin polarization originates from the HSP rather than merely from the surface potential gradient; further, these observations suggest the key factors affecting the HSP effect, such as the nonsymmorphic symmetry and

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orbital characters.



FIGURE 2. (a), (c) Band dispersion along M-X and Γ -X directions, respectively. The inset shows the BZ, with black dots indicating the momentum positions where the spin-resolved EDCs are measured. (b), (d) Spin-resolved EDCs and spin polarizations. Each panel's number corresponds to the momentum point denoted by the pink dashed lines in (a), (c). The green error bars indicate the statistical fluctuation in determining the spin polarizations (proportion $1/\sqrt{N}$; where N is the photoemission intensity).

In summary, combining spin-ARPES measurements and theoretical calculations, we report distinct spinmomentum-layer locking phenomena at different BZ positions in a centrosymmetric material BiOI. The measured spin polarization localized on a specific BiI layer is highly polarized along the BZ boundary but almost vanishes around the zone center due to its nonsymmorphic crystal structure. The layer-resolved spin texture, either Rashba or Dresselhaus type, reflects the symmetry of both real space and *k*-space. Our findings experimentally demonstrate the existence of the HSP effect and shed light on the design metrics to utilize high spin polarization in centrosymmetric materials by revealing the intimate interplay between spin, orbital, and layer degrees of freedom.

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Low-energy electron-boson coupling in Sr₂RuO₄

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Recently, spin-triplet superconductivity, in which individual electron spins are aligned in parallel in the electron pairs that form the superconductivity, has attracted much attention. Since most superconductors are spin-singlet superconductors with antiparallel electron spins, the elucidation of the mechanism of electron pair formation in spin-triplet superconductors is expected to provide essential guidelines for designing roomtemperature superconductors. The ruthenium oxide superconductor Sr₂RuO₄ has been extensively studied as a strong candidate for the spin-triplet superconductors. In particular, angle-resolved photoemission spectroscopy (ARPES) experiments have been widely believed to observe the electron-boson (phonon, magnetic fluctuation, etc.) coupling as a sudden change of the band dispersion, which might be involved in pair formation. Indeed, many previous ARPES results reported the existence of electron-boson interactions fingerprinted by a "kink" structure in the γ -band derived from Ru $4d_{xy}$ orbital. On the other hand, the latest high-resolution ARPES study, which measured the electronic states near the Fermi energy (E_F) , reported that the electrons and bosons are not strongly coupled [1]. Such a discrepancy could be attributed to the fact that the existing ARPES measurements only focused on the near- $E_{\rm F}$ region and could not accurately evaluate electron correlations with an energy scale 10 to 100 times larger than that of the boson mode ($\leq 100 \text{ meV}$). This suggests that we need to observe not only the band structures in the vicinity of the $E_{\rm F}$ but also the entire band structure for the accurate identification of coupling components by ARPES. In this regard, to separate and evaluate multiple types of the many-body effects, we have performed both soft X-ray (SX-) and vacuum ultra-violet (VUV-) ARPES by observing the entire band structure and detailed band structure in the vicinity of the E_F, respectively. SX- and VUV-ARPES experiments were performed at SPring-8 BL25SU and SSRL BL5-2, respectively, and preliminary VUV-ARPES experiments were performed at HiSOR BL-1.

Figures 1(a) and 1(b) show the Fermi surface and ARPES images using hv = 450 eV (SX) and 65 eV (VUV), respectively. In both SX-ARPES and VUV-ARPES results, the observed Fermi surfaces clearly show the three band-structures (α , β , and γ), originating in the bulk Ru 4d t_{2g} orbitals. First, we focus on the SX-ARPES image in the X-M-X direction, where the α band was observed entirely and showed a parabolic dispersion shape. This enables us to evaluate the electron correlation effects accurately because the α band shows negligible dependence on the perpendicular momentum (k_z) as well as the spin-orbit coupling in this direction. Next, we focus on the γ band in the Γ/Z -M direction because it shows the largest effective mass, namely, the electrons most strongly affected by the many-body interaction there. Then, we have determined the γ band dispersion by fitting the momentum distribution curves (MDCs) as shown in the blue-filled circles in Fig. 1(c), where a phenomenological model dispersion is also shown. The model dispersion was calculated by including the electron correlation effects with the estimated strength from the SX-ARPES results. One can see that the experimental dispersion is not reproduced by the model calculations, including the electron correlation effects. This indicates that the electron-boson coupling should be considered to explain the mass renormalization effects in the γ band.

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The electron-boson coupling could be more visualized in the real part of the self-energy shown in Fig. 1(d), induced by taking the energy difference between the experimental and model dispersion. Interestingly, we found a clear shoulder structure at ~ -8 meV, corresponding to the energy of the kink structure in the band dispersion as indicated by the orange line in Fig. 1(c). The kink energy is consistent with the Σ_3 phonon mode, the in-plane rotation of the RuO₆ octahedron, as observed by a neutron scattering experiment [2]. In addition, a strong coupling between the Σ_3 phonon mode and ferromagnetic fluctuations has been suggested by a scanning tunneling microscopy and theoretical study [3]. Therefore, we believe that our results reveal the strong electronic coupling to the ferromagnetic fluctuations mediated by the Σ_3 phonon mode. This may suggest the formation of the spin-triplet electron pair mediated by a magnon-phonon coupling.



FIGURE 1. (a) SX-ARPES data: Fermi surface and band dispersion along the M-X-M direction taken with a photon energy of 450 eV below 35 K with the circular polarization. The solid black line represents a phenomenological model dispersion ($\lambda_{EEI} = 1.0$). (b) VUV-ARPES data: Fermi surface and band dispersion along the Γ/Z -M direction taken with a photon energy of 65 eV below 10 K with the *p*-polarization. (c) The γ band dispersion in the vicinity of the *E*_F determined by the MDC fitting (d) Real-part of the self-energy very close to the *E*_F.

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Optimization of self-energy in high-*T*_c **cuprate superconductor La**_{2-x}**Sr**_x**CuO**₄

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Keywords: Cuprate, ARPES

For the revealing mechanism of high-temperature superconductivity in cuprates, many-body interactions have been extensively investigated by angle-resolved photoemission spectroscopy (ARPES). However, it had been challenging to obtain high-quality ARPES spectra from crystal systems having strong threedimensionality such as $La_{2-x}Sr_xCuO_4$ (LSCO) due to the roughness of a cleavage plane. On the other hand, in recent years, spectral quality has been improved as developing experimental equipment and performance, enabling us to obtain fine electronic states and study many-body interactions even in three-dimensional systems. Indeed, a recent ARPES study on an overdoped LSCO (x=0.23) examined quasiparticle scattering rate $\Gamma(\omega)=2Im\Sigma(\omega)$ as expressed by using the imaginary part of the self-energy, and claimed its energy dependence deviates from the Fermi liquid behavior [1]. However, since the analysis of the scattering rate is based on only electron-electron interaction, it is necessary to consider other many-body interactions such as electron-boson interaction (boson: phonon or magnon, etc.), which dominates the quasiparticle scattering in the vicinity of the Fermi level. In this work, we have thus examined the band structure in a wide energy range on an optimally doped LSCO using a high-resolution ARPES to understand the role of many-body interactions in this system.

High-quality single crystals of optimally doped LSCO (x=0.155, $T_c \sim 39$ K) were prepared by the traveling-solvent floating-zone technique. ARPES experiments were measured at the linear undulator beamline (BL-1) of Hiroshima Synchrotron Radiation Center (HiSOR) using an R4000 electron analyzer (Scienta Omicron). Clean surfaces of the samples were obtained by cleaving *in situ* under ultra-high-vacuum conditions (4×10⁻⁹ Pa) at a low temperature (~27 K). Present ARPES data were taken with the photon energy of 70 eV at 27 K in the *s*-polarization geometry.

Figure 1(a) shows the ARPES image of the optimally doped LSCO taken along the nodal direction, where the circles represent the band dispersions determined by fitting momentum distribution curves (MDCs). The ARPES dispersion was then compared with the calculated dispersion by the tight-binding (TB) model [2], as shown in Fig. 1(b). Assuming the TB model dispersion as a non-interacting or bare band, we found that the experimental dispersions show a larger effective mass in the vicinity of the Fermi level, while a smaller one in the higher energy region. This dispersion behavior is an indication of the high-energy anomaly widely observed in the strongly correlated electron systems. Moreover, we found that the maximum of the real part of the self-energy locates at around 0.3 eV, which agrees well with the energy-scale of the antiferromagnetic spin fluctuations as reported by resonant inelastic X-ray scattering (RIXS) measurements [3]. Our results thus indicate that the antiferromagnetic spin fluctuations play an important role in large energy-scale band renormalization effects in LSCO.

To visualize the renormalization effects more clearly, we extracted the real and imaginary parts of the self-energy as shown in Figs. 1(c) and 1(d), respectively. Here, we first fitted the experimental results (circles) by the model self-energies, including the electron-phonon interaction, the electron-electron interaction, and the final-states effects with the impurity scattering [4]. Then, using the obtained fitting

parameters, we calculated the real-part of the self-energy. As clearly seen in Figs. 1(c) and 1(d), the real and imaginary part of the self-energy shows the excellent agreement between the experimental and fitting results. The present results thus validate the experimentally induced self-energy and allow us to evaluate the coupling strength of the many-body interactions quantitatively. In this talk, we will discuss the coupling strength of the electron-electron and electron interaction in cuprate systems. Also, we will introduce a new analysis method based on machine learning for deducing an optimized self-energy and bare band.



Figure 1. (a) APRES image of optimally doped LSCO taken along the nodal direction at a photon energy of 70 eV below 27 K with *s*-polarization geometry. (b) Comparison of the MDC-derived band dispersion (circles) and TB model (solid line) band dispersion. (c) and (d) Imaginary and real parts of the self-energy, respectively: ARPES self-energy (circles) and model self-energy (solid line) including the electron-phonon interaction (orange line), the electron-electron interaction (blue line), and the final states effects with the impurity scattering (green line).

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Gap inhomogeneity in Bi₂Sr₂CaCu₂O_{8+δ} revealed by laser micro-ARPES

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Keywords: micro-ARPES, high-Tc superconductivity, Bi2212

Since the discovery of the high- T_c superconductivity in copper oxides (cuprates), the cuprate superconductors have been extensively investigated experimentally and theoretically. Nevertheless, the mechanism of the high- T_c superconductivity has not been clarified yet. The order parameter, the superconducting gap, of the high- T_c superconductivity has been particularly investigated. Angle-resolved photoemission spectroscopy is known as the powerful tool to prove the superconducting gap in a momentum-resolved manner, which fingerprinted the *d*-wave gap symmetry. On the other hand, scanning tunneling spectroscopy/microscopy allows to observe the superconducting gap, and the nano-scale inhomogeneity was in the real-space was reported in Bi₂Sr₂CaCu₂O_{8+δ} (Bi2212) [1]. However, such real-space inhomogeneity has not been fully considered in the conventional ARPES studies due to its poor spatial resolution (~ mm scale). To overcome this problem and study the evolution of the superconducting gap in the real- and momentum-space, we have performed high-resolution micro-ARPES experiments on underdoped Bi2212 ($T_c = 65$ K) using a micro-focused laser (hv = 6 eV) at the Hiroshima Synchrotron Radiation Center, Hiroshima University.

