Study on Defects in Iron Formed under Hydrogen Embrittlement Environment Using In-Situ Measurement Technique of Gamma-Ray Induced Positron Annihilation Lifetime Spectroscopy

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The incorporation of hydrogen into metals such as steel is known to cause embrittlement of the metal. In a previous study, vacancy clusters have been detected near the hydrogen embrittlement fracture surface by positron annihilation lifetime spectroscopy. However, conventional positron annihilation lifetime spectroscopy requires measurements after hydrogen charging, and therefore, in-situ positron annihilation lifetime measurements were desired to understand defect behavior during hydrogen charging. In this study, we irradiated pure iron samples with high-energy pulsed gamma-rays obtained from UVSOR and measured the positron lifetimes in-situ during hydrogen embrittlement tests or tensile tests using positrons induced inside the samples.

Well-annealed pure iron tensile test pieces (10 mm in width and 2 mm in thickness) were either (1) mounted in a 0.1 N NaOH aqueous solution containing 5 g/L NH₄SCN and charged with cathodic hydrogen by applying a current density of 50 A/m², or (2) mounted in a tensile testing apparatus and stretched to a nominal strain of 8% and held under a constant load. The samples (1) and (2) were irradiated with a pulsed gamma-ray beam for in-situ positron annihilation lifetime measurements.

Figure 1 shows positron annihilation lifetime spectrum obtained from a hydrogen-charged pure iron sample mounted in NaOH aqueous solution. A lifetime component of ~2 ns, corresponding to the annihilation of positrons in the aqueous solution, was observed with non-negligible intensity, indicating that further refinement of the measurement technique is needed. Figure 2 shows positron annihilation lifetime spectra obtained from a pure iron tensile-test piece under no load and under the load required for stretching to a nominal strain of 8%. The spectral shape clearly changed by applying the load, indicating the appearance of a defect component. Furthermore, focusing on the change in positron lifetime over time may reveal more than what can be obtained by conventional positron annihilation lifetime spectroscopy. A more detailed analysis of the obtained spectra is currently underway.

Fig. 1. Positron annihilation lifetime spectrum obtained from a hydrogen-charged pure iron sample mounted in NaOH aqueous solution.

Fig. 2. Positron annihilation lifetime spectra obtained from a pure iron tensile-test piece under no load (open squares) and under the load required for stretching to a nominal strain of 8% (open circles).
Momentum Microscope Study of a Kagome Superconductor CsV₃Sb₅

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The kagome lattice, consisting of a two-dimensional network of corner-sharing triangles with 3d transition metal ions, offers a fertile ground to explore exotic quantum phenomena originating from electron correlation and non-trivial band topology. Band structure of a simple kagome lattice is composed of a flat band, a Dirac cone, and a saddle point. Owing to such a unique band structure, the kagome lattice shows various interesting physical properties depending on the position of the Fermi level (Eᵋ).

Recently, a new family of kagome metals A/V₃Sb₅ (A = K, Rb, Cs) with a V kagome network has been discovered. A/V₃Sb₅ commonly exhibits superconductivity below T_c = 0.9-2.5 K and charge-density wave (CDW) below T_CDW = 78-103 K. To clarify the interplay among superconductivity, CDW, and electronic states, we have performed ARPES measurements of CsV₃Sb₅ (T_c = 2.5 K, T_CDW = 91 K) by using momentum microscope at BL6U in UVSOR [1].

Single crystals of CsV₃Sb₅ were synthesized with the self-flux method. ARPES measurements were performed using KREIOS 150 MM (SPECS) [2]. The energy resolution was set to be 35 meV.

Figure 1 shows the plot of ARPES intensity at Eᵋ as a function of kₓ and kᵧ, measured at T = 120 K (above T_CDW) measured with 106-eV photons corresponding to the k_z ~ 0 plane [3,4]. Photoelectrons in this wide momentum window were simultaneously collected by using a momentum microscope. One can recognize three types of Fermi surfaces, a circular pocket and a large hexagonal pocket centered at the Γ point and a small triangular pocket at the K point. The circular pocket at the Γ point originates from an electron band with the Sb 5pₓ orbital. On the other hand, the hexagonal pocket originates from linearly dispersive bands with the dominant V 3dₓ²−y² orbital character. The triangular pocket at the K point is associated with the Dirac-cone band with the Dirac point at E_D ~ 0.3 eV. This band is attributed to the V 3dₓ²−y² orbital, and forms the saddle point slightly above Eᵋ. Our high-resolution measurements below T_CDW (not shown) reveal the largest CDW-gap opening on this saddle-point band. Therefore, the saddle point plays a crucial role in stabilizing CDW in A/V₃Sb₅.

Fig. 1. ARPES-intensity map at Eᵋ plotted as a function of kₓ and kᵧ, measured at T = 120 K in CsV₃Sb₅. Red, purple, and blue dashed lines are guides for the eyes to trace the experimental Fermi surfaces.

Probing Vacancy-type Defects in Ce:LuAG Scintillators by GiPALS Experiment and DFT Calculation

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Positron annihilation lifetime spectroscopy (PALS) is a unique experimental technique that can visualize the existence of vacancy-type defects in solids. Taira et al., one of the authors, have developed gamma-ray induced PALS (GiPALS) using ultrashort pulsed gamma-rays generated by 90-degree inverse Thomson scattering [1]. We applied this method to the visualization of negatively charged cation vacancies, which trigger the formation of photocarrier traps associated with defect complexes of cation antisites and oxygen vacancies in Ce:Gd3Al2Ga3O12 (Ce:GAGG) crystals [2].

In the present study, GiPALS experiment has been performed at 300 K for Ce-doped Lu3Al5O12 (Ce:LuAG) crystals, which have the same crystal structure as Ce:GAGG. GiPALS spectra were analyzed according to the two-state trapping model of bulk and defect states. The lifetimes and relative intensities were determined by the least-square fitting using two exponential decay functions. Using these parameters, bulk- and defect-lifetimes were calculated, and were compared to those obtained from the theoretical calculation based on two-component density functional theory (TC-DFT).

Figure 1 shows the GiPALS spectrum of a Ce:LuAG crystals. The data were obtained at 300 K. The GiPALS spectra are reproduced by the sum of two exponential decay functions drawn by blue broken lines. The positron annihilation lifetime becomes longer at the negatively charged vacancy site, compared to the bulk state free from vacancy-type defects. Therefore, the short and long lifetime components are attributed to the positron annihilation at the bulk and defect states, respectively. The lifetimes \( \tau_i \) and relative intensities \( I_i \) were analyzed by the least square fitting of experimental data. The values of \( \tau_i \) and \( I_i \) are listed in Table I. The bulk lifetime \( \tau_B \) and trapping rate \( \kappa \) were estimated to be 166±2 ps and (1.53±0.07)×10^9 s^{-1}, respectively. Table II lists bulk \( \tau_B \) and defect lifetimes \( \tau_{24c}, \tau_{16a} \) and \( \tau_{24d} \), obtained by the present TC-DFT calculation. The subscripts indicate the Wyckoff positions of the lattice sites introducing cation monovacancies in the TC-DFT calculation. The experimental value of \( \tau_B \) is almost agreement with the calculated one. This result indicates the validity of our experiment and analysis.

In Table I, the value of \( \tau_2 \) corresponds to the vacancy-related lifetime. This value is similar to those of \( \tau_{24c} \) and \( \tau_{16a} \) in Table II. Thus, it is more likely that Al monovacancies are introduced at 16a and 24d sites. The existence of Al vacancies was suggested in Y3Al5O12 (YAG) [3].

![Fig. 1. GiPALS spectrum of a Ce:LuAG crystal measured at room temperature. Broken lines indicate the components due to positron annihilation at bulk and vacancy-related defect sites. The sum of them also was indicated by a red line.](image)

<table>
<thead>
<tr>
<th>( \tau_i (ps) )</th>
<th>( I_i (%) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tau_1 )</td>
<td>132±14</td>
</tr>
<tr>
<td>( \tau_2 )</td>
<td>226±1</td>
</tr>
<tr>
<td>( \tau_3 )</td>
<td>49.0±0.8</td>
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<tr>
<th>( \tau_i (ps) )</th>
<th>( I_i (%) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tau_{24c} )</td>
<td>51.0±0.8</td>
</tr>
<tr>
<td>( \tau_{16a} )</td>
<td>49.0±0.8</td>
</tr>
</tbody>
</table>

Table I. Lifetimes \( \tau_i \) and relative intensities \( I_i \) for GiPALS spectra of Ce:LuAG, analyzed using the two-state trapping model.

<table>
<thead>
<tr>
<th>( \tau_i (ps) )</th>
<th>( I_i (%) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tau_B )</td>
<td>162</td>
</tr>
<tr>
<td>( \tau_{24c} )</td>
<td>274</td>
</tr>
<tr>
<td>( \tau_{16a} )</td>
<td>239</td>
</tr>
<tr>
<td>( \tau_{24d} )</td>
<td>233</td>
</tr>
</tbody>
</table>

Table II. Bulk \( \tau_B \) and defect lifetimes \( \tau_{24c}, \tau_{16a} \) and \( \tau_{24d} \), obtained by the present TC-DFT calculation. The subscripts indicate the Wyckoff positions of the lattice sites introducing cation monovacancies in the TC-DFT calculation.

LCS-gamma Induced Positron Annihilation Study for the Dynamics of Defect Behavior in Bulk Materials

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The behavior of hydrogen atoms is attracting attention in a wide range of research fields such as high-strength structural materials and hydrogen storage materials. In such materials, hydrogen atom diffuses and has various interaction with defects and surface, consequently it is possible to make change the serious characteristic features. In particular, in the corrosion process of high-strength materials under high pressure and chemically harsh environment, the presence or absence of defects in the material is considered to have a great influence on the intrusion of hydrogen and oxygen and the interaction with constituent atoms in the material. It has been almost impossible to directly observe the atomic-level defects behavior that occurs inside the material during processes such as corrosion. This has been hampered by the need for high-energy acceleration of charged particles such as electrons, which are probes in various analytical methods used for detecting defects at the atomic level, and high-energy X-rays. On the other hand, positron annihilation methods are used defects research in materials powerfully. In normal defects research, a radioisotope (RI) and an accelerated slow positron beam are generally used for positron annihilation experiments. The maximum energy of positron emitted from most standard positron source of $^{22}\text{Na}$ is about 540 keV and almost positron beam is the order of 100 keV so that possible research area is near surface of materials. In order to investigate the dynamics of the internal defect behavior which is not possible to detect without destructing the material, mega electron volts accelerated fast positron is needed or positron production in target materials is useful. By utilizing high-energy gamma rays generated by injecting a laser beam from the outside into the electrons of the UVSOR synchrotron radiation storage ring, positron experiments for detecting defect behavior in bulk materials such as the latter become possible. We have developed positron annihilation Doppler broadening system using LCS gamma-beam at NewSUBARU synchrotron facility and successfully measured defects in bulk materials [1]. However, that beam line was closed at 2020. In this study, we have developed a device of in-situ measurement apparatus for tensile test. Figure 2 shows the results of positron lifetime and voltage change after stress applied. The initial drastic change in stress is due to elastic deformation at a moment of stress apply, and the subsequent slow increase is thought to be due to the introduction of dislocations and hardening due to plastic deformation. After applying stress, positron lifetime increased slightly but almost constant. This change corresponds to defect formation such as dislocations and vacancies. However, that change did not exactly match the stress change. Considering that the positron lifetime analysis is an average value, it is necessary to do multi component defects analysis on the positron data.

Fe sample, which is well annealed at 1073 K for 1 h to remove residual defects, was mounted on this apparatus for tensile test. Figure 2 shows the results of positron lifetime and voltage change as a function of time.

Fig. 1. Newly developed stress applying positron lifetime in-situ measurement apparatus at BLIU.

Fig. 2. Stress and positron lifetime change as a function of time.

Effect of the Particle Size on the Positron Annihilation Lifetime and Relative Intensity of CeO$_2$ Nanoparticles

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Recently, it has been reported that the presence of oxygen vacancies in CeO$_2$ catalysts affect their catalytic activity such as automotive exhaust gas purification, particulate matter and/or volatile organic compound oxidation [1]. Therefore, it becomes more and more important to analyze the presence and the concentration of oxygen vacancies in CeO$_2$ with high sensitivity.

Positron annihilation lifetime measurement is a powerful tool for the detection of lattice defects such as oxygen vacancies with high sensitivity. It was previously reported that two lifetime components were observed for CeO$_2$ catalysts: shorter lifetime component of 170-200 ps and longer lifetime component of ca. 400 ps [1]. Moreover, theoretical studies have estimated a positron annihilation lifetime of ca. 170 ps for the bulk of CeO$_2$ without oxygen vacancies [2]. This lifetime is in good agreement with the experimentally observed shorter lifetime component. However, there is no theoretical studies about the longer lifetime component (ca. 400 ps), and various arguments such as annihilation in oxygen vacancy clusters or at the surface have been experimentally made about this lifetime component.

In this study, positron annihilation lifetimes of CeO$_2$ catalysts with different primary particle sizes were measured to discuss the longer lifetime component in the positron annihilation for CeO$_2$ catalysts.

The particle sizes, which calculated from XRD analysis, of CeO$_2$ nanoparticles used in this experiment were 2.3 nm, 9.3 nm, 18.3 nm, and 26.7 nm, respectively. We have set up a gamma-ray spectroscopy system at the laser-Compton scattering (LCS) beamline of BL1U at UVSOR-III [3], and measured the lifetime of the annihilation gamma-rays at room temperature using BaF$_2$ scintillation detector. We used the software Lifetime9 (LT9) to analyze the spectra.

Figure 1 shows the positron annihilation lifetime spectrum of CeO$_2$ nanoparticle with a particle size of 2.3 nm. As shown in Fig. 1, this spectrum could be fitted with two lifetime components; ca. 155 ps ($\tau_1$) and ca. 390 ps ($\tau_2$). The positron annihilation lifetimes ($\tau_1$ and $\tau_2$) and relative intensities ($I_1$ and $I_2$; $I_2 = 100 - I_1$) analyzed using LT9 for CeO$_2$ nanoparticles with different particle sizes are listed in Table 1. Two lifetime components of ca. 170 ps and 390 ps were observed for all CeO$_2$ nanoparticles. The shorter lifetime component of ca. 170 ps is considered to be annihilation in the bulk of the CeO$_2$ nanoparticles, as previously reported. Furthermore, as the particle size decreases, the relative intensity of the longer lifetime component ($I_2$) of ca. 390 ps increases. The longer lifetime component for CeO$_2$ nanoparticles with a particle size of 2.3 nm is found to be more than 90 %. As particle size decreases, the ratio of surface to bulk increases. The longer lifetime component of ca. 390 ps observed in this experiment is dependent on the particle size, suggesting the annihilation at the CeO$_2$ surface. Theoretical calculations on the positron annihilation lifetime at CeO$_2$ surface will be performed in the future.

![Fig. 1 Positron annihilation lifetime spectra of CeO$_2$ nanoparticles with a particle size of 2.3 nm.](image)

<table>
<thead>
<tr>
<th>particle size</th>
<th>$\tau_1$ [ps]</th>
<th>$\tau_2$ [ps]</th>
<th>$I_2$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3 nm</td>
<td>155.0 ± 17</td>
<td>388.2 ± 1.5</td>
<td>93.5 ± 0.7</td>
</tr>
<tr>
<td>9.3 nm</td>
<td>188.0 ± 30</td>
<td>408.0 ± 21</td>
<td>85.1 ± 5.9</td>
</tr>
<tr>
<td>18.3 nm</td>
<td>174.7 ± 4.6</td>
<td>386.3 ± 3.1</td>
<td>66.3 ± 1.1</td>
</tr>
<tr>
<td>26.7 nm</td>
<td>176.7 ± 7.8</td>
<td>388.0 ± 30</td>
<td>53.6 ± 4.0</td>
</tr>
</tbody>
</table>

Mo LIII-Edge XANES Study of Highly Active MoC\textsubscript{x} Species in Mo-V Modified H-MFI Catalysts for Methane Dehydroaromatization

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For direct conversion from natural gases to useful petroleum compounds, innovative GTL (Gas To Liquid) catalysts are called for. A molybdenum- modified H-MFI zeolite (Mo/H-MFI) catalyst is a typical MTB (Methane To Benzene; \(6\text{CH}_4 \rightarrow \text{C}_6\text{H}_6 + 9\text{H}_2\)) catalyst with high activity for methane dehydroaromatization, which is a noted GTL process. Over the Mo/H-MFI catalysts, definite deactivation due to coke deposition has been a serious problem for enhancement of MTB reactivity, and thus, clarification of the deactivation process over the catalysts is one of the important points. A cause of the deactivation strongly depends on both coke deposition onto strong acid sites over H-MFI and structural deactivation of carbonized Mo species. One of the most important subjects for catalytically high and durable activity is the elucidation of active Mo-carbide sites. In this study, Mo L\textsubscript{III}-edge XANES is applied to characterize the active MoC\textsubscript{x} species on Mo/H-MFI and Mo-V co-modified H-MFI.[1]

Mo(5 wt\%)/H-MFI (Si/Al\textsubscript{2}=23) and Mo-V/H-MFI (Mo/V=10-40) catalysts were prepared as described in the previous paper.[2] The methane dehydroaromatization reactivity was evaluated at 1023 K. Mo L\textsubscript{III}-edge XANES spectra were obtained in BL2A of UVSOR-IMS in a total-electron yield mode using InSb double-crystal monochromator. A REX-2000 (Rigaku) software was used for normalization of each XANES spectra.

At Mo/V=40, maximum durability for catalytic MTB reactivity was shown at 1023 K. For L\textsubscript{III}-edge XANES spectra over Mo-V/H-MFI catalysts as shown in Fig. 1, deeply carbonized Mo species due to MoC\textsubscript{x} (x > 0.5) are formed. On the time course of the MTB reaction over Mo-V/H-MFI (Mo/V=40), decrease of edge energy due to rapid carburization of Mo ions is revealed in the initial step. At 60 min., the catalytic MTB reactivity was shown. After 105 min., the energy value relatively approached the \(\alpha\)-Mo\textsubscript{2}C. Because deactivation of MTB was shown after 60 min., the structural change due to formation of \(\alpha\)-Mo\textsubscript{2}C like species can be assigned the decrease of active MoC\textsubscript{x} sites. The rate of deactivation reduced by V co-modification, and thus, inhibition of excess carbonization by V co-modification is proposed. The result is likely to relate to a suppression effect of deactivation. For stabilize the active MoC\textsubscript{x} species, V co-modification is effective on Mo/H-MFI catalysts.

Table 1. Edge energy values obtained by 1st derivatives of LIII-edge XANES (shown in Fig. 1).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Edge Energy / eV</th>
<th>Time on Stream / min.</th>
<th>Edge Energy / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-free</td>
<td>2520.9</td>
<td>0</td>
<td>2522.0</td>
</tr>
<tr>
<td>Mo/V=10</td>
<td>2520.7</td>
<td>5</td>
<td>2520.7</td>
</tr>
<tr>
<td>Mo/V=40</td>
<td>2520.9</td>
<td>60</td>
<td>2520.6</td>
</tr>
<tr>
<td>(\alpha)-Mo\textsubscript{2}C</td>
<td>2521.0</td>
<td>105</td>
<td>2520.9</td>
</tr>
<tr>
<td>Mo Metal</td>
<td>2520.2</td>
<td>185</td>
<td>2520.9</td>
</tr>
</tbody>
</table>

Evaluation of the Electronic State of MgO by NEXAFS Spectroscopy

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Magnesium oxide (MgO) is used in various fields such as catalysts, electrical insulator and heat-resistant materials. In the development of organic solar cells, the introduction of a metal oxide layer improved functionality and efficiency [1]. For example, an MgO nanolayer is used as the electrode [1-3]. Therefore, it is important to evaluate the electronic state of the produced metal oxide.

We have been studying using Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy as a method for evaluating electronic states. Usually, the spectrum is carried out by the electron yield (EY) method and the fluorescence yield (FY) method. The EY method is a surface-sensitive method, and the FY method is a bulk-sensitive method.

In this paper, we investigated how the presence of defects changes the electronic states of the metal oxide surface and bulk.

The sample is MgO powder. Samples with defects were prepared by mechanically crushing. NEXAFS spectra of the MgO powders were measured at the beamline 2A of the UVSOR in the Institute of Molecular Science. For TEY, the drain current from the sample was measured. For PFY fluorescence X-rays were collected using an energy dispersible silicon drift detector (SDD). All experiments were performed at room temperature.

Figure 1 shows the Mg K-edge NEXAFS spectra of MgO powder obtained from TEY. The black line is the untreated sample and the red line is the defective sample. The overall shape of the NEXAFS spectrum is very similar. The inset is an enlargement of the rising edge of the spectrum. The rise of the spectrum of defect MgO shifted to the low energy side. This is due to the presence of reduced MgO.

Figure 2 shows the Mg K-edge NEXAFS spectra of MgO powder obtained from PFY. The black line is the untreated sample and the red line is the defective sample. The overall shape of the NEXAFS spectrum is very similar, but distorted by defects. The rising edge of the spectrum is shifted to the low energy side due to the defect, but it is smaller than that obtained by TEY.

The NEXAFS results obtained by the TEY method showed little difference between the untreated and crashed samples. On the other hand, the NEXAFS results obtained by the PFY method differed significantly. Since the mechanical crashing was done in the atmosphere, the defects inside the powder are chemically unstable and quenched. On the other hand, the defects inside the powder are retained.
Sintering Behavior of Mg-Doped Hydroxyapatite Nano Particles

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Hydroxyapatite (HAp) is a main inorganic component of human bones and teeth. It has good biocompatibility and thus it is used as materials for artificial bones and teeth. HAp in human bodies is not pure but contains various kinds of impurities. They affect properties of HAp such as solubility in water, mechanical strength and so on.

Artificial HAp was commercially available in various forms, powders, granules, pastes and sintered bodies. Doping into HAp have been attempted to control properties of HAp. However, some dopants induce Ca deficiency [1], which cause high-temperature instability. In this study, local environment of Mg in hydroxyapatite were investigated by X-ray absorption near edge structure (XANES) to reveal their effects to sintering.

Mg-doped HAp (Mg-HAp) samples were prepared by the solution-precipitation method. Starting materials were 0.10 mol/L of Ca(NO₃)₂ and (NH₄)₂HPO₄ aqueous solutions. The initial Ca/P molar ratio were set to 2.0, which is larger than that of stoichiometric HAp, to prevent formation of Ca vacancies. The (NH₄)₂HPO₄ aqueous solution was dropped into the Ca(NO₃)₂ aqueous solution under Ar atmosphere. Then, the solution was sealed in a PFA bottle and it was matured at 37 °C in a water bath for 72 h. After maturing, samples were washed by ion-exchanged water, filtrated and dried at 50 °C. A parts of samples were pressed into pellets and sintered at 1000 °C for 6 h.

Samples were characterized by powder X-ray diffraction (XRD), inductively coupled plasma optical emission spectrometry (ICP-OES) and XANES. Mg-K XANES were collected at BL2A in UVSOR by the partial fluorescence yield method using a silicon drift detector. [2] Samples were mounted on a metal plate using carbon tapes.

The XRD pattern of as-dried samples can be assigned to that of hydroxyapatite. Although stoichiometric HAp were obtained in the present condition, (Ca+Mg)/P molar ratio of Mg-doped samples was smaller than that of HAp, 1.67. This indicated that Mg⁺ in HAp are also associated with Ca vacancies and excess H [1].

Figure 1 shows Mg-K XANES of the samples. The spectrum of the sintered Mg-HAp has different features from that of as-dried Mg-HAp. The peak A and C shows formation of MgO. The shoulder D can be assigned to Mg-doped β-TCP. Therefore, Present Mg-HAp were partially decomposed to MgO and β-TCP during sintering. Since non-stoichiometric HAp are partially decomposed to CaO or β-TCP at 1000 °C [3], the low (Ca+Mg)/P molar ratio of the samples also cause the decomposition. Therefore, Mg-HAp and CaCO₃ were mixed to compensate lack of (Ca+Mg)/P molar ratio and they were sintered. However, its Mg-K XANES spectrum has the same features to that of MgO. This result means Mg²⁺ are ejected from HAp during sintering. High-temperature instability of Mg-HAp are not due to low (Ca+Mg)/P molar ratio but fundamental character.

Fig. 1. Mg-K XANES of (a) as-dried and (b) sintered Mg-HAp and (c) Sintered samples of mixture Mg-HAp and CaCO₃, respectively. Spectra of MgO and Mg-doped β-TCP were also shown as references.

Local Structure around Mg in Mg$_{1-x}$Ni$_x$Al$_2$O$_4$

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Spinel oxides with the general formula AB$_2$O$_4$ can be formed with various kinds of divalent A and trivalent B cations. Owing to their unique mechanical, electronic, and magnetic properties, the spinel oxides have gained considerable attention not only from the fundamental research fields but also from the industrial application point of view. Some spinel compounds accommodate a large degree of cationic disorder. The cationic disordering naturally affects the structural properties of the spinels. For example, magnesium aluminate (MgAl$_2$O$_4$) and nickel aluminate (NiAl$_2$O$_4$) spinels are generally known as normal and inverse spinel structures, respectively. However, their inversion degrees for synthetic specimens were also reported to be fluctuating between 0 and 1, respectively, due to the cationic disordering. Recently, the structure of Mg$_{1-x}$Ni$_x$Al$_2$O$_4$ was reported using neutron total scattering to understand the cationic disordering process [1].

X-ray absorption spectroscopy (XAS) is a powerful structure characterization method that uses an X-ray probe to reveal local atomic coordination and electronic structures. In this study, we focus on the local structures in MgAl$_2$O$_4$–NiAl$_2$O$_4$ solid solutions, particularly cationic-disordered structures.

The polycrystalline samples of Mg$_{1-x}$Ni$_x$Al$_2$O$_4$ ($x = 0, 0.05, 0.2, 0.5, 0.8$) were synthesized by a solid-state reaction. They were sintered in air at 1300 °C for 10 h followed by furnace. Mg and Al K-edge XANES measurements were performed on BL2A beamline at UVSOR Synchrotron Facility, Okazaki, Japan, using the partial fluorescence yield method. A KTiOPO$_4$ double-crystal monochromator gives Mg and Al K-absorption edges in the energy regions 1290–1340 eV and 1540–1610 eV, respectively. The measurements of Mg and Al K-edge XANES spectra were carried out in vacuum at a pressure and temperature of $1 \times 10^{-4}$ Pa and 20 °C, respectively. Fluorescence X-rays of Mg K$_\alpha$ and Al K$_\alpha$ were collected utilizing an energy-dispersible silicon drift detector.

The Mg K-edge XANES spectra for Mg$_{1-x}$Ni$_x$Al$_2$O$_4$ are shown in Fig. 1 with the composition values $x = 0, 0.05, 0.2, 0.5$, and 0.8. The intensity of each spectrum was normalized to a value of 1 at the photon energy of 1335 eV after the removal of the background intensity. All the Mg K-edge XANESs show similar spectra and no significant energy shifts or relative intensity changes at the major peaks are observed. It suggests that the local structure of Mg remains unchanged for the whole composition range of Mg$_{1-x}$Ni$_x$Al$_2$O$_4$, whereas the Mg concentration changes with respect to $x$.

Fig. 1. Mg K-edge XANES spectra of Mg$_{1-x}$Ni$_x$Al$_2$O$_4$.

Local Structure Investigations of Zn in ZnAl₂O₄ Induced on Swift Heavy Ion Irradiations

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Zinc aluminate oxide (ZnAl₂O₄) is one of the common spinel compounds. Since it shows a variety of interesting physical and chemical properties, its microstructure has been extensively investigated. A cationic disordered ZnAl₂O₄ spinel is represented by the formula of \([\text{Zn}_{1-x}\text{Al}_x](\text{Zn}_x\text{Al}_{2-x})\text{O}_4\), where the square brackets and the parentheses denote the tetrahedral and octahedral sites, respectively. The variable \(x\) is called the inversion parameter, which quantifies the cation disorder. Radiation with swift heavy ions (SHIs) interacts with materials and causes the structural change. It is therefore applied to material processing, modifications, etc. SHI irradiation provides high energy deposition through electronic stopping to the materials. SHIs in insulating solid materials are known to leave trails of damage along the ion path with a diameter of several nanometers. Structural change related to the cationic disorder has been also observed in ZnAl₂O₄ with SHI irradiation using transmission electron microscopy observation. In this study, we clarify local coordination of each cation element, on which we conducted synchrotron radiation-based X-ray analysis.