Figure 1(a) shows the ARPES image of the underdoped Bi2212 taken along the nodal direction (see inset) in the superconducting state (T= 20 K). We have then measured such a clear band dispersion from the nodal to the off-nodal direction (see inset) and evaluated the momentum dependence of the gap. In addition, we have also examined the real-space dependence of the superconducting gap by performing the same measurement while slightly changing the measurement position on the sample surface. Figure 1(b) compares the momentum dependence on the gap magnitude taken from the two different measurement positions (A and B). We found that the gap magnitude and its momentum dependence are clearly different in spite of the small difference (less than 0.1 mm) on the measurement position. To examine the momentum dependence quantitatively, we fit the experimental results by the gap function [2]: $\Delta(\theta) = \Delta^N \sin 2\theta + (\Delta^* - \Delta^N)(3\sin 2\theta - \sin 6\theta)/4$, where the Δ^N is the nodal gap (superconducting gap), the Δ^* is the antinodal gap (pseudogap), and the θ is the Fermi surface angle. The fitting analysis showed that the antinodal gap for position A is larger than one for position B, while the nodal gap for position A is smaller than one for position B. In other words, our results suggest the inverse correlation between the superconducting gap and the pseudogap in detail.



FIGURE 1. (a) ARPES image of underdoped Bi2212 (T_c = 65 K) taken along the nodal direction, where the inset shows the schematic diagram of the Fermi surface due to the antibonding band of Bi2212 (Blue line: nodal direction, red line: off-nodal direction). (b) The momentum dependence of the gap magnitude taken at the two different measurement positions (A and B). The arrows on both sides indicate the magnitude of the nodal and antinodal gap.

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Characterization of sp^3 content in amorphous carbon films

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Keywords: Amorphous carbon, films, sp³ content

Q-carbon (*quenched* carbon) is a newly discovered amorphous phase of carbon [1], and shows extraordinary physical properties such as room-temperature ferromagnetism and high-temperature superconductivity by boron doping [2]. Despite much interest, the research of Q-carbon is limited because of the difficulty in preparation of Q-carbon using rapid nonequilibrium laser processing. In this study, we prepared Q-carbon by adjusting the sp^3 content in diamond-like carbon (DLC) films and the laser energy density of pulsed laser annealing (PLA).

The amorphous DLC films are fabricated on sapphire Al₂O₃(0001) substrates using a pulsed laser deposition technique with a KrF excimer laser ($\lambda = 248$ nm). The *sp*³ content in the films varied between 20% and 42% by changing the laser energy density. To determine the *sp*³ content in the films, X-ray photoemission spectroscopy (XPS) measurements were carried out on the beamline BL-5, at the Hiroshima Synchrotron Radiation Center in Hiroshima University with non-monochromatic Mg K α X-ray source ($h\nu = 1253.6$ eV). C 1*s* core-level spectra were measured under an ultrahigh vacuum of ~10⁻⁷ Pa using a VSW hemispherical analyzer. The total energy resolution was about 1.8 eV. The binding energy of the films was corrected using the peak position of molybdenum spectra. Before measurements, the films were annealed at 100 °C under ultrahigh vacuum (~10⁻⁶ Pa) for 1 h to clean the film surface. PLA was performed on the DLC films using the KrF excimer laser with energy densities between 0.5 and 1.2 J/cm² at ambient atmosphere and temperature.

Figure 1 shows the XPS spectra of the C 1s core-level for the as-grown DLC films. A peak at the binding energy of ~284 eV was observed in the spectra for all the films. The peak position of the films moved towards higher binding energy, with slight broadening, as the laser energy density increased. Results of the spectral fitting are also shown in Fig. 1. After subtraction of a Shirley background, the C 1s spectra of the films were fitted using a Gaussian-Lorentzian mixed function. Lorentzian linewidth was set to 0.095 eV [3]. In this fitting process, for simplicity, symmetric line shapes were assumed, and one component for each sp^3 and sp^2 bond was considered. Full-width-half-maximum (FWHM) of peaks was set to the same value in each film. The experimental results were well reproduced by the three components with peak positions of 283.9, 284.9, and 286.5 eV. The peaks of ~284 and ~285 eV corresponded to sp^2 carbon atoms and sp^3 C-C bond, respectively [4]. The feature at 286.5 eV was assigned to C-O contamination formed on the film surface due to air exposure [5]. Gaussian linewidth was estimated from FWHM of peaks to be 1.7, 1.5, 1.8 eV for the films with laser energy densities of 0.4, 0.8, and 1.3 J/cm², respectively.

The sp^3 content in the films was determined from the ratio of the corresponding sp^3 peak area over the sum of sp^3 and sp^2 peak areas to be 20%, 35% and 42% for the laser energy density of 0.4, 0.8, and 1.3 J/cm², respectively. The sp^3 content in the films increased with increasing the laser energy density. This indicated that the sp^3 content in the DLC films was successfully varied by changing the laser energy density during deposition. These results are qualitatively in good agreement with the result recently reported by Joshi [6].

Since DLC films with different sp^3 content were obtained, PLA was performed on the DLC films. Consequently, for the combination of 20% sp^3 content and laser density of 1.0 J/cm², as well as 42% sp^3 and 0.5 J/cm², the films showed characteristic features of Q-carbon: filamentary nanostructures, the presence of a T peak in the Raman spectrum, room-temperature ferromagnetic behavior (Fig. 2), and ~80% sp^3 content. The results indicate that Q-carbon can be obtained by using a proper combination of sp^3 content in DLC films and an appropriate PLA energy density [7].



FIGURE 1. XPS spectra of C 1*s* core-level for the as-grown DLC films prepared with the laser energy density of (left) 0.4, (middle) 0.8, and (right) 1.3 J/cm². The results of spectral fitting are also shown. Open circles are experimental data, red lines are the fitting result, black lines are the Shirly background, blue lines are the component used for the fittings.



FIGURE 2. Field dependence of magnetization (M-H curve) for the 20-sp³ and 1.0-PLA film, measured at 300 K.

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Current activities of research and education on BL-5 (FY2020)

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Keywords: photoemission spectroscopy, photoelectron emission microscopy

We present an overview of our resent research and educational activities on beamline 5 (BL5) in the fiscal year 2020. Our beamline has two experimental stations in a tandem way. The first station is equipped with an angleresolved photoemission spectrometer (ARPES), a low energy electron diffraction (LEED) apparatus and an Xray source. The hemispherical analyzer of ARPES spectrometer (HA54, VSW) has a mean radius of 50 mm and is mounted on a twin axis goniometer in ultra-high vacuum chamber. Using this goniometer, one can perform ARPES and photoelectron diffraction (PED) measurements. It is also possible to perform resonant photoemission spectroscopy (RPES) measurements by using photon energy tunability of synchrotron radiation with X-ray absorption spectroscopy (XAS) measurement. With the X-ray source (XR2E2, FISONS), we can perform an X-ray photoelectron spectroscopy (XPS) measurement for the chemical state analysis and the PED. At the second station, we have installed a photoelectron emission microscope (PEEM, 'PEEM III', Elmitec). PEEM provides a magnified image of lateral intensity distribution of photo-emitted electrons from a sample surface. The spatial resolutions are several ten nanometers with Hg lamp and a few micrometers with synchrotron radiation. The sample is transferred between the ARPES and the PEEM chamber *in-situ*, and one can perform measurements at both stations for the same sample.

In the recent researches on BL-5, we have studied the electronic structure of potassium doped aromatic molecule (K_x picene) [1], iron-based superconductor (FeSe_xTe_{1-x}) [2], transition metal di-oxide films such as VO₂ thin films which exhibits a first-order metal-to-insulator transition at 340 K [3], CrO₂ thin films which are known as a half-metallic material [4], and TaO₂ film which is stabilized with a new technique developed in our group [5]. We have also studied the electronic structures of a high quality boron doped diamond film which shows a signature of the highest superconducting transition temperature of 25 K [6] and a high quality single crystal of YbFe₂O₄ which is one of multiferroic materials [7], by utilizing RPES at B-*K* and Fe- $M_{2,3}$ edges, respectively. In this fiscal year, we have studied the sp^3 content in diamond-like carbon films by using photoemission spectroscopy in order to optimize the conditions to produce Q-carbon (quenched carbon) which is a newly discovered amorphous phase of carbon with several exotic properties [8], as presented in this symposium. At present, we are preparing an auto-measurement system for photoemission holography.

We have used the BL-5 for education activity as well, for example, practical education for undergraduate students of Okayama University. The students have an opportunity to study the synchrotron radiation mechanism and to experience XPS measurement which is very useful for the surface science research. We accepted more than 100 students from 2006 to 2012. From 2014, we have started to join the practical lecture for experiments using the beamline end stations in HiSOR for both graduate school students of Hiroshima and Okayama Universities. In 2018, we have had a new project for education under a Japan-Asia youth exchange program in science supported by Japan Science and Technology Agency (JST), "Sakura Exchange Program in Science". We have accepted six students from Changchun University of Science and Technology in China.

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Origins of Thermal Spin Depolarization in Half-Metallic Ferromagnet CrO₂

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Keywords: Half-metallic ferromagnet, CrO2, Spin-resolved photoemission spectroscopy

In itinerant electron ferromagnets, interaction between conduction electrons and thermal spin fluctuation is of crucial importance for understanding the physical properties. As a many-body state dominating the transport properties of ferromagnetic metals, the nonquasiparticle (NQP) state, also called the spin-polaron state, was proposed in works on electron-magnon interaction [1,2]. For investigation of the behavior of the NQP state, half-metallic ferromagnets (HMFs), which have metallic electronic structures with an energy gap at the Fermi level (E_F) for one of the electronic spin state in the ground state, are ideal substances. This is because in half-metallic ferromagnets it is predicted that the effect of electron-magnon interaction is not masked by Stoner excitations unlike the usual itinerant ferromagnets, and it makes an observable modification of the electronic structure in the close vicinity of E_F [3,4]. However, only a few experimental studies suggesting the existence of NQP in HMFs have been published [5,6].

Chromium dioxide (CrO₂), which has a rutile-type crystal structure, is the simplest half-metallic oxide without carrier doping. CrO₂ shows almost 100% spin polarization, which is the highest value exhibited by a candidate HMF at low temperature, and this completely spin-polarized feature is suitable for exploring the many-body state. Theoretical studies based on the dynamical mean-field theory (DMFT) for CrO₂ showed that many-body effects broaden the bandwidth of a minority spin state above E_F and that the tail of the state cross E_F , meaning that NQP states are crucial for the occurrence of spin depolarization in CrO₂ [7,8]. Spin-resolved photoemission spectroscopy (SRPES) is a powerful technique to directly observe spin-polarized electronic structures and determine absolute values of spin polarization based on simple analyses. The pioneering works of SRPES on CrO₂, however, did not have sufficient energy resolutions to discuss depolarization near the E_F characteristic of the many-body effects. In this study [9], we have investigated the temperature dependence of the electronic structure and spin polarization of half-metallic CrO₂ (100) epitaxial films, by using laser-based high-resolution SRPES, in order to clarify the origin of the depolarization in CrO₂.

The CrO_2 (100) epitaxial films grown on a rutile-type TiO₂ (100) substrate were prepared by a closedsystem chemical vapor deposition method [10]. After the synthesis, the CrO_2 film was removed from the quartz tube and then immediately placed under high vacuum for SRPES measurements. During the procedure, the CrO_2 sample was exposed to the atmosphere for approximately three minutes. High quality of the sample surface prepared with the same procedure was verified by low energy electron diffraction (LEED) and surface-sensitive PES with a synchrotron radiation of 70 eV at HiSOR BL-5 [14]. Spin-integrated and spinresolved photoemission spectroscopy data were acquired by the laser-based spin-resolved angle-resolved photoemission spectroscopy (SARPES) apparatus in the Institute for Solid State Physics of the University of Tokyo [12]. We used a vacuum ultraviolet (VUV) laser (hv = 6.994 eV) with p-light-polarization as an excitation beam. During the measurement, the instrumental energy resolution was set to 20 meV and the base pressure was kept below 1 x 10^{-8} Pa. Calibration of $E_{\rm F}$ for the sample was achieved using a gold reference. We magnetized the CrO₂ (100) sample along the magnetic easy axis ([001] direction) by bringing the sample close to a magnet at room temperature. The approximate magnitude of the magnetic field at the sample position was 600 Oe.

A minority spin spectrum measured at 20 K (not shown) exhibits an energy gap of 10 meV below $E_{\rm F}$. which is much smaller than the previous estimation of about 500 meV [11,13]. This inconsistency can be attributed to a very small but non-negligible intensity from the surface contaminants (most probably Cr_2O_3), which will result in an underestimation of the spin polarization since the signals from Cr_2O_3 comprise unpolarized background. In order to eliminate this unpolarized background, we subtracted smoothed spectra of the minority spin spectra from both of the majority and the minority spin spectra. Figure 1 (a) shows the spin polarizations for various temperatures. The spin polarizations are normalized to their values at $E_{\rm B} = 80$ meV. It is clear that energy-dependent depolarization occurs at 80 K near E_F and it grows up at higher temperatures. Figure (c) and (d) are the spin-resolved energy distribution curves (EDCs) divided by the Fermi-Dirac (FD) function, showing that a minority spin state exists at $E_{\rm F}$ above 80 K (purple shaded region). This state is enhanced in the minority spin gap as temperature increases. This temperature dependence of the minority spin state is consistent with that of the NQP theories, which constitutes spectroscopic evidence for the appearance of a minority tail state attributed to a many-body effect. A thorough investigation of the fine spin-resolved electronic structure of HMFs will be important for understanding the many-body effect in itinerant electron ferromagnets and for realizing complete spin polarization at room temperature, which may accelerate the development of spintronic devices.



Binding energy (meV)

FIGURE 1. Minority tail states at finite temperature. (a) Spin polarizations for various temperatures obtained from majority and minority spin spectra with the background subtraction procedure. They are normalized to their values at EB = 80 meV. The error is indicated by bars. (b) Spin-resolved EDCs calculated from $I_{\uparrow} = (1 + P_{nor})I_{tot}/2$ (triangle-up) and $I_{\downarrow} = (1 - P_{nor})I_{tot}/2$ (triangle-down), where P_{nor} is the normalized spin polarization shown in panel (a). (c,d) Majority and minority EDCs divided by the FD function at the measured temperature convoluted with the experimental resolution.

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Electronic Structures and Chemical Natures of Inhomogeneous Gd-TM (TM = Co, Ni, and Cu) Metallic Glasses

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Recently, Ketov *et al.* [1] proposed a new type of the rejuvenation effect in metallic glasses, *i.e.*, a relaxation to a higher energy state, by a thermal cycle. According to their interpretation, if a glass is not elastically homogeneous, the thermal expansion coefficient has a distribution over the glass sample. By repeated temperature changes, magnitudes of thermal expansions are different depending on the positions in the glass, which surely induces shearing forces, and as a result, a rejuvenation effect occurs in the glass. They named this phenomenon as "Rejuvenation of metallic glasses by non-affine thermal strain". The validity of this logic is the subject to the discussion.

Yamazaki [2] intensively studied β -relaxation peaks in Gd-TM (TM = Co, Ni, and Cu) glasses. The β -peaks are remarkably larger than those of other metallic glasses, and thus, large heterogeneities are expected in these glasses. He also found that the heterogeneities highly depend on the transition metal elements, *i.e.*, Ni > Co > Cu.

In order to clarify the structural changes by the rejuvenation effect, we measured high-energy x-ray diffraction measurements. The rejuvenation of the glass samples was made by a thermal cycling between the liquid N₂ and room temperatures 40 times. The obtained pair distribution functions, g(r), have two distinct peaks, where the shorter and longer ones (0.29 and 0.35 nm) correspond to the Gd-TM and Gd-Gd correlations, respectively. After the thermal treatments, slight decreases and distance shifts are observed in these peaks. We also performed anomalous x-ray scattering experiments to further investigate partial structures relating to the rejuvenation effect.

In this study, we start to investigate this thermal rejuvenation effect from another point of electronic views. We have recently measured valence-band and core-level photoemission spectroscopy (PES) on these metallic glasses *before the thermal treatments*.

The amorphous samples were prepared by melt spinning with a single Cu roll installed at the Institute for Materials Research, Tohoku University, Sendai, Japan. Ribbon samples with a thickness of about 20 μ m and a width of ~ 2 mm were obtained.

The PES experiments were carried out by using a PES spectrometer installed at the beamline BL7 at Hiroshima Synchrotron Radiation Center in Hiroshima University, Higashi-Hiroshima, Japan. Ultraviolet photons generated from the HiSOR storage ring with the ring energy of 700 MeV and the ring current of 160-300 mA were monochromatized with a Dragon-type monochromator, covering the incident photon energy, hv, values from 20 to 450 eV. A PES spectrometer with a hemi-spherical photoelectron energy-analyzer (GAMMA-DATA, SCIENTA SES2002) attached to the analyzer chamber under the ultrahigh vacuum below 1×10^{-8} Pa at the end-station, was used for the PES experiments. The overall energy resolution, ΔE , of the spectrometer was about 0.1-0.5 eV depending on the hv values of 20-450 eV. The details of the PES experimental setup are given elsewhere [3].

All the PES spectra were collected at room temperature. Clean surfaces were *in situ* obtained by sputtering the samples with Ar^+ ions in a sample preparation chamber with the base pressure below 1×10^{-8} Pa. The

energies of all spectra were defined with respect to the Fermi energy, E_F , of the sample or a freshly evaporated Au film.

Figure 1 shows the Gd 4*d* core-level PES spectra of (a) Gd-Ni, (b) Gd-Co, and (c) Gd-Cu glassy alloys. As clearly seen in the figures by arrows, the Gd 4*d* core levels have at least two doublets of $4d_{3/2}$ and $4d_{5/2}$ levels, indicating that the Gd atoms have at least two chemical sites. In the near future, we will detect the spectral changes after the thermal treatments.



FIGURE 1. The Gd 4d core-level PES spectra of (a) Gd-Ni, (b) Gd-Co, and (c) Gd-Cu glassy alloys.

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P10

19AG043, 20AG064

ARPES study of the mechanically polished FeSi [001] surface

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FeSi is a nonmagnetic semiconductor at low temperatures. With increasing temperature, the magnetic susceptibility rises and the temperature dependence of the electric resistivity shows a crossover from the semiconducting state to the metallic state at ~300 K [1,2]. Thus, FeSi can be viewed as the Kondo insulator [3]. In order to investigate the electronic structure and electron-electron correlation effect in FeSi, the angle reserved photoemission spectroscopy (ARPES) measurements on FeSi [001] surface were carried out at HiSOR BL-1.

FeSi clean surface was successfully by mechanical polishing in air, and Ar ion sputter and annealing in the UHV chamber. After that procedure, the clear 1x1 LEED images were seen for the [001] surfaces (Fig.1).

Figure 2 shows the valence band dispersion along k_z (perpendicular to the sample surface), obtained by normal emission ARPES spectra from hv = 25 to 135 eV at 25 K. Assuming that the inner potential V_0 is 17 eV, the observed band structure are in agreement with the result of the GGA calculation along Γ -X line of the BZ (dashed curves). According to the result, it is found that one can examine the electronic band structure around Γ -X and X-M in the 4th bulk BZ with hv = 51 and 72 eV. respectively. We carried out the ARPES measurement with hv = 72 eV as shown in the Fig. 3. There are two dispersion bands between E_F and -1 eV, which approximately correspond to the calculated band structures along X-M (dashed curves). However, the observed dispersion bandwidths are narrower than the calculated ones. In particular, the observed bandwidth near E_F is approximately 0.6 times narrower than the calculated bandwidth. A similar bandwidth narrowing is found in the band structure along Γ -X (Fig. 2). We suppose that the bandwidth shrinking is derived from the strong electron-electron interaction.

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Fig.1 LEED image of FeSi [001] for E = 100 eV.



Fig.2 Plot of the normal emission ARPES intensity of FeSi [001] along k_z . Dashed curves represent the calculated band structures along ΓX .



Fig.3 Plot of the ARPES intensity with hv = 72 eV. Dashed curves represent the calculated band structures along XM.

20AU010

Electronic Structure of Antiferromagnet CeCoSi Revealed by VUV-ARPES

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Keywords: ARPES, strongly correlated physics, rare-earth compound, antiferromagnet, antiferroquadrupole

Strongly correlated electron systems have been known to show various emergent physical properties, as have been studied over recent decades. In such systems, a duality of "localization" and "itinerancy" of constituent electrons is the key to understand them; well localized *f*-electrons get to be itinerant when hybridized with conduction electrons (*cf*-hybridization). Magnetic or electronic ordered states develop when *cf*-hybridization is weak, while heavy-fermion emerges from strong *cf*-hybridization, namely in itinerant *f*-electron systems. The transition point from an ordered state to a heavy-fermion system defined in parametric space at zero temperature is called the quantum critical point (QCP). QCP has attracted a lot of theoretical and experimental attention for a few decades because some exotic phenomena, such as non-Fermi liquid, superconductivity, and Kondo destruction, have been reported in the vicinity of it [1].

Ternary cerium intermetallic compound, CeCoSi, has a tetragonal crystal structure (P4/nmm No. 129) (see Fig.1(a)). Antiferromagnetic (AFM) and antiferroquadrupole (AFQ) ordered phases were reported to take place at 9.4 K and 12 K at ambient pressure respectively, though the determination of the precise phase diagram has been controversial yet. The AFM transition temperature does not change against applied pressure very much, while that of the AFQ phase is stabilized up to 40 K at 1.6 GPa and vanishes around 2.4 GPa, implying the existence of QCP in the relevant pressure range [2, 3]. The different behaviors in AFM and AFQ phase indicate the existence of distinct mechanisms with different *cf*-hybridization strength because the large sensitivity to the applied pressure is often seen in rare-earth intermetallic compounds near the QCP [4, 5]. To reveal the mechanism of the AFQ phase, the information of the momentum-dependent *cf*-hybridization is important. Motivated by this, we have performed an angle-resolved photoemission spectroscopy (ARPES) of CeCoSi and its reference material, LaCoSi to elucidate the effect of *cf*-hybridization on the Fermi surfaces or band structures at HiSOR BL-9A.