Sintered ZnAl₂O₄ samples with the shape of 10 × 4 × 0.5 mm were used in this study. These specimens were irradiated with 340 MeV Au ions to fluences of \(1 \times 10^{11}\) cm⁻² at the H1 beamline of the tandem ion accelerator facility in the Japan Atomic Energy Agency (JAEA)-Tokai. At the beginning of each paragraph, two space characters should be inserted as an indent. Zn \(L_2,3\)-edge and Al \(K\)-edge XANES measurements were performed at the BL2A beamline of UVSOR Okazaki, Japan, using the partial fluorescence yield method (PFY). A Be₃Al₂Si₆O₁₈ (beryl) double-crystal monochromator gives Zn \(L_3\)-edge in energy regions 1000 – 1070 eV. In the cases of Al \(K\)-absorption edges, a KTiOPO₄ double-crystal monochromator scanned the energy region 1540 – 1610 eV. The samples were set with their surface perpendicular to the incident X-ray beam. Fluorescence X-rays of Zn \(L_α\) and Al \(K\) were collected using an energy dispersible silicon drift detector (SDD). All measurements of XANES spectra were carried out in vacuum of \(1 \times 10^{-5}\) Pa at room temperature.

The XANES spectra with the Zn \(L_3\)-edge are shown in Fig. 1 for the ZnAl₂O₄ samples before and after irradiation with 340 MeV Au ions at fluences ranging from \(1 \times 10^{11}\) to \(1 \times 10^{12}\) cm⁻². The intensities of spectra were normalized to a value of 1 at 1055 eV for Zn \(L_3\)-edge, after the removal of background intensities. As shown in Fig. 1, Zn \(L_3\)-edge XANES of the pristine ZnAl₂O₄ sample shows fine structures such as peaks \(A\) to \(H\). The Zn \(L_3\)-edge XANES of the ZnAl₂O₄ samples have not changed drastically from that of the pristine sample even with high fluence irradiation. However, the intensities at the peak \(B\) were decreased and spectral shape between the peaks \(F\) and \(G\) as indicated an arrow were slightly changed with increasing of the ion fluences.
UPS Spectroscopy of TFP Doped P3HT/PCBM Thin Films

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Organic solar cells (OSC) based on blends of polymers and fullerence derivatives are promising candidates for new renewable resource. However, the power conversion efficiency of OSC is low for commercial use. A bulk hetero-junction structure composed of poly (3-hexylthiophene (P3HT) and dphenyl-C61 butyric-acid-methyl ester (PCBM) showed an improvement of the efficiency. To achieve higher efficiency, it is necessary to improve the excition/charge transport. Recently, it was reported that by incorporating additives (i.e. doping) such as tetrafluorophthalnitrile (TFP), P3HT/PCBM system obtain high conversion efficiency [1]. In this study we observed photon- energy dependent photoemission of TFP doped P3HT/PCBM thin film to estimate the change of the electronic structure.

Photoemission measurements were performed at the beam line BL2B of the UVSOR storage ring at the Institute for Molecular Science. Incident photon energies of 28 eV 40 eV, and 90 eV were used. Incident angle of photon and take-off angle of photoelectron are 60° and 0° with respect to surface normal, respectively. At first RR-P3HT (Mn ~ 40000) was dissolved with 0.1wt% in chlorobenzene, followed PCBM adding with weight ratio of 1:0.9 to P3HT. TFP with 5 wt% and 7 wt% were then added to the P3HT/PCBM solution, followed by stirring for 30 min. at 50 °C. The solution consisting of P3HT/PCBM with or without TFP was spin-cast on the cleaned ITO substrate.

Figures 1 (a) and (b) show the measured UPS spectra of the secondary electron cutoff and valence top region, respectively. By TFP doping valence band top is shifted to Ef about 0.2 eV. It is expected that the gap states develop due to polaron and/or bipolaron on polythiophene chains of P3HT by TFP doping [2]. Figure 2 shows the measured UPS spectra at hv = 28 eV, 40 eV and 90 eV. In the UPS at hv = 90eV, the relative intensity of the peak at binding energy (EB) of 6.5 eV is larger than those at hv = 40 eV and 28 eV. By considering the photoionization cross-section of S 3p and C 2s and 2p [3], the peak at EB of 6.5 eV can be assigned to the π state included S 3p orbital in thiophene ring. The photon-energy dependent photoemission can provide the precise information on the electronic structure.

Fig. 1. UPS of secondary electron cutoff (a) and valence top (b) region at hv = 28 eV for P3HT/PCBM thin film with various TFP doping level.

Fig. 2. photon-energy dependent photoemission of P3HT/PCBM thin film with 5 wt% TFP doping level.

Valence and In-gap states of a Polyethylene Model Oligomer, C_{44}H_{90}, Film Studied by Conventional and High-Sensitivity Photoelectron Spectroscopy

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The electronic structures of materials are a key to understand and control the nature of materials. Not only their highest occupied molecular orbital (HOMO) but also weak density-of-states (DOS) in the energy gap has been focused to discuss the practical electric properties. Our research group has been developing high-sensitivity photoelectron spectroscopy (HS-UPS) which enables to directly probe such in-gap states of organic materials [1,2]. Recently, we have applied constant final state photoelectron yield spectroscopy (CFS-YS) to organic and inorganic materials, and a very weak in-gap states whose density is less than 10⁻⁶ of HOMO [3]. The observed in-gap states are believed to be in relation to defect and disorder of the films. However, the origin of in-gap states is still open question. To qualify the nature of the wave function of the in-gap states, photoelectron spectroscopy using synchrotron radiation (SR) is suited because of photon energy tenability and polarizability of light, although conventional SR light includes stray photons to increase background intensity, leading to low sensitivity. BL7U has a unique advantage that high-sensitivity measurement is enabled for less than 10 eV photon energy. We can expect that photon energy dependence and angular dependence of photoelectron could give a hint to identify the wave function nature of in-gap states. In this study, a model compound of polyethylene, tetratetarconate (TTC, C$_{44}$H$_{90}$) was investigated to clarify the valence and in-gap states by using BL2B (conventional UPS), BL7U(HS-UPS), and CFS-YS at Chiba University. Polyethylene is a basic polymer and applied to various products mainly as insulator. It is also interesting in relation to triboelectricity. The clarification of in-gap states is useful to understand its insulating nature.

TTC film was prepared by vacuum vapor deposition on an ITO-coated glass substrate, and the film thickness was 20 nm. The CFS-YS measurement was performed at Chiba University. SR measurements were performed at BL2B and 7U at UVSOR.

Figure 1 shows the UPS of TTC films for $h\nu$=120 eV@BL2B and 21.2 eV@Chiba U. The horizontal axis is the ionization energy relative to the vacuum level. The onset in 21.2 eV spectrum locates around 9 eV, which is consistent with the reported value of 8.9 eV [4]. The onset region is enhanced for 120 eV spectrum because of $h\nu$ dependence of photo- ionization cross-section of the HOMO, giving the onset around 7.5 eV, consistent with our CFS-YS results in the inset of Fig. 1. This result suggests that the reported ionization energy should be updated.

Figure 2 shows the results of HS-UPS at BL7U for TTC film with and without anneal. The valence top region in the figure exhibited the intensity difference. Blue spectrum gives more intensity than red one, suggesting that the in-gap states seems to be reduced by decreasing the degree of disorder due to annealing. The obtained spectrum is compared with our CFS-YS result as shown in the inset. The both spectra are very similar, demonstrating the feasibility of high-sensitivity measurement at BL7U. The angular dependence of the photoelectrons from the in-gap states (1 to 3 eV in the binding energy in Fig. 2) were isotropic. Now we are going to check the photon energy dependence to squeeze the information about the wave function nature of the in-gap states.

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**Structure Analysis on Helical Nanofilament of B4 Phase of Bent-core Liquid Crystals Mixed with Rod-like Cholesteric Liquid Crystals by Resonant Soft X-ray Scattering (RSoXS) at UVSOR**

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Due to the new intermolecular interactions, frustration and competition, soft matter is expected to have a new structure and new functionality. Liquid crystal is typical one of soft matter, and it exhibits various mesophases due to such an effect. For example, bent-core molecules show unique liquid crystalline phases called B1~B8. The B4 phase was the lowest temperature phase observed in the bent-core liquid crystals, and it shows spontaneously chiral separated domains despite of achiral molecules. After various experimental results, it is found that this phase forms a nano-helical structure.

Recently one of authors (YT) studied the binary system between a rod-like cholesteric liquid crystal (CLC) mixture and a bent-core liquid crystal showing a B4 phase [1]. The structure of the binary system composed of rod-like cholesteric liquid crystal mixture and bent-core molecules was analyzed in order to confirm whether nano-scale phase separation as observed in the 5CB – P-8OPIMB binary system is formed. As a summary, a new smectic structure that does not appear in only constituent molecules with wide temperature range was unexpectedly discovered. This structure seems to be fundamentally composed of rich concentration of rod-like molecules. On the other hand, there remains an open question with respect to the effect of the nano-helical filament of B4 phase formed by the bent-core liquid crystal.

In resonant X-ray scattering, using X-ray whose energy is coincident with a certain atom absorption edge, the structure factor becomes a tensor instead of the scalar in conventional X-ray diffraction. Recently, carbon K-edge resonant scattering has been applied to study, and successful in obtaining the precise structures of polymer blends, block copolymer, and liquid crystals. In this study, we report the local nanostructure analysis of B4 nano-helical filament using resonant soft-X-ray scattering (RSoXS) technique. Concentration dependence of rod-like molecules and temperature dependence were measured, and the mixing effect on the helicity and correlation of B4 nano-helical filament are discussed.

The experiment was performed at BL3U of UVSOR. For the measurement, a new vacuum chamber for small angle measurement was fabricated. Used achiral bent-core liquid crystal was P-8OPIMB, and a rod-like cholesteric liquid crystal (CLC) mixture was composed of a nematic mixture (ZLI-2293, Merck) doped with a chiral rod molecule (MLC-6248, Merck). Samples used were filled in the isotropic phase between two pieces of 100 nm-thick Si₃N₄ membranes (NTT-AT). The scattering was detected by CCD (ANDOR DO940P-BN). Incident X-ray beam was tuned between 270~300 eV. Typical RSoXS image was shown in Fig.1, and in this compound, carbon K-edge energy was 285.5 eV.

Figure 2(a) shows chirality concentration dependence of helical half pitch of B4 phase. By mixing CLC mixture, half pitch of nano-helical filament decreases from ca.120 nm to ca.80 nm, but pitch is independent of chirality. Figure 2(b) shows correlation length as a function of chirality concentration of CLC. Correlation length of mixtures is about three times longer than that of pure P-8OPIMB, and slightly increases with increasing the chiral dopant concentration. It suggests that helical pitch of the nano filament of bent-core molecules rich region is spatially homogeneous due to the influence of the rod-like molecule rich region.

![Fig. 1. Typical 2D RSoXS image from the helical nano-filament of the B4 phase.](image)

![Fig. 2. half pitch (a) and its correlation length (b) as a function of chiral dopant concentration.](image)

Recently, operation of particle detectors at higher counting rates has been required in a high-energy physics experiment. To satisfy this requirement, scintillators used in particle detectors need to have a short fluorescence lifetime to allow fast time response. For this purpose, we measured fluorescence spectra and decay curves of newly developed wavelength shifting fibers for the future project of neutral kaon rare decay experiment [1]. The fluorescence decay curves were measured by using light pulses from visible to near ultraviolet under single bunch operation, which enables a time-correlated single-photon counting.

Figure 1 shows the decay curve of a wavelength shifting fiber Y-11 for the 500 nm band under excitation at 424 nm at room temperature. The blue lines indicate experimental data. The lifetime was analyzed by using the data analysis framework ROOT [2].

We assumed that the obtained decay curves are fitted with the formula
\[ I(t) = \int P(t') \theta(t' - T_0) G(t - t') dt', \]
where
\[ P(t) = \sum_{i=1}^{n} A_i \exp\left(-\frac{t}{\tau_i}\right), \quad (n = 1, 2, 3 \text{ and } A_1 = 1) \]
and
\[ G(t - t') = \sum_{i=1}^{m} C_i \exp\left(-\frac{(t - t' - \mu)^2}{2\sigma_i^2}\right), \quad (m = 1, 2) \]

\( I(t) \) represents the observed decay curve, and \( P(t) \) represents the true fluorescence decay curve. If the true decay curve is composed of multiple components, it is described as the linear combination of exponential decay functions with the parameters of lifetime \( \tau_i \) and initial intensity \( A_i \). \( \theta(t' - T_0) \) is a step function to decide the time origin \( T_0 \). \( G(t - t') \) represents the resolution of the measurement system. The time structure of the beam, and so on, and is given by a single gaussian or a sum of two gaussians. The red line is the fitting curve which reproduce the experimental data. The fluorescence lifetimes of Y-11, YS4 and YS6, determined from our analyses, are summarized in Table 1.

![Fig. 1. Decay curve of Y-11 measured at room temperature under excitation at 424 nm obtained for the 500 nm photoluminescence band.](image)

![Fig. 2. Decay curves of YS4 (top) and YS6 (bottom) measured at room temperature under excitation at 416 nm and 418 nm. The former and latter are obtained for the 500 nm and 492 nm photoluminescence band.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \lambda_{EX} ) [nm]</th>
<th>( \lambda_{EM} ) [nm]</th>
<th>( \tau ) [ns] (Ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y-11</td>
<td>424</td>
<td>500</td>
<td>6.44±0.00</td>
</tr>
<tr>
<td>YS4</td>
<td>416</td>
<td>500</td>
<td>1.37±0.00</td>
</tr>
<tr>
<td>YS6</td>
<td>418</td>
<td>492</td>
<td>1.27±0.00</td>
</tr>
</tbody>
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[1] J. Comfort et al., Proposal for \( K_L \to n^0\nu\bar{\nu} \) Experiment at J-PARC (2006).
Thermoluminescence of LuAG Thick Film Scintillators Prepared via Chemical Vapor Deposition Process

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Scintillators are phosphor materials with conversion ability from radiation such as X-rays, γ-rays, and α-particles into UV–visible photons [1]. Scintillators have been used as radiation imaging systems coupled with photon detectors such as position-sensitive CCD. Recently, radiation imaging systems have been used in fields including non-destructive testing, nuclear medical imaging, and geological surveying [2–4]. Scintillator screens with excellent luminescence and emission wavelengths compatible with photon detectors are required for radiation imaging. Tl⁺ doped CsI films and Tb³⁺-doped Gd₂O₂S (GOS) powder phosphors are used as scintillator screens because of their high luminescence yield and well-matched emission band (500–800 nm) with CCD detectors [5]. Columnar and pixelated scintillators have been utilized to improve light yield and spatial resolution. Furthermore, thin scintillator screens of 10 µm or less can prevent light dispersion and are expected to be used in microtomography techniques [6].