The ARPES images of CeCoSi along the $\overline{\Gamma} - \overline{X}$ and $\overline{\Gamma} - \overline{M}$ lines (see Fig.1 (b)) measured using *s*-polarized light with its photon energy (*hv*) of 16eV are shown in Figs. 1(c) and 1(e), respectively. The results for LaCoSi are also depicted in Figs. 1(d) and 1(f) for comparison. We find a pair of bands crossing the Fermi level (E_F) as denoted with β along the $\overline{\Gamma} - \overline{X}$ and β' along the $\overline{\Gamma} - \overline{M}$ line for both CeCoSi and LaCoSi. It is recognized that the dispersion is quite anisotropic, where band β' is less steep (heavier) with an estimated effective mass of 13 m_e as compared with β (5.7 m_e). We have to note here that these bands are quite sensitive to light polarization. They actually disappear when excited with the *p*-polarized light, suggesting Co $3d_{x^2-y^2}$ orbital character. The band structures of LaCoSi and CeCoSi show a good agreement; the band structure of CeCoSi is well-reproduced by shifting the E_F about -0.1 eV, which suggests that the contribution of *f*-electrons to the Fermi surfaces are negligible, or the *f*-electrons in CeCoSi are well localized at ambient pressure.

Figures 2(a) and 2(b) show the magnified picture of the β band near E_F for CeCoSi and LaCoSi, respectively. The "kink" like structure is observed only for CeCoSi and its second derivative image visualizes a flat band and a gap in the β band. The flat band is not seen in LaCoSi and therefore can be ascribed to Ce 4f band. Since the gap opens at the crossing point of the flat band, it is thought that this gap is caused by cf-hybridization. Moreover, the flat band causing the cf-hybridization lies at about 11 meV below E_F which is identical with the size of the f-level crystal electric field (CEF) splitting caused through excitation as determined by the inelastic neutron scattering [6]. Therefore, it is thought that the cf-hybridization takes place between the Co $3d_{x^2-y^2}$ and the excited CEF level. Since AFQ moment becomes active only in the inter-orbital space made between the ground state and excited state, we believe that this hybridization is the key to understand the mechanism of the pressure-induced AFQ phase.



FIGURE 1. (a) Crystal structure of CeCoSi. Black arrows show magnetic moments in the AFM phase. (b) Bulk and surface Brillouin zones of *R*CoSi (R = La, Ce). (c)-(f) ARPES spectra of CeCoSi and LaCoSi along $\overline{\Gamma} - \overline{X}$ and $\overline{\Gamma} - \overline{M}$ lines.



FIGURE 2. (a), (c) Band structures of the β band of CeCoSi and LaCoSi along $\overline{\Gamma} - \overline{M}$ line near E_F . Two black arrows in (a) show characteristic energies of "kink" like structure. **(b), (d)** Second derivative spectra of panels (a) and (c). **(e)** Energy distribution curves in the region between cut k and k' shown in panel (a). Open circles and black squares show peak structures derived from the β band and the flat band, respectively.

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ARPES study of antiferromagnetic EuIn₂As₂

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Keywords: antiferromagnetism, axion phase, ARPES, bulk bands, two-dimensionality

Soon after the discovery of topological insulators, antiferromagnetic topological insulators defined by Z_2 topological invariant were also theoretically proposed [1]. This new form of magnetically ordered topological insulators can be characterized by the symmetry operation $S = \Theta \cdot T_{1/2}$ obtained by multiplying time-reversal symmetry operation Θ and the 1/2 lattice translation symmetry operation $T_{1/2}$, and is expected to realize an "axion phase". The axion phase has attracted a great deal of attention as a platform for the new topological electromagnetic effect. Recently, a gapped topologically non-trivial surface state of the layered antiferromagnetic MnBi₂Te₄ has been predicted and realized [2]. However, the energy gap in MnBi₂Te₄ is located well below Fermi level (E_F), which becomes an obstacle for the realization of topologically interesting phenomena. Therefore, there is an strong need for more ideal antiferromagnetic topological systems.

In this study, we focus on the antiferromagnetic EuIn₂As₂. This is the heterostructure compound that undergoes a phase transition to layered antiferromagnetic order below $T_{\rm N} = 16$ K [3]. It exhibits a large negative magnetoresistance near $T_{\rm N}$, which is known to occur in Weyl semimetals. As another interesting aspect, this material is predicted to be a higher-order topological insulator candidate accompanying topological hinge and corner states in the antiferromagnetic phase [4]. Previous angle-resolved photoelectron spectroscopy (ARPES) studies on this compound provided controversial results on the electronic band structures crossing the $E_{\rm F}$ [5,6,7], which were interpreted to be either bulk or surface origin. To make a decisive determination of the band structures, orbital and spin resolutions for the ARPES measurement is highly desired. Motivated by this, we have performed the ARPES with linearly polarized light at HiSOR BL-1 and BL-9A and the spin-resolved ARPES (spin-ARPES) at BL-9B.

Figure 1 shows the observed band structures of EuIn₂As₂ along the $\overline{\Gamma} - \overline{K}$ line acquired with a photon energy (*hv*) of 25 eV at BL-1. Most importantly, linearly dispersive hole like bands that cross E_F is observed. In order to confirm if these linear bands stem from surface or not, we have tried to measure incident photon energy dependence and found no k_z dispersion. Figure 2(a) shows the ARPES energy dispersion acquired at hv = 28eV and Fig. 2(b) shows the y component of spin polarization (P_y) and spin-resolved energy distribution curves along the yellow cut line [see Fig.2(a)] of the linear band, exhibiting no spin polarization. We note here that no recognizable spin polarizations are found also for P_x and P_z components.

Having considered the experimental results mentioned above, it can be safely concluded that the hole-like linear band stems from the bulk electronic states with high two-dimensionality.

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FIGURE 1. ARPES image of EuIn₂As₂ along $\overline{\Gamma} - \overline{K}$ line acquired at hv=25 eV.



FIGURE 2. (a)ARPES image taken at hv=28 eV with *p*-polarization. (b)Spin-resolved energy distribution curve along the line at an emission angle of 5 deg. (see yellow cut line).

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20AG57

Spin-polarized band structures of Ga-rich Fe₃Ga film as a promising material for high thermoelectric performance

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Keywords: Spin-ARPES, thermoelectric harvesting, anomalous Nernst effect

Thermoelectric materials are very promising for solving environmental problems because they can directly convert waste heat energy into electrical energy. They have so far been based on the so-called Seebeck effect, which generates an electric field in a direction to the heat flow. Since it is a one-dimensional phenomenon, it becomes an obstacle in minimizing the size and manufacturing cost. On the other hand, the anomalous Nernst effect (ANE) generates an electromotive force perpendicular to the magnetization and the heat flow in ferromagnetic materials. This three-dimensional nature makes it possible to apply it to complex curved surfaces. Therefore, the ANE has a great potential for application in energy harvesting technology.

Recently, a giant ANE up to 2.4 μ V/K, which is two order of magnitude larger than that of pure Fe, has been experimentally found in the disordered binary ferromagnetic alloy Fe_{1-x}Ga_x consisting only of earth abundant and non-toxic elements [1]. Later, it has reached 4 μ V/K in *D*0₃ phase Fe₃Ga thin film [2]. A recent theoretical study suggests that such a remarkable ANE originates from an intrinsic mechanism caused by a peculiar band structure [2]. To elucidate the mechanism of ANE and develop the thermoelectric device with higher performance, a direct observation of the band structures with spin resolution is essential. However, no experimental evidence on the spin resolved band structures have been missing so far.

Motivated by this, we have carried out a spin- and angle-resolved photoelectron spectroscopy (spin-ARPES) measurement on $D0_3$ phase Fe₇₂Ga₂₈ thin film. The thin film sample was deposited on MgO(001) substrate *via* magnetron sputtering method at NIMS (Tsukuba) and transferred to the spin-ARPES apparatus (Hiroshima Univ.) using the vacuum suitcase chamber. The experiment was performed at HiSOR BL-9B using the VLEED spin detector attached to the hemispherical analyzer [3].

Figure 1(a) shows the ARPES image acquired along [110] direction with a photon energy of 60 eV. We find steeply dispersive bands that cross the Fermi level (E_F) around $k_{||} = \pm 0.5 \text{ Å}^{-1}$. No recognizable features are observed for $|k_{||}| < 0.5 \text{ Å}^{-1}$ above $E \cdot E_F = 1.0 \text{ eV}$, whereas less dispersive features with the rather strong intensity are observed at $E \cdot E_F = -1.0 \sim -1.5 \text{ eV}$. The spin-resolved energy distribution curves (EDC) at $k_{||} = 0 \text{ Å}^{-1}$ (cut 1), 0.60 Å^{-1} (cut 2), 0.79 Å^{-1} (cut 3) and 1.12 Å^{-1} (cut 4) [see panel (a)] are

shown in Fig. 1(b). Minority-spin EDCs for cut 1 and 2 show a peak near $E-E_F = 0$ eV, which confirms a minority spin character for the steeply dispersive bands crossing E_F near $k_{||} = \pm 0.5 \text{ Å}^{-1}$. The minority-spin EDC at $k_{||} = 0 \text{ Å}^{-1}$ (cut 1) shows a single peak at $E-E_F = -1.1$ eV, while the majority-spin counterpart exhibits a broad feature at the similar energy that can be roughly decomposed into two intensity maxima at -1.0 and -1.2 eV. It tells us that the less dispersive feature shown in Fig. 1(a) near $k_{||} = 0 \text{ Å}^{-1}$ involves three distinctive bands possessing majority, minority and majority spin characteristics at $E-E_F = -1.0, -1.1$ and -1.2 eV, respectively. All of the experimental results shown here are reasonably explained by the theoretical band structures using the first principles calculation (*not shown*) when the theoretical E_F is shifted towards the lower energy (higher binding energy) by about 100 meV. Since the predicted nodal webs, which should be responsible for the higher Nernst coefficient, are still located above E_F , the further electron doping would be necessary to maximize the transverse thermoelectric performance.



Figure 1 (a) ARPES image of Fe₇₂Ga₂₈ thin film along [110] direction acquired at a photon energy of 60 eV. (b) Spin-resolved EDC in majority (red) and minority (blue) spin channels at k = 0 Å⁻¹ (cut 1), 0.60 Å⁻¹ (cut 2), 0.79 Å⁻¹ (cut 3) and 1.12 Å⁻¹ (cut 4).

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20U005

Evaluation Of The Self-healing Bio-assisted Cement-treated Clay With XAFS

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Keywords: XAFS, Cement-treated clay, Calcium carbonate.

1. Introduction

Cement is one of the most widely used materials for ground improvement. Recently, there has been increasing interest in the durability / robustness of cement-treated soil. In the marine environment, cement-treated soil is deteriorated by the percolation of salt from seawater [1].

As a countermeasure to this phenomenon, self-mediated cement treated clay with biomineralization is proposed to enhance the durability of cement-treated clay against seawater [2]. In this study, the morphology were of the cement-treated soil with biomineralization based self-heling cement treated clay was analyzed using X-ray absorption fine structure (XAFS).

2. Chemical reaction for deterioration mitigation

Calcium hydroxide, an important cementation component of cement-treated soil, reacts with magnesium salts in seawater to form highly water-soluble calcium salts, which are leached into seawater (Eq.1-2) [1]. In cement-treated soil with Bacteria and urea, urea is hydrolyzed to produce carbonate ions by bacterial function (Eq.3) [2]. The calcium ions resulting from the deterioration are reacted with the carbonate ions derived from urea, and they are reprecipitated as calcium carbonate (Eq.4) [2]. The above chemical reaction equation is described below.

$Ca(OH)_2 + MgCl_2 \rightarrow CaCl_2 + Mg(OH)_2$	(Eq.1)
$CaCl_2 \rightarrow Ca^{2+} + 2Cl^{-}$	(Eq.2)
$CO(NH_2)_2 \rightarrow urease \rightarrow 2NH^{4+} + CO_3^{2-}$	(Eq.3)
$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \downarrow (precipitation)$	(Eq.4)

3. Experimental method

Ordinary Portland cement was added to the marine clay and mixed. This sample was named "Sample A". "Sample B" was prepared by mixing urease-producing bacteria (*Sporosarcina aquimarina*) and urea to mixtures produced similarly to sample A. The samples at this point were used as the initial samples. These samples were filled into a mold and cured under sealed conditions. After curing, the specimens were exposed to 150 mL of artificial seawater for 196 days with only the top surface open. A sample of 5 mm was taken from the exposed surface of the specimen after exposure. The samples were dried in an oven at 105°C until there was no change in mass, and then finely ground using a mortar. In addition, samples of special reagent grade were prepared to simulate calcium hydroxide which are important cementation components of cement-treated soil and bacterial calcium carbonate, respectively.

XAFS measurements were performed at BL-11 of the Hiroshima Synchrotron Radiation Center (HiSOR) with the conventional transmission mode without calibrating the incident Xray energy.

4. Results and discussion

FIGURE 1 shows the XAFS spectra of samples and reference materials. Focusing on the reference samples, the peak of calcium hydroxide was observed at 4068 keV. Calcium carbonate (calcite), however, showed two peaks at 4066 keV and 4078 keV.

Both the initial samples showed peaks at 4068 keV, and the waveform was similar to that of the calcium hydroxide standard. For sample A (exposure), the peak was identified at 4068 keV, which was similar to that of initial sample. In sample B, a spectrum similar to calcite was obtained after exposure.



FIGURE 1 Calcium K-edge XAFS spectra of samples and reference materials

Based on these results, fractions of calcium hydroxide and calcite in the samples A and B were calculated using the spectra sum of reference materials. TABLE 1 shows the calculated results at the initial and the exposure stages. Before the exposure, both samples were found to be mainly composed of calcium hydroxide. After the exposure, sample B was almost completely converted to calcite. Calcium carbonate shows different structures depending on the type of urease-producing bacteria used as biocatalysts. Previous study where TG-DTA analysis was used, has shown that the calcium carbonate precipitated by *Sporosarcina aquimarina* is mainly calcite based, and our results strengthen the results of previous study [3].

TABLE 1 Calculated fractions of calculatin hydroxide and calcule in unknown samples.		
Sample name	Ca(OH) ₂	CaCO ₃ (Calcite)
Sample A(initial)	0.756	0.244
Sample A(exposure)	0.541	0.459
Sample B(initial)	0.751	0.249
Sample B(exposure)	0.190	0.810

 TABLE 1
 Calculated fractions of calcium hydroxide and calcite in unknown samples.

5. Conclusion

In this study, the authors used XAFS analysis to investigate the structure of the crystals formed in cement-treated clay mixed with urease-producing bacteria when it comes into contact with seawater. The results showed that most of the calcium hydroxide was converted to calcium carbonate by the microbial function in the sample exposed to seawater, while the calcium hydroxide was the main component in the sample before exposure. Moreover, calcium carbonate turned out to be calcite.

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20AG049

Polarization dependent sulfur K-edge XAFS measurements of P3HT thin films for determination of film orientations with the improved sensitivity

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Keywords: XAFS, conversion electron yield, angular dependence, P3HT

1. Introduction

X-ray absorption fine structure (XAFS) measurements in the soft X-ray region are widely conducted with a total electron yield (TEY) method under the vacuum owing to the difficulties in preparing samples of appropriate optical thickness for the transmission method, and the X-ray fluorescence yield (XFY) method is supplementary employed for other cases. We have been employing a conversion electron yield (CEY) method that utilizes the ionization of surrounding He gas molecule by the energetic Auger electrons from a sample. The CEY is advantageous in the sense of S/N compared to the XFY. However, the use of an electrode that prevents created electron-ion pairs from recombination has generally made the geometrical restrictions for angular dependent measurements. We have developed a new device that can make the angular dependent XAFS measurements using CEY method. And we report the results of determination of the orientation for P3HT thin films using the developed device.

2. Experimental

2.1 A CEY device

A principle of the CEY measurements is similar to that of X-rays with an ionization chamber except for the source of the gas ionization. Therefore, a planer electrode has been adopted in the experimental setup at BL11 [1]. To realize the angular dependent measurements we have developed a new device shown in Fig.1. The device is equipped with a rod-shaped electrode. The diameter of the electrode in the new device was 6 mm, and the relatively wide diameter of the anode has maintained the strength of the electric field within the region of the ionization chamber. The cross section of the anode was semicircle, and the electrodes are placed above and below the beam height.



FIGURE 1. A photograph of the new device for the angular dependent CEY measurements (left), and a schematic layout of the sample geometry including glancing angle, θ and the azimuthal angle, ϕ (right).

2.2 XAFS measurements

XAFS measurements were performed at BL-11 of HiSOR. Incident X-rays were monochromatized with a Si(111) double crystal monochromator. The XFY was detected with a silicon drift detector (SDD) in a He filled chamber. A poly(3-hexylthiophene) (P3HT) film on ITO glass substrate was utilized as a sample having an anisotropy in sulfur K-edge XAFS spectra. A chlorobenzene solution of P3HT(Rieke Metals, Mw=58000) was spin-coated on a special ITO/glass substrate, and the surface of the substrate was previously brushed with a velvet fabric. The majority of backbones of edge-on oriented molecules are expected to be aligned in the brushing direction [2]. The azimuthal angle, φ was defined to be 0 when the electric field of the incident X-rays was normal to the brushing direction.

3. Results and Discussion

FIGURE 2 shows the azimuthal angle, φ dependence of S K-edge XAFS spectra from a P3HT thin film at $\theta = 80^{\circ}$. The 1s to π^* peak (π^*) showed strong peak under the condition of $\varphi = 0^{\circ}$. A plot of the intensities of π^* peak is shown as a function of azimuthal angle (FIGURE 3). We consider a three-component system that includes edge-on orientation (uniaxial and random) and face-on as components of orientation. But the almost direct incidence condition suggests that the contribution from the face-on orientation of the molecules is negligible, and the obtained π^* data can be attributed to molecules in the uniaxial edge-on direction and those in the random edge-on direction. This anisotropy could be expressed by the $\cos^2\varphi$ function. On the

azimuthal other hand, the dependence of the σ *S-C peak (FIGURE 4) should include the contribution of molecules in the face-on orientations. As the anisotropy of the σ *S-C peak was originated from the molecules in the uniaxial orientation, analysis of these two curves enabled us to determine the fractions of three components, and the fraction of the uniaxial orientation (edge-on) was determined to be 35 %.



FIGURE 2. Azimuthal angle dependence of S K-edge XAFS spectra $(\theta=80^\circ)$ from uniaxial edge-on oriented P3HT thin film.







FIGURE 4. A plot of the σ^* peak intensities as a function of the azimuthal angle.

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20AG034

Structure of a Novel Amorphous Organic-Inorganic Hybrid Tin Cluster Exhibiting Nonlinear Optical Effects by Low-Energy XAFS Measurements

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Keywords: Amorphous structure, low-energy XAFS, non-linear optical effect

Tailored light sources have greatly advanced technological and scientific progress by optimizing colour and brilliance, improving energy efficiencies or the quantum properties of light. So called supercontinuum generators are premier examples for media with nonlinear optical (NLO) effects – far superior in some respects to other sources such as phosphorescent white light-emitting diodes (LEDs). However, unlike LEDs, most of these advanced light sources are only used for scientific purposes, as they require extreme electric field strengths which are commonly realized by high-power pulsed lasers. In contrast, the materials of interest for this research project represent a new generation of supercontinuum emitters that are readily obtained from ubiquitous resources in a simple synthesis.

These compounds are of the general composition Sn4S6R4 (R=Methyl, Phenyl, Naphtyl, Cyclopentadienyl) and exhibit strong NLO effects, making it possible to use them as cheap and efficient warm-white supercontinuum emitters when driven by a commercially available low-power continuous-wave infrared laser diode [1]. Quantum chemical calculations suggest that these compounds consist of Sn4S6 clusters. On the other hand, it was also confirmed that the NLO effect is linked to the amorphous nature of the materials, but the structural properties of the amorphous phase, and thereby the apparent origin of this effect, is difficult to determine [2].

Recent investigations indicate that the relative orientation of neighboring clusters comprise key information concerning the strength of the NLO effect.[3] These inter-cluster correlations can be probed by low-energy EXAFS measurements, which were conducted at BL11 for a sample with R=Methyl. The analysis is complicated by the multitude of different EXAFS paths, therefore a good resolution in



FIGURE 1. S K-edge EXAFS data (a) in comparison with Sn K-edge EXAFS data, and their fitting results. The model used for the fit is shown in (c), where the organic side groups are omitted for clarity.

real-space, corresponding to a wide *k*-range in the raw data, is essential. A simplified model based on the calculation of the dimer structure [3] gives a very good fit to the data (Fig. 1a) and is also in agreement with higher energy EXAFS data from the Sn K-edge (Fig. 1b). The model is illustrated in Fig. 1c, and comprises two different inter-cluster S-S distances, one short (about 3.70 Å) and one long (about 3.85 Å) distance.

The results indicate an inter-cluster S-S coordination number of 0.7, tantamount to a dimerization of the Sn4S6R4-clusters (expected CN is 0.66). A formation of a further network of arranged clusters (equivalent to a larger inter-cluster S-S coordination number) is demonstrated to be unlikely for the clusters with Methyl side groups. Further work is necessary to investigate samples with other organic side groups to reveal possible links between the network formation and the NLO effect.

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19BG047

Circular Dichroism Study of Magainin 2-Membrane Interaction: Evidence for β-Strand Formation upon Membrane Association

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Keywords: peptide-membrane interaction; antimicrobial peptide; synchrotron radiation circular dichroism.

The biological function of antimicrobial peptide magainin 2 (MG2) largely depends on the lipid binding properties of the peptide but one conclusion from a number of reports on the lipid membrane association of MG2 is that this peptide interacts with membrane, inducing the conformational change from random coil to α -helix, and forms the membrane pore [1, 2]. However, the molecular mechanism of the interaction is still a matter of debate. In this study, to gain further insight into the interaction on a molecular level, a synchrotron radiation circular dichroism (SRCD) spectroscopy was used to characterize the conformation of MG2 associated with dipalmitoyl-phosphatidylglycerol (DPPG) liposome membrane.