Lu₃Al₅O₁₂ (LuAG)-based scintillator shows a high stopping power for radiation, excellent light yield, and a fast scintillation decay. Because of the excellent hardness of LuAG, LuAG thick film with less than 10 µm was hardly obtained via mechanical polishing. Crystal growth from the vapor phase is a promising process for the preparation of LuAG thick films. However, the vapor-grown LuAG thick film was only reported using the pulse laser deposition method, the resultant film was only 140 nm. In the previous work, we have demonstrated the preparation of 5 µm-thick Ce³⁺:LuAG films via a chemical vapor deposition process at a high deposition rate [7]. The thick film showed an excellent light yield and a fast decay time compared with the Ce³⁺:LuAG grown single-crystal by the melting-growth process. The reason for these excellent scintillation properties is not well known. Defect information is useful to explain the variation in scintillation properties of crystals grown by different methods. In this report, we have demonstrated the thermoluminescence (TL) properties for the sake of obtaining the defects in the vapor-grown Ce³⁺:LuAG thick film.

In BL3B of UVSOR facilities, we measured TL properties from 18 K to 300 K (room temperature) for vapor-grown Ce³⁺:LuAG film and melting-grown Ce³⁺:LuAG single crystal. The crystals were irradiated at 165 nm for 10 minutes at a low temperature of 14–18 K. After the irradiation, the sample temperature was slowly raised and luminescence intensity was measured with a CCD detector. The TL emission spectrum for the Ce³⁺:LuAG thick film at 220 K was similar to that for the Ce³⁺:LuAG single crystal at 140 K as shown in Fig. 1 (a). These emission peaks were originating from 5d–4f transition of Ce³⁺ ions. The TL glow curves of the thick film and single crystal are shown in Fig. 1 (b). The curve for the single crystal had continuous emissions up to room temperature while one peak was found at 140–150 K. In contrast, the thick film had two bands at ~80 and 220 K in the curve. These TL results suggested that types and amounts of defects existed in the single crystal scintillator were more and larger than those in the film scintillator.

![Fig. 1. (a) TL spectra and (b) glow curve of LuAG thick film and LuAG single crystal.](image-url)

**Temperature Dependence of Photoluminescence Properties of Li$_2$HfI$_6$**

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We have developed Cs$_2$HfI$_6$ (CHI) scintillator [1] for radiation monitoring in the Fukushima Daiichi Nuclear Power Plant. CHI has an emission wavelength of approximately 700 nm and light yield of 60,000 photons/MeV. Such a red emitting scintillator can be attached to an optical fiber for use in remote radiation monitoring [2]. However, CHI has low neutron sensitivity, and neutron muttering is also required due to nuclear debris including [3].

Most conventional neutron scintillators have an emission wavelength of 500 nm or less, and these scintillation materials are not suitable for the remote monitoring system with the optical fiber. We have developed a neutron scintillator with red and infrared emission by replacing Cs in CHI with Li. Here, $^6$Li has a large neutron capture cross section. In this study, we measured the temperature dependence of the luminescence properties to estimate the band gap energy ($E_{\text{gap}}$) and to discuss the luminescence mechanism.

A Li$_2$HfI$_6$ crystal specimen was synthesized by the vertical Bridgman growth method in our laboratory using 99.9 % pure LiI powders and 99 % pure HfI$_4$ powders. We measured the photoluminescence excitation and emission spectra at 15, 50, 100, 150, 200, 250, 300 and 350 K. Multi-Gaussian fit was operated on the obtained spectra to analyze emission bands.

Figure 1 show the photoluminescence excitation and emission spectra of Li$_2$HfI$_6$. At 15K, Li$_2$HfI$_6$ had an emission band of ~660 nm. The photoluminescence band stably existed from 15 K to 50 K. This emission band can be originating from charge transfer emission or self-trapped exciton.

On the other hands, Li$_2$HfI$_6$ had two emission bands from 100 K to 250 K. The one band located at ~550 nm was observed excited by ~305-nm photons. The other band had the broad red emission peak at ~660 nm. At The emission intensity of such bands gradually decreased as temperature increase. No luminescence was observed at room temperature due to thermal quenching.

To determine the emission mechanism exactly, we measure the temperature dependence of decay time in the future.

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Samarium monosulfide (SmS), in which two electronic configurations (insulator (4f)6 and metal (4f)5(5d)1) of Sm energetically compete, is known as valence fluctuation materials. The electronic state of Sm undergoes the transition to (4f)5(5d)1 from the (4f)6 state by applying pressure and chemical doping, while the (4f)6 state is stable under ordinary pressure and temperature condition [1]. It is promising to be applied to materials for negative thermal expansion (NTE) and actuators by controlling these electronic states [2] since this phenomenon is accompanied by a large volume change up to 10 %. To study changes in the electronic states due to the valence transition, we conducted systematic optical reflectivity measurements of Sm1-xYxS single crystalline samples, covering wide energy and compositional region [3]. It is clarified that a characteristic structure, which showed the changes in electronic states induced by the valence transition, became appeared in the optical spectra at Y composition of 0.28 [3]. For the application of the electric-field-driven actuator, the changes in the electronic state during the valence transition induced by the application of the electric field must be studied. It is also necessary that SmS can be applied electric field enough to induce the valence transition.

In this work, we prepared a Sm0.9Ca0.1S single-crystalline sample to enhance the insulation, and conducted the optical reflectivity spectral measurements at room temperature at no electric field first. Normal incident reflectivity spectra were collected at 295 K by using a Fourier-type interferometer (0.005–1.6 eV) and a grating spectrometer (1–3 eV) installed with a microscope. For the measurements from visible to the vacuum-UV region (2–30 eV), we used synchrotron radiation at BL3B of UVSOR, Institute for Molecular Science.

Figure 1 shows the electrical resistivity of Sm0.9Ca0.1S single crystal. By comparing to the non-doped SmS, it is clearly shown that the electrical resistivity significantly increased by more than two orders of magnitude. We succeeded in the valence transition to the metallic phase of this sample by applying the electric field of 300 V/cm at the liquid nitrogen temperature (data not shown). The optical reflectivity spectra of Sm0.9Ca0.1S are shown in Fig. 2. The spectra in the lower energy region (Fig. 2(a)) show that both Ca-doped and non-doped SmS are characteristic of the insulator, in terms of low reflectivity in the far-IR region except for phonon peak. The reflectivity spectrum of Sm0.9Ca0.1S also demonstrated an appearance of the reflectivity dip around 40 meV, strongly suggesting further insulation by the Ca doping. On the other hand, for the reflectivity spectra in the higher energy region (Fig. 2(b)), problems in the data consistency remain. The reflectivity data above 5 eV must be reconsidered for precise discussion on the changes in the electronic state due to the Ca doping, whereas fine structures below 5 eV are reliable. To elucidate the changes in the electronic states by the valence transition induced by the electric field, it is necessary to construct a measuring system that the reflectivity spectra in the wide energy region can be collected at the liquid nitrogen temperature and under the electric field in the future.

Fig. 1. Electrical resistivity of Sm0.9Ca0.1S single crystals.

Fig. 2. Optical reflectivity spectra of Sm1-xCa,xS at 295 K: (a) from far-IR to visible and (b) from visible to vacuum-UV regions.

Optical Investigation on Fluoro-olefins in Vacuum-Ultraviolet for New Refrigerant Gas Development

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Chlorofluorocarbon (CFC), hydrochlorofluorocarbon (HCFC), and hydrofluorocarbon (HFC) have been used as a refrigerant. These gases have high global warming potential (GWP) over 100. Recently, the hydrofluoroolefin (HFO) gases are expected as new low environmental load refrigerant due to its low GWPs since olefin gas is unstable and easily decompose by ultraviolet light in nature. In order to put HFO into practical use as a refrigerant, it is necessary to clarify the physical characteristics of HFO such as UV absorption and decomposition process. In this study, we measured the vacuum ultraviolet (VUV) light induced decomposition of HFO.

The decomposition spectra measurements were carried out in BL3B in UVSOR facility. Trans-C₂H₄F₂ gas was flowed into vacuum chamber through the capillary tube. The pressure in vacuum chamber was kept less than 3×10⁻⁴ Pa. The VUV light from 8 to 30 eV was irradiated on sample gas and the ionized molecular fragments were detected TOF-mass spectrometer shown in Fig. 1.

Figure 2 shows the decomposition spectra of C₂H₄F₂. We could clearly observe the ionization energies of each fragments. The decomposition from C₂H₄F₂ to CH₂F₂ and HF arise with 14.9 eV. With higher energy about 18 eV, the C₂H₄F₂ dissociate to CHF and CHF. From our previous results, the trans-C₂H₂F₂ has the absorption from 135 nm (9.2 eV) to 190 nm (6.5 eV) as shown in Fig. 3. The absorption at 145 nm is attributed to the stretching and twisting of carbon double band and the 190 nm is the transition from π to π* in C=C bonds, respectively [1]. However the ionization and decomposition threshold is quite higher than these absorption. These results show that the higher photon energy over 14 eV is needed for trans-C₂H₂F₂ to be decomposed in the air. However, we notice that other components exist such as oxygen and nitrogen which react with fluoro-carbon in real case.

In conclusion, we could observe the optical properties and ionization energy of decomposition process of C₂H₄F₂ in VUV region. The results let us know the UV- or VUV-induced decomposition dynamics of fluoro-olefins as refrigerant in next-generation.

Fig. 1. Schematic image of the experimental setup in BL3B.

Fig. 2. Decomposition spectra of trans-C₂H₂F₂.

Fig. 3. Absorption spectrum of C₂H₂F₂.

Absorption Bands of Ti⁺ Centers in CsI-based Ternary Crystals

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The optical properties of the Ti⁺ centers in alkali halide crystals have been extensively investigated [1]. The Ti⁺ centers in alkali halide crystals with the NaCl-type crystal structure exhibit the typical A, B, and C absorption bands. On the other hand, the Ti⁺ centers in cesium halide crystals with the CsCl-type crystal structure have absorption bands different from the typical A, B, and C bands; in particular, the appearance of absorption bands in CsI:Ti⁺ is unusual [2,3]. It has been regarded that the unusual absorption spectra of the Ti⁺ centers in cesium halide crystals originate from the different ionic configurations around the Ti⁺ ion in the NaCl- and CsCl-type crystal structures [2]. To provide a better understanding of these observations, we investigated absorption bands of CsCaI₃:Ti⁺, CsBa₂I₅:Ti⁺, Cs₄CaI₆:Ti⁺, and Cs₄SrI₆:Ti⁺ crystals, which were prepared by a cell method [4].

Figure 1 shows the absorption spectra of CsCaI₃:Ti⁺, CsBa₂I₅:Ti⁺, Cs₄CaI₆:Ti⁺, and Cs₄SrI₆:Ti⁺ crystals at 10 K. For reference, the absorption spectrum of CsI:Ti⁺ is also demonstrated in the top of Fig. 1. In CsCaI₃:Ti⁺, the absorption bands having no extremely different absorption intensity are observed at 4.54, 5.14, and 5.55 eV. A absorption band is observed at 4.32 eV for CsBa₂I₅:Ti⁺. In Cs₄CaI₆:Ti⁺ and Cs₄SrI₆:Ti⁺, the absorption band with a doublet structure is observed at about 4.23 eV and the band with the largest absorption intensity is observed at 4.94 eV. In addition, the weak absorption bands are observed at about 5.18 and 5.33 eV. The 4.23 eV band with a doublet structure and the 4.94 eV band in Cs₄CaI₆:Ti⁺ and Cs₄SrI₆:Ti⁺ may be assigned to the A and C bands of the Ti⁺ centers, respectively, from the intensity ratio between them. On the other hand, it is hard to assign the absorption bands of CsCaI₃:Ti⁺ and CsBa₂I₅:Ti⁺ to the A, B, and C bands, just like the absorption bands in CsI:Ti⁺.

The CsI-based ternary crystals above have various crystal structures; orthorhombic (CsCaI₃) [5], monoclinic (CsBa₂I₅) [6], and trigonal (Cs₄CaI₆ and Cs₄SrI₆) [7] structures. In the host lattice, the Ti⁺ ions which replace the Cs⁺ ion, have various coordinations of the I⁻ ions. That is to say, the Ti⁺ ions in the ternary iodide crystals have different coordination of the I⁻ ions from the Ti⁺ ion in the CsI crystal. Despite the difference of the coordination, the absorption bands of CsI:Ti⁺ seem to appear at the energy positions which the absorption bands of the Ti⁺ centers in the ternary iodides are observed. For example, the lowest absorption band of CsI:Ti⁺ is located at 4.27 eV, which is close to the lowest bands of Cs₄CaI₆:Ti⁺ and Cs₄SrI₆:Ti⁺ in the energy position. The 4.52 eV absorption band of CsI:Ti⁺ is located at the energy position close to the lowest 4.54 eV band of CsCaI₃:Ti⁺. The energy positions of the absorption bands in CsI:Ti⁺ may be related to the coordination states around the Ti⁺ ion.

The intrinsic luminescent scintillators with the chemical formula of $A_2BX_6$ ($A$: monovalent cation, $B$: tetravalent cation, $X$: halogen ion) are attracting large attention due to their high light outputs and high energy resolutions. We reported Cs$_2$HfI$_6$ and Rb$_2$HfI$_6$ as the novel red-emitting scintillators with the high light output over 40,000 photons/MeV [1-5]. While the candidate compositions of $A_2BX_6$ scintillators are actively studied, the detailed mechanism of intrinsic luminescence is still unclear. We have studied the photoluminescence properties of $A_2BX_6$ scintillators to understand the basic luminescence behaviors and compare them with the that of conventional phosphors using the beamline of BL3B, UVSOR.

In the UVSOR activity report 2020, we reported the low-temperature photoluminescence properties of Cs$_2$HfI$_6$. Cs$_2$HfI$_6$ showed two photoluminescence bands at 10K. The origin of each band was unclear. In order to compare the effect of $B$ cation on the photoluminescence properties, we grew Cs$_2$ZrI$_6$ crystal and evaluated the temperature dependence of photoluminescence emission spectra. A single crystalline Cs$_2$ZrI$_6$ specimen was obtained by the vertical Bridgman growth method in our laboratory from 99.95 %—pure ZrI$_4$ and 99.999 %—pure CsI powders.