MG2 peptide (amino acid sequence: GIGKFLHSAKKFGKAFVGEIMNS) was synthesized in GenScript Biotech Corp. (New Jersey, USA). DPPG lipid molecule ($T_m = 41$ °C) was purchased from Avanti Polar Lipids, Inc. Each sample was dissolved with 10 mM phosphate buffer (pH 7.0). DPPG liposome suspension with 100 nm diameter was prepared by an extrusion technique, and then mixed with MG2 solution at lipidto-peptide (L/P) molar ratio from 0 to 26. The SRCD spectra of MG2 in the presence of DPPG liposome were measured at BL-12 beamline in HiSOR. Temperature was controlled with a Peltier device, and varied between 25 °C and 55 °C. A sufficient number of SRCD spectra covered the whole ranges of L/P molar ratio was analyzed using the singular value decomposition (SVD) method. The L/P-dependent data were fitted using adsorption model based on scaled particle theory (SPT), whose procedure is briefly described below. The final solution of SPT for adsorption of a large self-associating ligand is described by

$$Kc_{\rm f} = \Phi_1 \gamma_1(\Phi_1, \Phi_z), \qquad \Phi_z = z K_{1z} \frac{\gamma_1(\Phi_1, \Phi_z)^z}{\gamma_z(\Phi_1, \Phi_z)} \Phi_1^z, \tag{1}$$

where K is the association constant, z is the number of subunits of adsorbed aggregation, c_f is the concentration of the peptide free in solution (or native state), $\Phi_1 = nc_1/c_L$ and $\Phi_z = nc_z/c_L$, c_1 and c_z are the concentrations of bound monomer and z-mer, respectively, c_L is the total lipid concentration, n is the number of lipid molecules covered by a single peptide, γ_1 and γ_z are the activity coefficient of adsorbed monomer and z-mer, respectively, K_{1z} is the equilibrium constant for the formation of z-mer [3]. Initial values of K, K_{1z} , n, and z were set, and then c_f , c_1 , and c_z at each L/P were calculated according to Eq. (1), outputting them as matrix C. The matrix of component spectra S was calculated by $S = (C^T C)^{-1} CD$ (D: data matrix) [4], and then the 2-norm for the error matrix E = CS - D was calculated. This process was repeated to minimize the 2-norm. The secondary-structure contents of MG2 in native state, membrane-binding monomer state, and z-mer state were determined from respective SRCD spectra using SELCON3 program [5, 6].

Figure 1 shows SRCD spectra of MG2 in the presence of DPPG liposome at L/P molar ratio from 0 to 26. The SRCD spectra of MG2 at 55 °C clearly exhibited an iso-dichroic point around 204 nm, while the spectra of MG2 at 25 °C did not show such a point. SVD analyses for the SRCD spectra at 25 °C and 55 °C indicated that the SRCD spectra at entire ranges of L/P molar ratio can be explained by three and two components, respectively, within experimental errors (data not shown). These results suggested that MG2 involved three-state and two-state conformational transitions at 25 °C and 55 °C, respectively, when interacting with DPPG membrane.



FIGURE 1. SRCD spectra of MG2 in the presence of DPPG liposome at L/P from 0 to 26 at 25 °C (a) and 55°C (b).



FIGURE 2. Component spectra of MG2 at 25 °C (solid line: native state; dashed line: membrane-binding monomer state; dotted line: z-mer state) (a) and 55°C (solid line: native state; dashed line: membrane-binding monomer state) (b). The inset of (a) shows the dependence of fractional population of the membrane-binding monomer state (closed square: experimental plot; dashed line: fitting curve) and z-mer state (open circle: experimental plot; dotted line: fitting curve) on the L/P molar ratio. The inset of (b) shows the dependence of fractional population of the membrane-binding monomer state (closed square: experimental plot; dashed line: fitting curve) on the L/P molar ratio.

Figure 2 shows component SRCD spectra of MG2. The L/P-dependent data could be fitted when *z* is greater than 3. The component spectra obtained under z = 5 is shown in figure 2 as a sample case. Native MG2 exhibited a negative CD peak at 200 nm, which is a characteristic peak of random coil structure. MG2 in the membrane-binding monomer state showed two negative peaks at 208 and 222 nm, and a positive peak around 193 nm, which are characteristic of α -helix structure. These results are corresponding with previous research [2]. On the other hand, MG2 in z-mer state showed two negative peaks around 220 nm and 190 nm, and a positive peak at 200 nm, which is a characteristic peak of β -strand structure. The secondary-structure analyses by SELCON3 showed that MG2 in native state, membrane-binding monomer state, and z-mer state at 25 °C included 8 %, 70 %, and 1 % α -helix, respectively, and 28 %, 11 %, and 46 % β -strand, respectively. These results suggested that MG2 self-associated to form β -strand structure when interacting with DPPG membrane, and also indicated that membrane fluidity is an important factor for the interaction of MG2 with membrane because T_m of DPPG is 41 °C. The result of β -strand formation of MG2 upon membrane association is supported by experiments of fourier transform infrared spectroscopy and solid-state nuclear magnetic resonance spectroscopy as well [7].

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Study of Membrane-Bound Conformation and Pore Formation of Magainin2 using Vacuum-Ultraviolet Circular-Dichroism Spectroscopy

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Keywords: Antimicrobial Peptide, Lipid membrane, Circular dichroism

Magainin2 (MG2) is an antimicrobial peptide consisting of 23 amino acids, and its antimicrobial activity occurs due to the interaction with membranes followed by the formation of transmembrane pores. The activity closely relates to the membrane-bound conformation of MG2 and it largely depends on the characteristics of constituents of membrane or lipid molecules. Recently, it found that the characteristics such as the void-space within membrane and the fluidity of membrane contribute to the membrane interaction of proteins [1, 2]. Hence, to clarify the contribution of MG2 in the presence of four types of membranes which were prepared from DLPC, DMPC, DPPC, or DSPC lipid molecules were analyzed by a vacuum-ultraviolet circular dichroism spectroscopy.

MG2 formed a random coil structure in native state (without membrane) and its structure altered the helical structure in the presence of DLPC and DMPC lipid membranes at 25°C (FIGURE1), meaning that MG2 interacted with the both membranes. On the other hand, MG2 retained its random coil structure in the presence of DPPC and DSPC lipid membranes, implying non-interaction. Since the phase transition temperature (T_m) of these lipid molecules are -2°C for DLPC, 24 °C for DMPC, 41 °C for DPPC, and 55 °C for DSPC, it was suggested that MG2 could interact with the membrane of liquid state. To enhance the fluidity of DPPC and DSPC lipid membrane or to get their liquid states, the temperature was raised above T_m of the both lipid molecules. After decreasing the temperature until 25°C, we found that MG2 formed helix structure in the DPPC lipid membrane



FGURE1 VUVCD spectra of MG2 in the presence and absence of DMPC lipid membranes at 25°C.

but retained the random structure in the DSPC lipid membrane. The differences of DPPC and DSPC lipid molecules were their spontaneous curvatures (positive for DPPC and negative for DSPC), which affected the void-space within membrane (internal void-space for DPPC and external void-space for DSPC). Since DLPC and DMPC lipid membranes had the internal void-space, the internal space would be key factor for promoting the membrane-interaction of MG2.

These results suggest that the internal void-space in membrane and the increment in the membrane fluidity would be driving force of MG2-membrane interactions.

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Optical Activity Measurement of Amino Acid Films by Circular Dichroism Spectroscopy

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Keywords: Homochirality, Amino Acid, Optical Activity, Circularly Polarized Light, Circular Dichroism

The origin of homochirality in terrestrial biomolecules (L-amino acid and D-sugar dominant) remains one of the most mysterious problems in the research for the origins of life. Rational explanations for the chiral asymmetry introduction into biomolecules are required through interdisciplinary collaborations. One of the most attractive hypotheses in the context of astrobiology is "Cosmic Scenario" as below [1, 2]; (1) Asymmetric reactions of prebiotic molecules on interstellar dust surfaces in molecular cloud circumstances were introduced by asymmetric radiation sources in space, that is "chiral radiations". (2) The chiral products were transformed into the complex organic materials including amino-acid precursors as "chiral seeds". (3) The complex organic materials as "chiral seeds" were transported with meteorites or asteroids to primitive Earth resulting in terrestrial biomolecular homochirality.

Several ground experiments to validate the scenario have been investigated asymmetric photochemical reactions in simple biochemical molecules using circularly polarized light (CPL) from high-energy particle accelerators [3]. Presently, we are carrying out irradiation experiments by using CPL with different wavelengths to investigate the photon energy dependence of photochemical chiral reactions [4]. As for the sample, we formed thin solid films of racemic mixture of alanine on quartz substrates from crystal powders of DL-alanine by using a thermal-crucible vacuum-evaporation system in HiSOR. The thin solid films of racemic mixture of alanine wavelengths using the undulator beam line BL1U of UVSOR-III [5]. In case of CPL irradiation in shorter wavelengths than 200 nm, the samples were set in a vacuum sample chamber preventing attenuation by air absorption. On the beam entrance side of the vacuum sample chamber, a gate valve with an MgF₂ vacuum sealing window was mounted. The irradiated CPL wavelengths were 180 and 155 nm corresponding to photon absorption bands of alanine molecule. The total doses of irradiated photon energy were measured with photoelectron current of a silicon photodiode (International Radiation Detectors, Inc.) settled at the sample position.

Circular dichroism (CD) spectra of the CPL irradiated films were measured at beam line BL-12 of HiSOR to clarify the optical activity emergence by CPL irradiation. CD spectroscopy can detect optical activity with a high accuracy because CD spectra sensitively reflects the steric structures of chiral molecules. Fig.1(a) and (b) are CD spectra of DL-alanine films irradiated by L- or R-CPL at 180 nm and 155 nm in wavelength, respectively. In order to delete the effects of linear components, the CD spectra at sample rotation angles (0, 45, 90, and 135 degrees) were individually measured and averaged them. The observed spectral profile strongly depends on the irradiated CPL wavelength and the polarization (L- or R-CPL) [6]. The measurement and theoretical calculation of CD spectra of L-alanine molecule has revealed that the chromophores such as carboxyl and amino groups are derived from the characteristic electronic transitions (π - π * and n- σ *) corresponding to the wavelengths as shown on Fig.1(c) [7, 8]. It is strongly suggested that optical activity emergence depends on photon energy of the irradiated CPL. Detailed analysis of CD spectra is in progress supported by quantum chemical calculations.

Presently, we are also planning the further irradiation experiment using CPL at 121.5 nm in wavelength, which is corresponding to hydrogen Lyman-alpha line. The clarification of full mechanism of the optical activity emergence potentially has relevance to the origin of terrestrial bioorganic homochirality stimulated by "chiral photon radiation".



FIGURE 1. CD spectra of the L- or R-CPL irradiated DL-alanine films measured at BL-12 of HiSOR. The CPL irradiation wavelengths were (a) 155 nm and (b)180 nm at BL1U of UVSOR-III. (c) The measured and theoretical calculated CD spectra of L-alanine molecule [7, 8].