Figure 1 shows the measured spectra of Cs$_2$ZrI$_6$. The emission wavelength of Cs$_2$ZrI$_6$ was ~630 nm at 300 K, and shifted towards shorter wavelength as cooled down reaching ~720 nm at 10K. Cs$_2$ZrI$_6$ had only one photoluminescence band at all temperature, while Cs$_2$HfI$_6$ had two bands at 10K. Therefore, the numbers of photoluminescence bands of Cs$_2$HfI$_6$ were determined to be two when $B$ is Hf and to be one when $B$ is Zr. The tetravalent cation $B$ might play the important roll in the luminescence phenomena of $A_2BX_6$ scintillators. For future study, we would continue to study $A_2BX_6$ compounds to reveal the rolls of $A$, $B$ and $X$ ions.

Structural Analysis of Unvulcanized Rubber by Scanning Transmission X-ray Microscopy

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Reduction of consumption of limited resources is nowadays a critical issue to maintain our daily life. Rubber is one of the important resources and its demand is assumed to increase especially according to growth of car industries. Therefore, further improvement in wear-and destruction-resistant of rubber is necessary to reduce its consumption. Then, control of crosslinking of sulfur in rubber is a key technology. Heterogeneity of network of crosslinking in rubber has been confirmed by small-angle neutron scattering [1]. This heterogeneity causes destruction of rubber because it gathers internal stress under deformation. Therefore, dispersion of a crosslinking reagent in the rubber is important to make the crosslinking network homogeneous.

To achieve the above goal, it is important to measure the relationship between the dispersion and various parameters of synthesis. Thus, this dispersion has been conventionally tried to depict by using electron microscopy. However, its observation was not easy because the rubber contains only small amount of the crosslinking agent. Moreover, the crosslinking agent is consisted of light elements and is easily damaged by electron beam. Then, scanning transmission X-ray microscopy (STXM) can be an alternative approach. STXM can probe the crosslinking agent by using near-edge X-ray absorption fine structure (NEXAFS). The advantages of STXM are high spatial resolution around 30 nm and much lower radiation damage than the electron microscopy. In this report, the distribution of crosslinking agent in unvulcanized rubber is investigated by STXM.

An ultra-thin section of the unvulcanized rubber of 250 nm thick was prepared as a sample by a cryo ultra-microme. In the case of STXM observation, the sample was cooled down to ~ -90 degree with cryo-cooling setup to suppress the radiation damage [2].

Figure 1(a) shows an X-ray fluorescence image at N-Kα line by using transmission electron microscopy with an energy dispersive detector. Since signal intensity of N-Kα line is low, the image is noisy and does not have any structures. Even though the detection of the X-ray fluorescence brings high sensitivity to the analytical system, the crosslinking agent could not be detected. We assumed that the crosslinking agent was damaged by irradiation of the electron beam.

The STXM image acquired at the X-ray energy of 401 eV is shown in Fig. 1(b). The observed image shows many dark domains with high absorption. X-ray absorption spectra of these dark domains (Fig. 2(a)) are compared with references of the crosslinking agent “A” and “B” by comparing with the reference spectra (Fig. 2(b)). Matrix of the rubber has quite lower nitrogen signals than the dark domains, which implies heterogeneity of the distribution of the crosslinking agent. As a result of linear combination fitting, these dark domains are consisted of the crosslinking agent “A” and “B”.

Fig. 1. (a) Images of unvulcanized rubber acquired by transmission electron microscopy with an energy dispersive detector acquired at N-Kα line and (b) that by STXM at N-K edge (401 eV).

Fig. 2. (a) X-ray absorption spectra of the unvulcanized rubber in the dark domain (solid line) and matrix (dashed line) in Fig.1(b) around N-K edge and (b) those of the crosslinking agents for “A” (solid line) and “B” (dashed line).

Adding filler materials such as carbon black to elastomer materials such as synthetic rubber can significantly change mechanical properties: stress properties, tensile strength, and abrasion resistance [1]. The factors that cause the changes in mechanical properties are not well understood, and the type and the amount of filler materials added to obtain the desired mechanical properties are known empirically. In addition, it is known that the structure of an elastomer material differs at each scale and exhibits a hierarchical structure [2-4]. Among the hierarchical structure, we presume that the chemical state and the 3D structure of the bound-rubber structure formed between filler particles at the nm scale determine the overall mechanical properties. In the study, we will add filler materials and/or reagents to elastomer materials that the mechanical properties are known, then the chemical states of the bound rubber structure and its spatial distribution will be measured using the STXM in BL4U. We believe that this process will clarify the origin of the mechanical properties.

In the measurement, compounds were prepared from an elastomer material with a filler material and various reagents, and styrene-butadiene rubber (SBR) and modified SBR are used as the elastomer materials. The fabricated compounds were cut into sections and used in the STXM measurements. The measurement was performed with a spatial resolution of 100 nm and an exposure time of 2 msec per point. The obtained soft X-ray images clearly distinguish the position of the added filler material. Based on the preliminary NEXAFS results, spectral measurements were performed focusing on the difference between the π*- and the σ*- structures of the C-K absorption edge. The obtained nanoscopic spectra around bound-rubber structures in a same compound showed a similar spectral shape with a change in peak intensity depending on the presence or the absence of the filler and/or reagents. Different spectral shape was observed around a bound-rubber structure according to a modification of the SBR. An example of the spectral change in shape is shown in Fig. 1. By the energy positions of the peaks, we estimate the origins of peaks as that: peak A is a transition from C1s orbital to π* orbital due to the C=C bond, peak B is a transition to C-H* orbital, and peaks C and C' are transitions to σ* orbital [5].

Fig. 1. C-K edge spectra of SBR and modified SBR with same filler and reagents. Curves are smoothing results for guide to see.

Analysis of Materials for Secondary Batteries by STXM

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In order to improve the performance of secondary batteries such as lithium-ion batteries (LIB) and develop innovative electrode materials, investigation on the electronic state of electrode materials under charge/discharge condition is required. This is because the electronic state determined by redox conditions is one of the critical factors for the energy density such as charge/discharge capacity and operating voltage of battery. Since soft X-ray absorption spectroscopy (XAS) is sensitive to the change of local electronic state, it is suitable analytical method for electrode materials [1,2].

In addition, study of facet is also important to control of the stability of the interface between the electrode active material and the electrolyte. To elucidate the behavior of the facet, analysis for spatial distribution of electronic state at interface is required. For spatially selective analysis, various techniques of electron microscopes have been developed. For example, TEM-EELS and TEM-EDS are widely used as elemental analysis with a high spatial resolution. However, in order to understand the electronic state of the active materials, synchrotron radiation soft X-ray spectroscopy is advantageous in terms of the energy resolution and lower beam (X-ray) damage than the damage by electron beams in electron microscopes. Moreover, the scanning transmission soft X-ray microscopy (STXM) with a spatial resolution of several tens of nm is highly effective for analyzing the electronic-state distribution in one particle of the electrode material because the particle size is in the order of several micrometers.

So far, we have mainly focused on cathode materials like transition-metal oxides, but now we apply STXM analysis to 2D carbon materials used for the anode as well. Figure 1 shows the STXM image of 2D carbon nanosheets at 320 eV and the C $K$-edge XAS spectrum of selected area. Graphite-like $\pi^*$ and $\sigma^*$ peaks are observed. We believe that STXM is important for carbon materials as well because it enables analysis for the distribution of local electronic structure to discuss the stability of the material.

Fig. 1. STXM image and spectrum of selected area.

Probing the Electronic Structure of Ni-Co Binary Oxide/Graphene Nanocomposites as Supercapacitor Electrodes by Scanning Transmission X-ray Microscope

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Nickel and cobalt-based oxide are considered as promising materials for supercapacitors owing to the multiple oxidation states and excellent electrochemical redox activity. The conductive carbon materials (such as graphite, carbon nanotubes, and graphene) serve as a conductive component can created the possibility to form the conducting interconnection between carbon materials and transition metal oxides, allowing fast ions and electrons transport inside interior space of transition metal oxide pore/channel structure, thus dramatically enhanced the electrocatalytic activity. In this study, Ni-Co binary oxide were synthesized on the graphene to obtain Ni-Co binary oxide/graphene (NCG) nanocomposites as supercapacitor electrodes. NCG nanocomposites were tested with the applied voltage of 0.3 and -0.1 V to evaluate pseudocapacitive behavior toward studying the change of the local chemical environment of a selected element using STXM. Figure 1 show the optical density images, STXM stack mapping, and XANES spectra of NCG at C K-edge and O K-edge under applied voltage of 0.3V and -0.1V. The C K-edge XANES spectra has several distinct features (Gₐ, G₆, and G₇). Features G₆ and G₇ at 284.6 and 290.9–291.9 eV are associated with the transitions from C 1s to the unoccupied π* and σ* orbitals, respectively, reflecting the bonding perpendicular to the ring plane and within the ring plane. Features G₆ consist of three peaks G₆, at 286.3 eV, G₆₂ (287.5 eV), and G₆₃ (288.5 eV) correspond to C–O π* (hydroxyl or ether), C=O π* (carbonyl groups), and O=O π* (carbonyl, lactone, or carboxylic acids). The O K-edge XANES spectra reveals Ha and Hb features at 532.8 and 540.0–545.0 eV. These features are associated with C=O π* states of carbonyl groups and the O–H σ*, C=O σ* and C=O σ* symmetry states from carbonyl, carboxylic acid, and hydroxyl groups. The spectral profile in Figs. 1(g) and (h) changes with the bias potential applied from selected regions of the edges (yellow) and the center (red) that indicate favorable structural and chemical reversibility during the charge/discharge process, suggesting that the oxygen-containing functional groups provide pseudocapacitance through Faradaic reactions that occur near the surface of the graphene-based materials: \( >\text{C}=\text{O} + \text{H}^+ + e^- \leftrightarrow \text{COOH} <\text{C}=\text{O} + \text{H}^+ + e^- \), and \( >\text{C}=\text{O} + e^- \leftrightarrow \text{C}=\text{O}^- \) [1-3]. Further studies at Ni and Co L-edge are expected to provide detail information of the energy storage mechanisms.

Fig. 1. Optical density images of NCG under (a) 0.3 V and (d) -0.1 V. (b,e) C K-edge and (c,f) O K-edge STXM. (g) C K- and (h) O K-edge STXM-XANES of NCG from different regions (yellow and red).

Development of Reflection XMCD Measurement Setup for the Investigation of Inner Structures of Magnetic Thin Films at UVSOR BL4B

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Magnetic thin films/multilayers with complex depth structures exhibit a wide variety of magnetic phenomena due to the interactions between layers [1]. Furthermore, multilayer structures have been used to realize useful properties in recording media, which is an important application of magnetic materials. Direct observation of the magnetic distribution in the depth direction of such magnetic multilayers has been used to elucidate the mechanism of evolution of magnetic structures in thin films.

We installed an experimental setup for reflectance x-ray magnetic circular dichroism (XMCD) method [2] in the soft X-ray region at BL4B and experiments were performed on test samples as shown in Fig. 1.

The sample and the detector can be rotated independently to obtain reflectivity. X-rays were detected by a photodiode (AXUV100G, Optodiode inc.). The magnetic field was about 0.35T, and measurements were made at room temperature. The magnetic field was applied by two pairs of Nd magnets disposed oppositely. The magnets can be rotated and the relative positional relationship between the magnetic field and the sample was kept constant. The setup is schematically depicted in Fig. 2.

We used off-axis components of x-rays from the bending magnet to obtain circularly polarized light. The x-rays are elliptically polarized. XMCD intensity was measured by changing the direction of magnetic field.

The sample was CoFeB and an oscillating structure was observed due to the interference of the cap layer and the underlying layers. We observed the difference corresponding to XMCD by changing the direction of magnetic field, which is consistent with the simulation results. The same measurements were made around the absorption edges and spectroscopic information was extracted. These results can be reproduced by the simulation based on the full matrix algorithm and the magnetooptical effects of the elliptically polarized x-rays were treated explicitly. Although there have been previous studies using XMCD of reflectance, there are few studies that extends this method to obtain spectroscopic information. We also conducted spectroscopic measurements and obtained photon energy and reflection angle dependence to analyze the depth-resolved magnetization information.

Fig. 1. The experimental setup installed at BL4B.

Fig. 2 The illustration for the XMCD reflectivity measurements.

BL5U

**Dirac Fermions and Topological Phase Transition in $X\text{Mg}_2\text{Bi}_2$ ($X = \text{Ba and Sr}$)**

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The search for novel fermions is recently becoming an exciting challenge in condensed-matter physics, as highlighted by the discovery of two-dimensional (2D) Dirac fermions in graphene and helical 2D Dirac fermions at the surface of three-dimensional (3D) topological insulators. The recent discovery of 3D Dirac fermions in topological Dirac semimetals (TDSs) further enriches the category of exotic fermions. TDSs show exotic quantum phenomena such as high carrier mobility and giant linear magnetoresistance governed by the linearly dispersive Dirac-cone energy band. Also, TDSs provide a fertile playground for realizing a variety of topological phases, e.g., by breaking the time-reversal/crystalline symmetry or by chemical substitution. However, despite many theoretical predictions for TDS candidates, TDSs that have been experimentally verified are still rare. Moreover, topological phase transition from TDSs has been scarcely realized partly because of the difficulty in substituting constituent elements of known TDSs. Thus, it is highly desired to explore new TDS materials that overcome such difficulties.

Here we demonstrate that ternary compound BaMg$_2$Bi$_2$ is a new TDS and serves as a useful platform to study topological phase transition [1].

High-quality single crystals of $X\text{Mg}_2\text{Bi}_2$ ($X = \text{Ba and Sr}$) were synthesized by the self-flux method. ARPES measurements were performed with micro-focused VUV synchrotron light at BL5U. Prior to the ARPES measurements, samples were cleaved in an ultrahigh vacuum.

Figure 1(a) shows the ARPES intensity near $E_F$ measured along a momentum ($k$) cut crossing the $\Gamma$ point. One can see linearly dispersive bulk valence band (VB) which crosses $E_F$. To search for a possible band touching of VB and conduction band (CB) predicted in the calculation, we deposited K atoms onto the surface in an ultrahigh vacuum. One can clearly see in Fig. 1(b) that the hole bands in K-deposited BaMg$_2$Bi$_2$ are shifted downward due to the electron doping to the surface. Intriguingly, VB in the negative $k$ region appears to almost continuously disperse across $k = 0$ and cross $E_F$ at positive $k$, without losing its intensity at $k = 0$, indicative of the formation of Dirac-cone dispersion. In contrast to the case of K-deposited BaMg$_2$Bi$_2$, the spectral weight associated with the CB is absent and no Fermi-edge cut-off is observed in K-deposited SrMg$_2$Bi$_2$ [Fig. 1(c)]. This observation demonstrates that an intrinsic band gap opens in SrMg$_2$Bi$_2$, suggesting the occurrence of topological phase transition from the TDS state to the ordinary insulator phase upon replacing Ba with Sr [Fig. 1(d)].