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Electronic Relaxation Process in Fluorinated Aromatic Monolayers Studied by Core-Excited Ion Desorption

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Keywords: Self-assembled monolayers (SAMs), Resonant core-electron excitation, Site-selective bond breaking, Ion desorption, Molecular conductivity

Core-electrons are localized to each atom in the molecule, and their binding energy varies depending on the types of element and the surrounding chemical environment. Therefore, by selecting the energy of the incident light, it is possible to selectively excite the inner-shell electrons of specific atoms in the molecule. After core resonant excitation, various reaction pathways occur (Figure. 1). Desorbed ions include site selective ion desorption (red arrow) and non-selective ion desorption through energy redistribution within the molecule (blue arrow). In the case of surface molecules, these reactions compete with energy deactivation by charge transfer to substrate (green arrow), so the faster the charge transfer to the substrate occurs, the more the slower reactions are suppressed. Site non-selective ion desorption is slower than site selective ion desorption. So, we tried to evaluate the charge transfer rate from the site selectivity of ion desorption.

Measurements of near edge X-ray absorption fine structure (NEXAFS) were performed at the beamline BL-13 of HiSOR, and time of flight (TOF) mass spectroscopy was measured at the beamline BL-2B of KEK-PF. NEXAFS spectra around the C K-edge were recorded in total electron yield (TEY) mode by measuring a sample drain current. TOF spectra were measured with pulse selector [1] in the hybrid mode operation at PF.

Figure. 2 shows the schematic drawings of self-assembled monolayers (SAMs) used in this study. SAMs were prepared by immersing Au substrates into 1.0 mM ethanol solutions of MBB ($HSC_6H_4C_6H_4COOCH_3$), MBF ($HSC_6F_4C_6H_4COOCH_3$), and MFB ($HSC_6H_4C_6F_4COOCH_3$). It has been reported that these samples have different charge transfer rate [2]. All samples have methyl ester groups as terminal groups at topmost surfaces, and conductive phenyl rings as molecular chains.

Figure 3 shows the NEXAFS spectra measured for MBF and MFB changing the incident angle. NEXAFS spectra show features derived from fluorine substitution, especially in the peak



Figure 1. Reaction pathways after core resonant excitation.



Figure 2. Molecular structures of SAMs used in this study; MBB, MBF, and MFB SAMs.

splits of the first (~285eV) and second peaks(~288eV). From the intensity of first peaks, MBF and MFB were estimated to be oriented at 74° and 69° from the surfaces, respectively. Even though the orientation angles of MBF and MFB are almost the same, the ion fragmentation in MFB is more intense than that in MBF in terms of its CH_n^+ (n=0-3) ion desorption yield. These ions are produced by further fragmentation of CH_3^+ due to the excess energy it has when it is desorbed from the terminal group. The excess energy in MFB is estimated to be higher than that in MBF. We estimated the ratio of site selective vs. non-selective processes by reproducing the ion fragmentation pattern by adding together the site selective and non-selective model fragmentation patterns. As a result, selective:non-selective ratios were 0.81:0.19 for MBF and 0.98:0.02 for MFB. The results show non-selective ion desorption in MFB is faster than that in MBF because energy deactivation by charge transfer to substrate in MFB is faster than that in MBF. This result is consistent with the charge transfer rate in MBF and MFB (MBF: ~8.8fs, MFB: ~6.6fs) [2]. Therefore, the difference in conductivity depending on the fluorine substitution position was evaluated from the site selectivity of ion desorption.

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Figure 3 TEY spectra for (a)MBF and (b)MFB. The angles in the figure are the incident angles from the sample surfaces. MBF and MFB were estimated to be oriented at 74° and 69° from the surfaces, respectively.

20AG055

Comparison of soft X-ray absorption spectra of transition metal sulfates

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Keywords: Soft X-ray absorption spectrum, 3d transition metal sulfate, H2O, SO42-, bond length

The 3*d* transition metal (Fe, Co, Ni, Cu, and Zn) sulfates make an octahedral structure with 6 coordination containing some water molecules. Those complexes have various numbers of the coordinated water such as FeSO₄_7H₂O, NiSO₄_6H₂O, and CuSO₄_5H₂O. Only copper combines directly with SO₄²⁻ in five elements. Four H₂O are coordinated in the same plane and two SO₄²⁻ are coordinated out of plane (Figure 1). To investigate how the electronic states of coordinated water molecules are affected by the central metal atoms, soft X-ray absorption spectra have been measured in the energy range of 530~545 eV (O1s) and 690~1050 eV (metal 2*p*) of the 3*d* transition metals at BL-6 [1] of the HiSOR.

Figure 2 shows the total electron yield (TEY) spectra of the 3d transition metal sulfates in the O1s edge. The lowest peaks are observed around 532.8 eV and their energies depend on the 3d transition metals. There are two kinds of oxygen atoms (H₂O and SO₄²⁻) in the present complexes. To distinguish them, the TEY spectrum of anhydrous copper sulfate (CuSO₄) is also measured and compared with CuSO₄_5H₂O (Figure 3, top panel). The lowest peak observed only in CuSO₄_5H₂O is thus ascribed to contribution of the coordinated water molecules. The difference spectrum is calculated by normalizing the two spectra with the number of oxygen atoms (Figure 3, middle panel) and compared with the spectrum of a gaseous water molecule [2] (Figure 3, bottom panel). Comparing to the 4a₁ peak of gaseous water molecule, the lowest peak of the coordinated water is shifted to lower energy side by about 1 eV and broadened. The lowest peak energies of the 3d transition metals are summarized in Table 1 with the average bond length of X-OH₂ (X= Fe, Co, Ni, Cu, and Zn). The shorter the average bond length of X-OH₂, the higher the lowest peak energy except Ni.

TEY spectra are also measured at metal 2p edge. There observed spin-orbit separation peaks of $2p_{3/2}$ and $2p_{1/2}$ to 3d transitions with the energy separation of $13\sim21$ eV except Zn, which has no hole in the 3d orbit. Comparing the experimental transition energies of $2p_{3/2}$ to 3d with the calculated differences of binding energies between 2p and 3d electrons, the largest discrepancy for Cu is considered to be ascribed to direct coordination of SO_4^{2-} to the central metal.

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FIGURE 1. Schematic diagram of CuSO₄_5H₂O.



FIGURE 3. TEY spectra of (top) CuSO4_5H2O and CuSO4, (middle) calculated ligand (H2O) component, and (bottom) H2O (gas).



FIGURE 2. TEY spectra of *3d* transition metal (Fe,Co,Ni,Cu, and Zn) sulfates at the O*1s* edge.

TABLE 2 The lowest peak energies of the 3d transitionmetal sulfates and the average bond length of X-OH2(X= Fe,Co,Ni,Cu, and Zn).

	Peak energy (eV)	Average bond length (Å)
FeS0₄_7H₂0	532. 0	2. 123
CoSO₄_7H₂0	532. 4	2. 092
NiSO₄_6H₂O	532. 0	2. 051
CuSO₄_5H₂0	532. 8	1.956
ZnS0₄_7H₂0	532. 0	

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Soft X-ray Polarization Measurement and Evaluation at HiSOR BL-13 Using Electron Orbitally Oriented Samples

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Keywords: NEXAFS, SAMs, HOPG, polarization

Linear polarization is an important parameter for the study of sample orientation and anisotropy of reaction dynamics by X-ray absorption spectroscopy (XAS). Therefore, it is necessary to understand in advance the polarization characteristics of the beamline to be used. Usually, for evaluating the polarization of beamlines, however, it is necessary to insert expensive X-ray polarizers into the beamlines, an ion detection system for anisotropic dissociation induced by polarized SR light, or a photoelectron spectrometer for gaseous molecules.

Recently, the evaluation method of polarization using highly oriented pyrolytic graphite (HOPG), a sample with oriented electron orbitals, was reported [1]. This method makes it possible to easily evaluate polarization by simply rotating the tilted sample in-plane. In this study, the polarization of BL-13 was determined from the dependence on the incidence angle and the validity of the obtained polarization was evaluated by using self-assembled monolayers (SAMs).

HOPG is a solid sample with highly oriented electron orbitals that can maintain its planarity, and it was fixed on a sample stand with an tilted angle of 30° (Fig. 1). In a typical sample arrangement, only the horizontal component of the electric field vector can be evaluated.



FIGURE 1. Photos of the tilted HOPG sample introduced to BL-13.

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The angle dependence of the X-ray absorption fine structure (NEXAFS) spectra was measured at various azimuthal angles (ϕ) as shown in Fig. 2. The intensity of the $\pi^*(C=C)$ transition peak at 285 eV increases as the azimuth angle increases. On the contrary, the intensity of the peak from the $\sigma^*(C=C)$ transition around 292eV to around 312eV and 330eV decreases as the azimuth angle is increased. The polarization of BL-13 was determined from the analysis of such angle dependence.

The obtained result was applied to the determination of the orientation angle of alkanethiol SAMs with respect to the gold substrate (Fig. 3) and the obtained orientation angles were compared with the literature values. In addition, biomembranes prepared only by dropping lipid solution onto substrates was also evaluated by polarized SR light. The spectra showed clear polarization dependence, indicating the layered conformation of biomembranes formed by such simple method.



FIGURE 2. Azimuthal angle dependence of NEXAFS spectra of HOPG.



FIGURE 3. Schematic diagram of SAMs.

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Inner Shell Excitation Spectroscopy of Gold Nanoparticles Coated with Aromatic Molecules

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Keywords: Self-assembled monolayers (SAMs), Gold nanoparticles, Laser ablation, Resonant core-electron excitation

Gold nanoparticles have been used commercially since the 4th century B.C. Gold nanocolloid solutions have a reddish purple color [1]. On the research front, it was found that organic molecules with thiol groups chemisorb onto the gold surface to form self-assembled monolayers (SAMs) in 20th century [2]. In recent years, next-generation materials and in vivo sensors based on gold nanoparticles modified with organic molecules have been developed. A lot of knowledge has been obtained about aliphatic SAMs. On the other hand, aromatic SAMs, which are expected to be applied as conductive materials, have not been fully understood. In this study, we compared the core excitation spectra of aromatic SAMs adsorbed on gold with different surface geometries and investigated the molecular states of the nanoparticle surface.

In this experiment, methyl 4-mercaptobenzoate (MP0) molecules with a methyl ester group (CH₃COO–) were used (Figure 1a). MP0-coated gold substrates (MP0S, Figure 1b) were prepared by immersing gold substrates in MP0 solution. The gold nanocolloid solution prepared with pulsed laser ablation in liquid (PLAL) technique. MP0-coated gold nanoparticles (MP0N, Figure 1c) were produced by adding MP0 to

gold nanocolloid solution. Field emission scanning electron microscopy (SEM) image (Figure 2) and surface plasmon resonance (SPR) absorption spectrum (Figure 3) were used to evaluate the size of gold nanoparticles. Near-edge X-ray absorption fine structure (NEXAFS) spectra and X-ray photoelectron spectra (XPS) have been observed at HiSOR BL-13. In the NEXAFS measurements, the incident angle of the soft X-rays was varied from normal (90°) to grazing (40°) incidence with respect to the sample surface.

The size of gold nanoparticles was determined at 7 nm from the SPR peak wavelength shown in Figure 3 based on the analytical equation by Haiss et al [3]. The XPS spectrum of the carbon 1s peak consisted of four peaks, (i) C=C, (ii) H–C–O, C–S–Au, (iii) C=O, and (iv) π – π * shake off satellite (Figure 4), and the peak intensity ratio (i)/(ii)/(iii) = 5/2/1 was corresponded to the carbon number ratio of MP0. Since the same result was obtained MP0N, it was found that MP0 molecules were densely chemisorbed onto the nanoparticles regardless of their surface shapes.