![Fig. 1. (a)-(c) ARPES intensity plot near $E_F$ in BaMg$_2$Bi$_2$, K-dosed BaMg$_2$Bi$_2$, and K-dosed SrMg$_2$Bi$_2$. (d) Schematic band diagram of $X\text{Mg}_2\text{Bi}_2$.](image)

Band-structure Reconstruction of Ca$_3$Ru$_2$O$_7$ Induced by K Adsorption

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Application of external perturbations to Mott insulators often leads to dramatic changes in the electronic structure. For example, the Mott insulator Ca$_2$RuO$_4$ can be metallized by chemical substitutions [1,2], physical pressure [3], and electric current [4]. Changing the number of the RuO$_2$ layer in the unit cell from one (Ca$_2$RuO$_4$) to two (Ca$_3$Ru$_2$O$_7$), the system can also become metallic down to low temperatures [5]. Instead, Ca$_3$Ru$_2$O$_7$ exhibit a first-order phase transition at $T = 48$ K that involves lattice and spin degrees of freedom [6]. At 48 K, antiferromagnetically ordered spins change their orientation from the $a$ to $b$ crystalline axis and the lattice undergoes slight compression along the $c$ axis. This phase transition makes a significant influence on the transport properties such as resistivity, Hall effect, and Seebeck effect [7], suggesting dramatic changes in the band structure near the Fermi level. Indeed, our recent angle-resolved photoemission spectroscopy (ARPES) study [8] has revealed a clear band-structure reconstruction into a Dirac-semimetallic state upon cooling across 48 K.

Recently, alkali-metal adsorption is being recognized as an efficient way to dope a solid surface with electrons. This methodology has been applied to Mott insulators such as iridates [9] and cuprates [10] and the occurrence of metal-insulator transition has successfully been demonstrated through in-situ ARPES measurements. With this technique, electrons can be doped at the surface even in the case where bulk electron doping by chemical substitutions is impossible. Ca$_3$Ru$_2$O$_7$ is one such case where electron doping has never been realized.

We have dosed K on Ca$_3$Ru$_2$O$_7$ and carried out ARPES measurements at BL5U at $T = 10$ K. Figure 1 shows energy distribution curves in a wide energy range. As K is adsorbed on the surface, a peak at the binding energy of ~1.7 eV, which is a remnant of the lower Hubbard band, loses its intensity and instead a spectral weight accumulates at the Fermi level. This spectral-weight re-distribution suggests that the electronic state changes away from the Mott insulating state. The change is even more clearly seen in the ARPES spectra in Fig. 2. Notably, the hole-like dispersion around the $\Gamma$ point expands, which is opposite to what is expected from electron doping. It is therefore likely that the effect of adsorbed K atoms goes beyond simple electron doping to cause the observed band structure reconstruction.

Quadrupole Electronic Structure in Mn$_{3-x}$Ga Studied by Angle-resolved Photoemission Spectroscopy

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Magnetic ordered alloys have attracted significant attention for use as spintronics materials because they are highly likely to exhibit perpendicular magnetic anisotropy (PMA). Tetragonal Mn$_{3-x}$Ga alloys are widely recognized as hard magnets which exhibit highly anisotropic, ferrimagnetic, and metallic properties [1]. We have investigated the mechanism of PMA and large coercive fields in Mn$_{3-x}$Ga by x-ray magnetic circular and linear dichroisms (XMCD /XMLD) [2]. The origin of PMA in Mn$_{3-x}$Ga alloys can be explained by the quadrupole contribution along the $z$-axis by the charge asphericity. The specific crystalline structures provide the elongated $c$-axis direction, which induces the anisotropic chemical bonding, resulting in the anisotropy of electron occupancies in 3$d$ states and charge distribution. However, orbital magnetic moments in the Mn sites are almost quenched because of half-filled occupation.

Although the site-specific charge distributions can be accessed by x-ray absorption spectroscopies, the origin of quadrupole-induced PMA from the viewpoint of the band structures in Mn$_{3-x}$Ga alloys is not fully understood. Here, we employ the angle-resolved photoemission spectroscopy (ARPES) to unveil the anisotropic band structures in Mn$_{3-x}$Ga by the comparison with the density-functional theory (DFT) calculations.

30-nm-thick Mn$_{3-x}$Ga samples were prepared on MgO (001) substrate using sputtering technique. On the surface of Mn$_{3-x}$Ga layer, Mg and MgO capping layers were deposited. The MgO layer was removed by Ar-ion sputtering and the Mg layer was removed by annealing just before the ARPES measurements. We construct the method to remove the Mg layer which does not react chemically with Mn atoms at the interface. Clear low-energy electron diffraction (LEED) patterns were also obtained. ARPES was performed at BL5U, UVSOR, where the photoemission chamber is connected to the sample preparation chamber. The measurement conditions were set at 15 meV energy resolution and 10 K. Linear polarized beams of $s$- and $p$-polarization were used to detect the orbital symmetry. We employ the photon energy ranges of 60 – 80 eV to enhance the Fe 3$d$ photo-ionization cross section, where the $Γ$-X(M) line is scanned by the angular mode of $±$ 15°.

Figure 1 shows the Fermi surface mapping taken at photon energy of 80 eV. Four-fold symmetric lines are detected, which is consistent with the LEED patterns. High intensity spots appear at both $Γ$ and X points. Nodal lines are also developed from each symmetric point. Energy-momentum ($E$-$k$) dispersion curves also exhibit the intensities at $Γ$ and X points with the dispersive bands. These bands are comparable with the DFT calculation. The band from the $Γ$ point has a character of $yz$ orbital, which can be detected by the $s$-polarized beam in vertical geometry.

We discuss the quadrupole formation. In the DFT calculation, the virtual spin-flip transitions from occupied up-spin $yz$ to down-spin $z^2$ orbitals correspond to the finite matrix element to the PMA in the perturbation. Therefore, occupied $yz$ orbitals detected by ARPES contribute to spin-flipped $yz$-$z^2$ oblate quadrupole charge distribution, resulting in the PMA. Our finding explains the origin of PMA in Mn$_{3-x}$Ga comes from not orbital moment anisotropy but elongated charge distribution through the spin-flipped transition in specific orbitals, whose results are also supported by XMCD and XMLD.

Fig. 1. ARPES images of Mn$_3$Ga taken at $hν=80$ eV using $s$-polarized beam. (a) The $k_x$-$k_y$ mapping. (b) Band dispersions along $Γ$-X direction in primitive Brillouin zone. Dot curves in (b) show the results of DFT calculation.

Change of the Fermi Surface of Bi$_2$Sr$_2$Cu$_2$O$_8$+δ Observed by ARPES


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It has been known that the cuprate superconductors show a high superconducting (SC) transition temperature ($T_c$) and exotic physical properties, on the other hand, the SC mechanism has been unclear yet. In order to understand the mechanism of high-$T_c$ cuprates, Bi$_2$Sr$_2$CaCu$_2$O$_8$ (Bi2212) is one of the promising candidates to study the electronic structure and reveal the physical properties. Bi2212 has two CuO$_2$ planes in the unit cell and shows the high $T_c$ around 95 K at the optimally doped sample. Superconductivity occurs upon hole doping into the CuO$_2$ plane and the amount of hole doping can control $T_c$, and therefore, carrier doping (hole/electron concentration) plays an important key parameter in cuprates [1,2]. According to the previous report, we consider that differences of the electronic states in Bi2212 depending on the sample with several compositions might exist, even though samples are expected to be the same hole concentration, where the optimally doped sample shows the maximum $T_c$ ($T_{c\text{,max}}$); however, the compositions are different, which shows a different $T_{c\text{,max}}$ [1,2]. Therefore, in the present study, we have performed an angle-resolved photoemission spectroscopy (ARPES) measurements to study the Fermi surface changes of Bi2212 due to differences in sample compositions.

We have demonstrated ARPES measurements to investigate the electric structure on wide momentum space for Bi2212 with two compositions. ARPES experiments were carried out at BL5U and we measured two optimally doped samples: Bi$_2$Sr$_{1.5}$CaCu$_2$O$_{8.5}$ ($T_c \sim 85$ K) and Bi$_{2.1-x}$Pb$_x$Sr$_2$CaCu$_2$O$_{8.5}$ ($x = 0.66, T_c \sim 95$ K) in the SC and the normal states. High quality single crystals of Bi2212 were cleaved in-situ in the ultrahigh vacuum (~4 $\times 10^{-9}$ Pa).

Figures 1(a) and 1(b) show the Fermi surfaces taken at $h\nu = 60$ eV and $T = 30$ K in the SC state for Bi$_2$Sr$_{1.5}$CaCu$_2$O$_{8.5}$ and Bi$_{2.1-x}$Pb$_x$Sr$_2$CaCu$_2$O$_{8.5}$ ($x = 0.66$), respectively. Fermi surfaces are clearly observed in wide momentum space for both samples. In Fig. 1(a), in addition to the main Fermi surfaces as shown by a red arrow at -0.4 Å$^{-1}$ in momentum space on the horizontal axis, the spectrum at -0.2 Å$^{-1}$ in momentum space is observed, indicating that the modulation from the BiO layer, so called replicas, is observed as shown by a blue arrow. If replicas are observed in the ARPES results, we cannot understand the electric structure precisely in momentum space because the main and replica bands are overlapped. Figure 1(b) shows Fermi surfaces of Bi$_{2.1-x}$Pb$_x$Sr$_2$CaCu$_2$O$_{8.5}$ ($x = 0.66$). Substitution of the Bi site with Pb suppresses the modulated structure from the BiO layer and as a result, the replica is strongly suppressed. In Fig 1(b), the replicas on Fermi surfaces are well suppressed and the main bands are dominantly observed.

We have analyzed the ARPES spectra around the nodal region for each sample and determined the Fermi momentum ($k_F$) for each Fermi surface by fitting of momentum-distribution curves (MDCs) with a Lorentzian. The $k_F$’s are plotted as shown by red dots (Fig. 1). As a result, we have found that two samples with different compositions show that the distance between two nodal points has a different value. This means that the Fermi surface might change due to differences in sample compositions. As a future work, we will demonstrate ARPES experiments in a different composition and doping level.

![Fig. 1. Electronic structure of Bi2212. (a) Fermi surfaces of Bi$_2$Sr$_{1.5}$CaCu$_2$O$_{8.5}$ in the superconducting state (30 K). (b) Fermi surfaces of Bi$_{2.1-x}$Pb$_x$Sr$_2$CaCu$_2$O$_{8.5}$ ($x = 0.66$) in the superconducting state (30 K). Main Fermi surfaces are shown by a red arrow. Red dots are the Fermi momentum estimated from the MDC peak near the Fermi level.](image)

CDW-induced Electronic Reconstruction in a Kagome Metal $A\text{V}_3\text{Sb}_5$

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Recently, a new kagome-lattice material $A\text{V}_3\text{Sb}_5$ ($A$ = K, Rb, and Cs) has been discovered. $A\text{V}_3\text{Sb}_5$ undergoes a charge-density wave (CDW) transition below $T_{\text{CDW}} = 78$-103 K, accompanied by the in-plane unit-cell doubling with the $2 \times 2$ periodicity. This CDW state shows an intriguing entanglement with the superconductivity (transition temperature $T_c$ of 0.9-2.5 K) and non-trivial topological surface states. Also, exotic properties, e.g., strong anomalous Hall effect and possible time-reversal symmetry breaking have been reported, highlighting the unconventional nature of CDW.

Despite intensive studies, the origin of CDW in $A\text{V}_3\text{Sb}_5$ is highly controversial. In particular, the type of structural distortion responsible for the CDW has yet to be clarified. First-principles calculations proposed two types of distortions sharing the same space group to account for the in-plane $2 \times 2$ periodicity. One is the “Star-of-David” (SoD) distortion of V atoms. The other is an inverse type of the SoD distortion, where V atoms show an opposite displacement compared with the SoD case, resulting in a periodic arrangement of triangular and hexagonal patterns, called “Tri-Hexagonal” structure. It is experimentally highly controversial which distortion actually takes place.

To gain insight into the origin of CDW from the electronic structure perspective, we have performed high energy and spatial resolution ARPES of KV$_3$Sb$_5$ by using a micro-focused beam at BL5U in UVSOR [1].

Figure 1 shows a side-by-side comparison of the ARPES intensity plots along the M-M cut measured in the normal and CDW states (left and right panels, respectively). In the normal state, one can see a strong intensity near the Fermi level ($E_F$) at the M point, together with a hole-like dispersion topped at slightly below $E_F$ at the M point. One can recognize an obvious difference in the intensity distribution in the CDW phase. A new shallow holelike bands crossing $E_F$ appear at the middle of the two M points, as also identified from the momentum distribution curve at $E_F$ (white curves shown in the inset; folded bands are highlight by white triangles). This indicates the CDW-induced band folding. A comparison of the observed electronic reconstruction with the band structure calculations assuming SoD/ThH structural distortion would help to clarify the origin of CDW.

Fig. 1. ARPES intensity measured along the M-M cut at $T = 120$ K (left) and 20 K (right), respectively. White curve in the inset shows the MDC at $E_F$.

Electronic Structure of VNb₃S₆: a Transition-metal Intercalated NbS₂

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Transition-metal dichalcogenides MX₂ host a rich variety of physical phenomena such as superconductivity [1] and charge density wave [2], and thus have attracted intense interest for decades. In 1970-1980’s, there have been extensive attempts to modulate its electronic structure by intercalation of 3d transition metals T [3]. Thus made TM₃X₆ takes crystal structure with broken inversion symmetry and shows various types of magnetic order depending on the intercalated 3d transition metal. Out of these, CrNb₃S₆ has been most intensively studied because of the special type of magnetic order called chiral soliton lattice.

In Recent years, due to the breaking of both the inversion and time-reversal symmetries, TM₃X₆ is attracting interest from a topological perspective. Especially, VNb₃S₆, which shows a ferromagnetic order below T_C ~ 44 K, has been theoretically predicted to possess a magnetically induced Weyl point. Indeed, a recent study has demonstrated large anomalous Hall conductivity potentially associated with the proposed Weyl point [4]. While there recently appears increasing number of ARPES reports made for CrNb₃S₆ [5,6], MnNb₃S₆ [7], FeNb₃S₆ [8], CoNb₃S₆ [8-10], and NiNb₃S₆ [7,8], to the best of our knowledge there have been no such studies on VNb₃S₆. We therefore attempted an ARPES measurement to reveal the low-energy electronic structure of VNb₃S₆.

Single crystals of VNb₃S₆ were grown by the chemical vapor transport method from polycrystals with iodine as the transport agent. ARPES measurements were performed at BL5U of UVSOR at temperatures ranging from 10 to 200 K.

Figures 1(a) and (b) show the Fermi surface and band dispersions through the Brillouin-zone center of VNb₃S₆, respectively, recorded at 10 K. From these, three hole-like Fermi surface sheets centered around the zone center can be clearly identified. This result is distinct from the observations for the antiferromagnets FeNb₃S₆, CoNb₃S₆, and NiNb₃S₆ [7-10], where there is only single Fermi surface. Instead, the Fermi surface structure resembles what was reported for the ferromagnet CrNb₃S₆ [5,6]. In the case of CrNb₃S₆, from temperature dependent systematic APRES measurements across T_C [6], the emergence of multiple Fermi surface sheets has been ascribed to the effect of ferromagnetism. In contrast, as for VNb₃S₆, the band structure is remarkably robust against temperature variations up to 200 K (Fig. 1), far above T_C ~ 44 K. Therefore, the peculiar band structure is likely not rooted in magnetism. Comparisons with first-principles band structure calculations both in the magnetic and non-magnetic states would pave the way to understanding the origin of these observations.

Angle-resolved Photoemission Study of Zr$_3$SnC$_2$

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MAX phase compounds, i.e., M$_{m+1}$AX$_n$ where M is a transition metal, A belongs to groups 13-16 and X is the C or N element, have recently been attracted much attention due to their possible application for new class of two-dimensional systems called MXenes by removing A atoms [1]. Zr$_3$SnC$_2$ is so called 312 MAX phase in which Zr$_3$C$_2$ layers separated by Sn layer, then two dimensionality becomes higher than 211 phase. In addition, relatively stronger spin-orbit interaction of Zr and Sn 4d is expected to affect its physical properties.

In this study, we have performed angle-resolved photoemission spectroscopy (ARPES) on MAX phase compound Zr$_3$SnC$_2$ to directly investigate the electronic structure of this system.

ARPES measurements were performed at the UVSOR-III BL5U. Data were acquired at $T=30$ K with $h\nu=82$ eV which enables us to trace around the $\Gamma M$ plane with inner potential of $V_0=17.7$ eV estimated from the photon energy dependent measurement (not shown).

Figure 1 shows the obtained Fermi surface (FS) image on the $\Gamma KM$ plane of Zr$_3$SnC$_2$. Along the $\Gamma M$ and $\Gamma KM$ high-symmetry lines (orange lines), we have extracted the band structure image as shown in Fig. 2.

We have found that the electronic structure near the Fermi level ($E_F$) consists of two hole-pockets around $\Gamma$ point and relatively intense dispersive feature just below $E_F$ around M point. While the former seems to be similar with DFT calculation, the latter feature has appeared in the blank of bulk DFT bands around the M(L) point. Therefore, we assigned the dispersive feature around the M(L) point to be surface state. From the band structure near $E_F$ (Fig. 3(a)), the observed surface state was formed by characteristic saddle-like dispersive feature (Fig. 3(b)), in which the saddle-point locates around 150 meV at the M(L) point. From the saddle-like dispersion, it has been expected that the narrow dispersive feature along MK line forms pair of triangular FS around M point, which has been clearly observed in Fig.1. To clarify the essential role of the surface states, further studies with using liner/circular polarization and spin-resolved ARPES are intended.

Fig. 1. Fermi surface image of Zr$_3$SnC$_2$. Orange thick lines indicate the high-symmetry lines on which the ARPES image has been extracted in Fig. 2.

Fig. 2. Band structure (lower panel) and MDC spectra at $E_F$ (upper panel) along $\Gamma M$ and $\Gamma KM$ lines of Zr$_3$SnC$_2$. Blue solid and dashed lines are DFT calculation along the $\Gamma M\Gamma$ and $\Gamma K\Lambda$ lines, respectively.

Fig. 3. (a) Band structure near $E_F$ around M point of Zr$_3$SnC$_2$. (b) Example of saddle-like dispersive feature, in which M point corresponds to the saddle point.

Fermi Surface Measurements of TiSe$_2$ with the CDW Transition

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Transition metal dichalcogenides (TMDs) are a class of materials attracting high scientific interest in recent years. They are layered materials where the interlayer distance is considerably larger than the intralayer atomic distance yielding a quasi-two dimensional character. Charge density wave (CDW) transition, which is a transition accompanying a periodical superlattice formation below the transition temperature, is one of the typical phenomena of the low-dimensional system, and has been attracted many researchers. Among TMDs, (1T-)TiSe$_2$ exhibits very unique character; its CDW transition provides the $2a \times 2b \times 2c$ superlattice formation where the interlayer periodic distortion occurs. Although several studies, including ARPES studies, have been made for revealing the driving force of the CDW transition in TiSe$_2$, rather few were made for investigating the interlayer interaction. In this work, we investigate the change in the Fermi surface of TiSe$_2$ along the interlayer axis due to the CDW transition by measuring the photon-energy dependent ARPES.

The experiments were carried out at BL5U of UVSOR. The temperature of the cleaving/measurements of single-crystalline TiSe$_2$ were 300K and 10K, which are respectively above and below the CDW transition-temperature (about 200K). The (lateral) CDW formation at 10K was examined by the folding of the valence band from $\Gamma$(A) point to M(L) point in the ARPES spectrum. Figure 1 show intensity maps of the photoelectron at the Fermi level, demonstrating the Fermi surface along the $\Gamma$-M-L-A plane. The horizontal axis is along the $\Gamma$-M(A-L) line derived from the angular distribution of the photoelectron, and the vertical axis is along the inter-layer axis ($k_z$) derived from the photon-energy dependent measurements. For deriving value of $k_z$, the free-electron final state is assumed, and 13.5eV is used as the inner potential after the reference[1].

At 300K [Fig. 1(a)], the Fermi surface of the electron-pocket near the M(L) point shows a tilted elliptical shape. This structure is periodic (except the variation of the intensity) along the $k_z$ axis with a $2\pi/c$ distance which is the periodicity of the inverse lattice. This is consistent with the DFT calculation (not shown here). When the CDW transition occurs at 10K, meanwhile, the periodicity of the Fermi surface along the $k_z$ axis shrieks as half of that at 300K [Fig. 1(b)]. It is due to the superlattice formation whose lattice constant along the inter-layer axis $c^* = 2 \times c$. It is a very clear evidence of the CDW transition of TiSe$_2$ accompanies the periodic interlayer distortion. Further studies for investigating the driving force of the interlayer CDW transition in TiSe$_2$ is under progress with a help of the DFT calculation.

Fig. 1. Intensity maps of the photoelectron at the Fermi level of TiSe$_2$. The horizontal axis is along the $\Gamma$-M(A-L) line derived from the angular distribution of the photoelectron, and the vertical axis is along $k_z$ axis derived from the photon-energy dependent measurements. The sample temperature is 300K (a) and 10K (b).

BiCh$_2$ compounds are quasi-two-dimensional materials with a layered structure typically represented by the composition of REO$_{1-x}$F$_x$BiCh$_2$ (RE=rare earth; Ch=S, Se). It can be doped electrons by replacing oxygen with fluorine atoms, and electron-doped samples exhibit superconductivity below 2-10 K. Several experimental and theoretical studies have indicated the possibility of unconventional superconducting mechanisms [1]. Since the superconducting transition temperature is sensitive to the pressure applied to the BiCh$_2$ planes, the effects of many elemental substitutions have been intensively studied [1-2]. Elemental substitution effects are important for understanding the superconducting mechanism, although there are few reports on the electronic structure. Pb-doped La(O,F)BiS$_2$ shows an anomalous behavior with a sharp decrease in electrical resistance around 100 K, but the origin of this behavior is unknown [2]. In this study, we performed temperature-dependent angle-resolved photoemission spectroscopy (ARPES) measurements of Pb-doped La(O,F)BiS$_2$ above and below the temperature at which an anomaly in electrical resistance appears in order to investigate the cause of the anomalous electrical resistance.

The measurements were performed using the LaO$_{0.5}$F$_{0.5}$Bi$_{0.9}$Pb$_{0.1}$S$_2$ single crystals synthesized by the flux method [2]. The temperature at which the anomaly appears is estimated to be about 100 K from the temperature dependence of the electrical resistance. ARPES measurements were performed at BL5U of UVSOR III. We used the 70 eV photons, and the energy resolution was 35 meV. All samples were cleaved in situ on the (001) plane in an ultrahigh vacuum of less than 5.0×10$^{-9}$ Pa. The temperature dependence of the electronic structure was measured in the range of 50-150 K.

Figure 1 shows the Fermi surface mapping from the ARPES intensity between ±25 meV of the Fermi energy ($E_F$) measured at 70 K and 150 K. Figure 2 shows the angle-integrated energy distribution curves (EDCs) in the X-M and Γ-X directions measured at 70 K and 150 K. The Fermi surface shape was found to be in good agreement with the previously reported La(O,F)BiS$_2$ (F concentration = 0.5) [3], with no significant difference in the Fermi surface shape at 70 K and 150 K, respectively. On the other hand, the EDC intensity in the X-M and Γ-X directions at 70 K decreased from $E_F$ to around 0.2 eV and increased around 0.3-0.6 eV, compared to those at 150 K. Reproducibility of the results were checked for several samples. Therefore, this EDC change is considered to be a change in the electronic structure due to an anomaly in the electrical resistance.

Fig. 1 Temperature dependent Fermi Surfaces map of LaO$_{0.5}$F$_{0.5}$Bi$_{0.9}$Pb$_{0.1}$S$_2$ at (a) 70 K and (b) 150K.

Fig. 2 Angle-integrated EDCs in each direction (top: X-M, bottom: Γ-X). Spectral intensities were normalized by area intensity in the range $E_B = -0.1$-0.8 eV. The angles are integrated about ± 6° around the X point.

High-$T_c$ cuprate superconductors have attracted much interest since their discovery in 1986 for their high $T_c$ as well as unusual physical properties such as bad metal states and formation of density waves [1, 2]. However, the high-$T_c$ mechanism has not been fully understood yet, and therefore, it is necessary to study the physical properties from the microscopic point of view. Angle-resolved photoemission spectroscopy (ARPES) is one of the most effective and direct experimental methods to investigate the electronic structure in solids. ARPES spectra are related to the imaginary part of the one-particle Green’s function and give the quasiparticle excitation spectrum. The one-particle Green’s function includes the self-energy derived from the many-body interactions such as the electron-phonon, electron-electron, and electron-impurity interactions. By analyzing the ARPES spectral lineshape quantitatively, one can directly evaluate the magnitudes of each many-body interaction.

The previous ARPES studies of cuprates have focused on the investigation of the electron-boson interaction at the vicinity of the Fermi level [3]. In the previous studies, the real part of the self-energy due to the electron-electron interaction was usually estimated by a line [4]. However, the energy dependence of the self-energy due to the electron-electron interaction is not trivial in the wide energy range. It is assumed to induce a so-called “waterfall” structure or a sudden spectral intensity suppression in the ARPES spectra [5]. To understand the mechanism of the high-$T_c$ cuprate superconductivity, it is also important to quantify the magnitudes of the electron-electron interaction as well as electron-phonon(boson) interaction [3].

In this study, to quantitatively evaluate the electron-boson interaction and the electron-electron interaction simultaneously, we have performed a high-resolution ARPES study using synchrotron radiation on the Bi-based high-$T_c$ cuprate (Bi,Pb)$_2$Sr$_2$CuO$_{6+x}$ (Pb-Bi2201) in the wide momentum and energy ranges. We have selected overdoped Pb-Bi2201 with $T_c = 6K$ because it has a relatively simple electronic structure which allows us to precisely evaluate the self-energy in the normal state (i.e., normal self-energy). While it has been expected that heavily hole-doped cuprates would behave as the 2D Fermi Liquid, ferromagnetic fluctuation has been found recently [6].

Figures 1(a) and 1(b) show ARPES intensity plots taken at $h\nu = 60$ and 75 eV, respectively. Based on the lineshape analyses using the tight-binding model (here we only considered the $x^2-y^2$ band), we have evaluated the self-energy in the wide energy range. Figure 1(c) shows the simulation of the ARPES intensity plot using the evaluated self-energy. We clarified that the real part of the self-energy crosses the zero line at the energy of $E - E_F \approx -0.5$ and the imaginary part of self-energy has the maximum at that energy (Dashed line in Fig. 1). Because the imaginary part of the self-energy gives the spectral linewidth, the waterfall structure is caused by the suppression of the spectral intensity due to the significant broadening of the linewidth at $E - E_F \approx -0.5$ eV due to the electron-electron interaction. In order to further reproduce the spectral intensity, the matrix element and contribution from other bands at the bottom of the $x^2-y^2$ band is required.

Fig. 1. Electronic structure of Pb-Bi2201. (a), (b) ARPES intensity plots taken at $h\nu = 60$ and 75 eV, respectively. (c) Simulated ARPES intensity plots using the evaluated self-energy. A solid black curve is the $x^2-y^2$ band in the tight binding model.

Multi-atom Resonance Photoemission from the Valence Band of TiSe$_2$

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“Multi-atom resonant photoemission” (MARPE), which is an interatomic resonant photoelectron emission from neighboring atoms of the core-excited atoms, was reported first for the O1s photoelectron emission at the Mn-2p excitation edge in MnO [1], and attracted significant attention. In this report, we report the MARPE effect on, for the first time, the valence band in TiSe$_2$ analyzed with the momentum-resolved constant initial state (MR-CIS) spectroscopy using the “Momentum Microscope” apparatus recently installed at BL6U in UVSOR-III, IMS [2].

Figure 1(a) shows a CIS spectrum of TiSe$_2$ at the Ti-L$_3$ edge for the whole valence band (0-5.5 eV). The spectrum is well represented by two symmetric Lorentzian peaks. Meanwhile, in Fig. 1(b), the MR-CIS spectrum for a specific state [M-point at the binding energy of 2.0 eV; shown in Fig. 1(c)] is well reproduced by the sum of two Fano-shaped strongly asymmetric curves. According to our photon-energy dependent ARPES studies and DFT calculations (not shown here), this state is mainly provided by Se-4p, while most of the valence band is provided by Ti-3d. The symmetric shape in Fig. 1(a) indicates that the interference between the direct photoexcitation from Ti-3d and the intra-atomic Auger process does not occur since the former probability is so small at this photon energy range [3]. On the contrary, it is suggested that the probability of the photoemission from Se-4p is comparable to that of the inter-atomic Auger decay of Ti-2p core hole, and the interference yields the Fano-type asymmetric shape. It should be noted that the Fano parameter $q$ is negative in the present case, contrary to the conventional resonant photoelectron emission. More work will be needed to reveal the physical origin of negative $q$.