We have succeeded to observe the polarization dependence of the carbon K-edge NEXAFS spectra of MP0S (Figure 5a, b). From the fitting analysis of the first π^* peak (~285 eV) based on Stohr's analytical formula



FIGURE 1. (a) Molecular structure of MP0. Schematic drawings of (b) MP0S and (c) MP0N.



FIGURE 2. SEM image of MPON. Inset shows the photograph of obtained MPON nanocolloid solution.

[4], the tilting angle of MP0 molecule from the surface normal have been determined. On the other hand, the polarization dependence of MP0N was not observed in the carbon K-edge NEXAFS spectra (Figure 5c, d), because the gold nanoparticles synthesized in this study were confirmed to be spherical by SEM images (Figure 2). Recently, time-of-flight mass spectrometry was performed at Photon factory BL-2B, and different CH_n^+ ion fragment distribution was obtained between MP0S and MP0N, which are being analyzed from the view point of surface morphology.

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FIGURE 3. Visible spectrum of gold nanocolloid solution. The wavelength of SPR peak was 521 nm.



FIGURE 4. Carbon 1s XPS of MP0S. The four peaks were assigned to (i) C=C, (ii) H–C–O, C–S–Au, (iii) C=O, and (iv) π – π * shake off satellite, respectively.



FIGURE 5. Carbon K-edge NEXAFS spectra of (a) MP0S and (c) MP0N, and difference spectra between the normal (90°) and grazing (40°) incidence spectra of (b) MP0S and (d) MP0N. The energy positions of the resonance peaks were consistent between MP0S and MP0N.

Splitting of Dirac band on Cr₂O₃/Graphene/Ni(111)

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Graphene is one of the most promising Dirac electronic systems. By functionalizing graphene, a sizable local magnetic moments and spin-orbit coupling can be induced in graphene. The main known mechanism responsible for the π band modifications including: the spin-dependent hybridization with the d states of the transition metal (proximity exchange), spin splitting due to inversion symmetry breaking (Bychkov-Rashba splitting) and the sublattice-symmetry breaking (pseudospin splitting). Recently, it has been predicted that a nontrivial band gap opening in the graphene Dirac bands asymmetric between K and K valleys at antiferromagnets Cr₂O₃/graphene interface, which is mediated by symmetry protected boundary magnetization of Cr2O3 and proximity effect induced SOC. The fabrication of this structure has been realized by Picone's group successfully on Ni(111) substrate. Moreover, a narrowed band gap of ultrathin α -Cr₂O₃ than that of crystal was observed by STS. While this progress is impressive, it is recognized that the size of bulk material often largely exceeds the characteristic for inducing a large proximity spin-orbit coupling in graphene. Directly experimental evidence of a Dirac band gap opening induced by Cr₂O₃ is still lack. From this perspective, it is beneficial to direct describe band structure of ultrathin Cr₂O₃/graphene. Here, we report a observable giant π band splitting in ARPES experiment induced by depositing ultrathin Cr₂O₃ film on graphene(Gr)/Ni(111). We speculate the evolution of graphene π band from n-doping-type to splitting-type comes from a nontrivial sublattice-symmetry breaking.



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Growth mode and interface structure of Co ultrathin films evaporated on h-BN/Ni(111)

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Keywords: epitaxial growth, hexagonal boron nitride, Auger electron spectroscopy

Magnetic tunneling junction (MTJ) structures, where ferromagnetic electrode layers sandwich an insulating barrier layer, show tunnel magnetic resistance (TMR) effect that is widely applied for spintronics devices such as magnetic random access memory. One of important performance factors of TMR element is magnetic resistance (MR) ratio, which is sensitive to not only electronic and magnetic status in the magnetic electrode layers but also the interface structure between the barrier layer and each magnetic layer. Conventionally, metal oxide layers like aluminum oxide have been utilized for the barrier layer in the device structures, where improvement of MR ratio is limited because of disorder of crystal structures at the interface, arises from lattice mismatch, inter-diffusion or defect inclusion. In recent years, much attention and intensive studies have been devoted to hexagonal boron nitride (h-BN) whose structure is composed of two dimensional honeycomb layers formed by stable chemical bonding. Monolayer h-BN is one of good candidates for the ideal burrier layer of TMR devices because the h-BN layer is expected to form a sharp and abrupt interface without pinhole defects with typical magnetic elements. A ultrathin MTJ structure of Co/h-BN/Ni(111) is also considered to form ideal interface from good lattice matching between the h-BN layer and magnetic transition metals. Although the commensurate interface of h-BN/Ni(111) is well established by previous studies, the growth mode and interface structure for Co/h-BN has not been clarified as yet.

In this study, we have investigated growth mode of Co films on h-BN/Ni(111) in manner of quantitative analysis of Auger electron intensity that is depending on Co thickness in several monolayer region. The sample of Co/h-BN/Ni(111) was prepared in ultra-high vacuum by means of MBE evaporation of Co on h-BN/Ni(111), where high quality h-BN monolayer was fabricated on the clean surface of Ni(111) by cracking of borazine (B₃N₃H₆) [1]. Figure 1 shows intensity ratio of Co (LMM) to Ni (LMM) in Auger electron spectra (AES), whose thickness dependence is clearly revealed. Simple exponential expansion of Co signal has not found from data fitting analysis, leading to a failure of complete layer-by-layer growth. We can suggest initial islanding growth followed by two dimensional epitaxial growth above 4 ML.



FIGURE 1. Co thickness dependence of intensity ratio of Auger electron of Co (LMM) to Ni (LMM) obtained from differential Auger electron spectra from Co/h-BN/Ni(111). Some of fitting models are also shown on the right panel.

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20AU018

High-resolution ARPES of heavily overdoped Bi2201: evaluation of coupling parameters

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Keywords: High-T_C Superconductor, ARPES, Many-body interactions

High transition-temperature (T_C) cuprate superconductors have attracted much interest since their discovery in 1986. While there have been extensive studies, there exist unsettled physical phenomena such as bad metal, density waves, magnetic fluctuations, and nematic phases [1-4]. These states are emergent from the competing charge, spin and lattice degrees of freedoms. To understand the origin of the physical properties of cuprates, it is desirable to disentangle these competing interactions and quantify each contributions.

To this end, here we focus on the Bi-based high- T_C cuprate, $(Bi,Pb)_2Sr_2CuO_{6+\delta}$ (Bi2201). The Fermi surface of Bi2201 is relatively simple because there exists a single CuO₂ plane in the unit cell. We start from the overdoped region, where the electronic state is expected to behave as the Fermi Liquid [3]. However, recently, Kurashima et al. found a ferromagnetic fluctuation close to the vanishing T_C region, and the ground state properties in this region should be investigated [3]. Previously Meevasana et al. have done angle-resolved photoemission spectroscopy (ARPES) and examined the self-energy due to the electron-electron and electron-phonon interactions especially for the heavily overdoped Bi2201 with no superconducting transition [5]. However, each contribution from the electron-phonon (or electron-boson) and electron-electron interactions as a function of hole concentration is still not clearly determined. Our purpose is, therefore, to systematically clarify the evolution of these interactions as a function of hole concentrations.

Here we have examined the electronic structure of as grown Bi2201 single crystal with $T_C=6$ K. We have done linear-polarization dependent ARPES experiments on BL-1 [6] to investigate the Fermi surface and energy band dispersion in the wide energy range. To examine the fine details of the electron-phonon interaction near the Fermi level, we have done high-resolution ARPES using 6.3 eV ultraviolet laser (μ -Laser ARPES machine) [7].

Figure 1(a) shows the observed Fermi surface taken at hv=90 eV at 50 K. In addition to the hole-like Fermi surface, we have observed additional Fermi surfaces moved by (π,π) , which suggests antiferromagnetic fluctuation or superstructure formation. To analyze the Fermi surface shape quantitatively, we have adopted the two band tight-binding (TB) model [8]. The red lines in Fig. 1(a) show the best fit result of the TB model.

Figure 1(b) and 1(c) show the band structures along the nodal direction (cut 1) and the antinodal direction (cut 2) taken at hv=40 eV. We measured cut 1 (cut2) using p-(s-)polarization geometry taking into account the diple selectrion rule [6,9]. One can see the reduction of the group velocity near the Fermi level compared with the TB model. The deviation is assumed to derive from the self-energy due to the electron-electron interaction. We have also overlaid the LDA result [10] for Bi2201 in Fig. 1(b). One can see that the deviation of the group velocity is not so strong compared with the two band TB model.

We have also measured fine details near the Fermi level using the μ -Laser ARPES machine and have observed a clear kink structure around -90 meV. In the poster presentation, we show the self-energy due to the electron-phonon and electron-electron interactions using the two band TB model.



FIGURE 1. (a) Fermi surface of Bi22012 taken at hv = 90 eV at 50 K. The read lines show calculated Fermi surface using the two-band TB model. ARPES image plot along (b) the nodal direction (cut 1) and (c) the antinodal direction (cut 2) respectively taken at hv=40 eV at 25 K. Red lines in (b) and (c) show band dispersions calculated by the TB model. The white line in (b) shows a band dispersion obtained from the LDA calculation. Blue dots in (b) and (c) show the band points evaluated by the MDC analyses.

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Topological Surface State in Sb, Te, and Se Based Single Crystals

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Three-dimensional topological insulator (TI) belongs to new quantum state of matter family, which has attracted great attention over the past decade because of their unique physical properties and potential future applications [1]. TI has an energy gap in the bulk bands but has metallic topological surface states which are robust against perturbations as far as the topological properties of the energy bands are conserved. Here we report the electronic band structures of the topological insulators Sb₂Te₃ and Sb_{1.9}Sn_{0.1}TeSe₂ using angle-resolved photoemission spectroscopy (ARPES). These samples are *p*-type semiconductors and have the Dirac point inside the bulk band gap, which is favorable for dissipationless spin-based electronic devices because the scattering from the surface to bulk states is suppressed [2,3].

We have done ARPES experiments on the linear undulator beamline BL-1 [4] with the *p*-polarization geometry. We cleaved high quality Sb₂Te₃ and Sb_{1.9}Sn_{0.1}TeSe₂ single crystals in the ultrahigh vacuum to get clean surfaces. First, we did ARPES experiments changing incident photon energies to resolve the surface and bulk-derived structures. Figures 1 and 2 respectively show the ARPES intensity plots obtained from Sb₂Te₃ and Sb_{1.9}Sn_{0.1}TeSe₂ along the K- Γ -K high symmetry direction. In Fig. 1, one can clearly see the Rashba-type band splitting in Sb₂Te₃ around the Γ point taken at hv=25 eV at 22 K. Note that the Rashba-type band splitting was only visible for certain photon energy range and along the K- Γ -K high symmetry direction. On the other hand, in the case of Sb_{1.9}Sn_{0.1}TeSe₂As in Fig. 2, the linewidth becomes broadened and we could not observe the Rashba type band splitting around the Γ point.

In the poster presentation, we will discuss the band structures of these TIs in more details.

0.6

Κ



Κ

hv = 25eV

0

-0.2

-0.6

-0.8

-1.0

Binding Energy (eV)

Figure 1. ARPES image of Sb₂Te₃



Figure 2. ARPES image of Sb1.9Sn0.1TeSe2

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