Fig. 1. (a) CIS spectrum for the whole valence band at the Ti-L$_3$ edge, (b) The MR-CIS spectrum at the specific states (M-points at the binding energy of 2.0 eV), which are shown as bright spots in the photoelectron intensity map (c), where the hexagon is the Brillouin zone of TiSe$_2$.

Temperature-dependent Electronic Structure of $\eta$-Mo$_4$O$_{11}$ Revealed by Photoelectron Momentum Microscopy

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$\eta$-Mo$_4$O$_{11}$ is a pseudo two-dimensional material that consists of alternating layers of octahedral structure, which contributes to electrical conduction, and tetrahedral structure, which do not contribute to electrical conduction. Owing to the connection of octahedral structure in a form of one-dimensional chain, $\eta$-Mo$_4$O$_{11}$ can be classed as a material with hidden one-dimensionality. A two-step anisotropic charge density wave (CDW) transition at 109 K ($T_{C1}$) and 30 K ($T_{C2}$) has been reported for this material by temperature-dependent conduction measurement [1], and this transition was supported by the observation of change in lattice periodicity [2]. However, though a gap opening and band folding is predicted in case of CDW transition, such phenomena were not observed in the band structure [3]. Therefore we have performed photoemission measurements of $\eta$-Mo$_4$O$_{11}$ at different temperatures in order to observe traces of CDW in the band structure.

Figures 1 and 2 show the Fermi surface and the band dispersion at $k_y=0$ Å$^{-1}$ measured at $T=20$ K. The thin solid black lines in Figs. 1 and 2 represent the Brillouin zone boundaries. The Fermi surface in Fig. 1 looks different from that reported previously in Ref. [3], probably due to the difference in the energy of the excitation light. The energy used in the present study would make the band visible only in the first Brillouin zone, but not in the second one. In other words, we can explain the results in Ref. [3] by considering the bands in the second Brillouin zone.

Figure 3 shows the photoelectron intensity distribution near the Fermi level. As can be seen in this figure, no band gap opening or band folding can be observed even when the temperature is varied across the transition temperatures, and metallic electronic states are always observed. This result suggests that the charge density wave transition in $\eta$-Mo$_4$O$_{11}$ may be a metal-metal transition. The nesting vector determined in previous studies is $q_{c1}=0.23b^*$ and $q_{c2}=0.55a^*+0.47b^*+0.28c^*$, suggesting that the charge density wave phase has a fairly long period structure. As a result of the minute modulation of each atom, we consider that the band structure of the metallic phase may not be much affected. This idea is consistent with the slow increase of resistivity below $T_{C1}$, and the decrease in resistivity indicating the metallic character of this material below $T_{C2}$.

![Fig. 1. Fermi surface of Mo$_4$O$_{11}$ measured at $T = 20$ K.](image1)

![Fig. 2. Band dispersion at $k_y=0$ Å$^{-1}$.](image2)

![Fig. 3. Temperature-dependent photoelectron intensity distribution near the Fermi level.](image3)

Chemical vapor deposition (CVD) is a promising method to synthesize high-quality transferrable graphene sheets for device applications. We have previously reported growth of high-quality graphene on Ir(111)/α-Al₂O₃(0001) by a low-pressure CVD method and demonstrated the reusability of the substrates [1-2]. In this study, we characterized the crystallinity of graphene/Ir(111)/α-Al₂O₃(0001) and the electronic interaction between graphene and Ir(111) using photoelectron momentum microscope (PMM) [3].

We carried out CVD growth of graphene on the Ir(111)/α-Al₂O₃(0001) substrates, using CH₄ and H₂ as precursors at 1000 °C. The gas flow rate of hydrogen and methane were 100 : 10 (#1), and 200 : 10 (#2), respectively. For both #1 and #2, the 2D and G peaks for graphene were observed in the Raman spectra. We characterized the samples (#1 and #2) by valence-band photoelectron spectroscopy (VB-PES) using PMM at the linearly polarized soft X-ray beamline BL6U of the UVSOR Synchrotron Facility, Institute for Molecular Science, Okazaki 444-8585, Japan.

Through this study, we found that the relationship of crystal orientations and the degree of electronic interaction between graphene and the Ir(111) depended on the CVD growth conditions of graphene, for which PMM is a powerful complementary characterization tool to conventional methods (e.g., Raman spectroscopy and AFM) for comprehensive characterization of graphene/Ir(111).

Fig. 1. Iso energy cross sections of 2D band dispersion at Fermi energy for (a) #1, (b) #2.

Fig. 2. Momentum-resolved VBP spectra of graphene for (a) #1 along KTK direction, (b) #1 along MIM direction, (c) #2 along KTK direction, and (d) #2 along MIM direction.

Vibrational Spectroscopy of Pentacene Single Crystals in the Mid to Far Infrared Region and its Temperature Dependence

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Charge transport in organic semiconductor molecules has become an important issue in the pursuit of organic semiconductor devices with excellent efficiency. However, the decrease in carrier mobility due to molecular vibration is a particular problem for organic semiconductors, and the elucidation of the vibrational interactions that limit the charge carrier transport efficiency is one of the most important subjects in the field of organic semiconductors. In this study, we carried out mid-to-far infrared absorption spectroscopy on the single crystal pentacene (C$_{22}$H$_{14}$), a typical p-type organic semiconductor material, and attempted to track its temperature dependence.

First, single crystals of pentacene were prepared using the physical vapor transport (PVT) method and fixed to chemical-vapor-deposited (CVD) diamond substrates (5 mm × 5 mm × 0.4 mm). Infrared (IR) absorption measurements were performed in a transmission configuration at room temperature (RT) or low temperatures (100 K, 40 K). A blank CVD diamond substrate as a reference sample was also measured in identical conditions.

The measurement results are expressed in the top panel of Fig. 1 in terms of the IR absorbance which was derived from the relative transmittance of the pentacene/diamond sample with respect to the blank diamond sample. Quantum-chemical calculation results (Gaussian09, b3lyp, 6-31g*) for intramolecular vibration modes and calculated intermolecular $A_b$ and $A_c$ phonon modes of the pentacene single crystals taken from a literature [1] are shown in the lower panels of Fig. 1. To track how the absorption intensity and peak positions change when the effect of thermal vibration is reduced by cooling, the measurements were performed at three different temperatures (RT, 100 K, and 40 K). Figure 1 shows two peaks around 460–500 cm$^{-1}$ for the spectra at RT and 100 K. Whereas, the calculation results predict three modes around 480–500 cm$^{-1}$, the former two modes were presumed to be merged in the experimental spectra. Although, the two peaks appeared in a low wavenumber region compared to the calculated positions. On the other hand, the spectrum at 40 K exhibited a single peak, instead of two, at approximately the same wavenumber as the calculation results. The reason for this is unclear at this stage, but may be attributed to changes in intermolecular interactions as previously reported as shifts in Raman bands for amorphous thin-films of $N,N'$-di-naphthaleyl-$N,N'$-diphenyl-1,10-biphenyl-4,4'-diamine and copper-phthalocyanine [2].

For the spectral features below 200 cm$^{-1}$ observed in Fig. 1 are not able to be assigned to which vibrations at this stage mainly due to a poor signal-to-noise ratio. More accurate and reliable measurements in this wavenumber region are future subjects to identify plausible phonon/vibration modes that inhibit the electrical conduction at RT.

Fig. 1 Far-infrared spectra of a pentacene single crystal sample measured in a transmission configuration at various temperatures (RT, 100 K, 40 K). Calculated intramolecular vibrational modes using the ab-initio density functional theory and lattice phonons of pentacene single crystals taken from Ref. [1] are also presented.

Spectral Evidence of Current-Induced Local-to-Nonlocal Transition of SmS

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Samarium monosulfide SmS shows a pressure-induced insulator-to-metal transition from a black-colored semiconductor to a golden-colored metal (BGT) [1,2]. Even though BGT was discovered more than 50 years ago, its origin remains unclear. One possible origin has been proposed as a transition between the Bose-Einstein condensation (BEC) and the BCS state of excitons [3], but no definitive evidence has been obtained.

Recently, Ando et al. reported that the nonlinear relationship between voltage ($V$) and electric current ($I$) occurs with increasing $I$ at temperatures lower than 100 K, which suggests the electronic state changes by applying current [4]. However, whether the current-induced electronic state change is related to the BGT is now under debate. To clarify the origin of the nonlinear $V/I$ curve and the link to the BGT, we investigate the current and temperature dependence of the reflectivity spectrum, which reflects electronic structure, in the nonlinear $V/I$ region. We have already reported the rapid increase of the effective carrier density at the nonlinear $V/I$ region by observing the THz reflectivity spectrum [5], which suggests the appearance of the current-induced local-to-nonlocal transition of the electronic structure. To clarify the whole picture of the current-induced electronic structure change, we measured the current dependence of the mid- and near-infrared reflectivity spectrum using THz and IR microscopes at BL6B.

The single crystalline SmS with a typical sample size of $1\times1\times1$ mm$^3$ was sandwiched by the electrodes connected to the current source and mounted in a liquid-helium-cooled cryostat.

Figure 1 shows the $I$-dependent reflectivity spectra at temperatures of 50 and 100 K. With increasing $I$, the reflectivity intensity below 0.1 eV increases, suggesting the carrier density increase. The peak at 0.6 eV corresponds to the exciton peak of the direct bandgap at the X point in the Brillouin zone [6,7]. The peak was broadened and slightly shifted to the higher energy side with increasing $I$. The spectra at 50 K (a) and 100 K (b) qualitatively showed the same behavior. In the case of a normal insulator-to-metal transition, the bandgap size decreases toward the metallic phase. However, this change in Fig. 1 is the opposite of that expected. The spectral shift is consistent with that with increasing temperature [2]. Our THz reflectivity spectrum results suggest that the current-induced increase of the carrier density could not be explained by the increase of lattice temperature [5].

From these results, the current flow induces the delocalization of electrons without increasing lattice temperature. However, the golden-colored metallic phase does not appear by the current. This result suggests that the BGT needs other factors, such as lattice deformation.

Fig. 1. Current dependence of mid- to near-infrared reflectivity spectra of SmS at 50 K (a) and 100 K (b).

Recently, fiber biomaterials such as cellulose fiber and peptide fiber have been getting attention in medical and materials fields. The common feature in their structures is a rigid sheet-like conformation, and it is usually difficult to regulate the stacking format without uses of extreme heating and organic solvents. As an alternate approach, physical technique such as high-power radiation can be proposed to control the fiber structure. Here, two-kinds of terahertz waves were applied to regulate the cellulose fiber: one is terahertz free electron laser (THz-FEL) and the other is submillimeter wave from gyrotron [1]. The THz-FEL has a double pulse structure that is composed of micropulse and macropulse where the duration of the former is 10-20 ps and that of the latter is about 4 μs. The oscillation wavelength covers from 30 to 300 μm, and the irradiation power is given as avg. 5 mJ per macropulse. The submillimeter wave from the gyrotron is a single pulse (1-2 ms half width) having 10 W power. After the cellulose fiber was irradiated by the THz-FEL that was tuned to 80 μm and the submillimeter wave that was tuned to 720 μm under atmospheric conditions at room temperature, those samples were added on metal-coating plate and analyzed by using BL6B synchrotron-radiation infrared microspectroscopy. The measurement was performed by reflection mode with 64 scans.

In the FT-IR spectrum of cellulose (Fig. 1), strong band at 1050 cm⁻¹ and middle peak at about 1300 cm⁻¹ were observed (Black). The former band corresponds to stretching vibrational mode of glycoside bond (vC-O), and the latter peak can be assigned to bending vibrational mode of H-C-O, respectively [2]. After THz-FEL irradiation (blue), the former peak was decreased and the latter peak was increased. On the other hand, the former peak was largely increased accompanied by slight increase of the latter peak after the submillimeter wave from gyrotron (red). These spectral changes indicate that submillimeter wave gave the irradiation effect on cellulose fiber opposite to THz-FEL. Interestingly, when the cellulose fiber was irradiated by submillimeter wave following THz-FEL (green), the whole spectral pattern was almost the same as that of the non-irradiation sample (black). One interpretation on this phenomenon is that the cellulose fiber was dissociated to the monomeric chain by the THz-FEL irradiation, and the cellulose monomers were re-associated by the submillimeter wave radiation to produce the original cellulose fiber.

We have ever found that amyloid fibrils that form fiber structure like cellulose can be dissociated by the THz-FEL and be promoted to form the aggregate by the gyrotron. [3,4]. Therefore, it can be enough considered that cellulose fiber can be dissociated and re-associated by those terahertz waves similarly with amyloid fibrils. The high-power terahertz waves can be expected as a physical tool for regulation of the fiber biomaterials in future.

Fig. 1. Infrared spectra of cellulose fiber after irradiation by terahertz waves. Black: non-irradiation; blue: cellulose irradiated by THz-FEL; red: cellulose irradiated by submillimeter wave from gyrotron; green: cellulose irradiated by submillimeter wave behind THz-FEL.

BL7U

Low-energy ARPES Study of Iron-chalcogenide High-temperature Superconductors

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Since the discovery of high-temperature superconductivity in LaFeAs(O,F), iron-based compounds are attracting great attention. Among known iron-based superconductors, iron selenide FeSe is the structurally simplest material. It exhibits various exotic properties such as anisotropic superconductivity and electronic nematicity without long-range magnetic order. These properties are sensitive to chemical substitution, high-pressure application, and/or carrier doping. Therefore, FeSe provides an opportunity to investigate the interplay between nematicity and superconductivity while controlling some physical parameters. In particular, isovalent-substituted FeSe1-xTeX and FeSe1-xSx films offer an excellent platform. Nematicity is realized in FeSe (x = 0) as in bulk FeSe, and the highest Tc of 23 K among non-carrier-doped FeSe-based compounds has been reported at the critical Te concentration x_c of ~0.2 at ambient pressure [1]. On the other hand, for the S-substituted counterpart, large Tc enhancement is absent and possible emergence of magnetism has been reported [2]. Comparative studies on these contrasting behaviors would provide a key to understand the origin of exotic properties.

In this study, we performed low-energy angle-resolved photoemission spectroscopy (ARPES) study of FeSe1-xTeX and FeSe1-xSx films. High-quality thin films were grown by the pulsed laser deposition method. ARPES measurements were performed using a MBS-A1 spectrometer at BL7U in UVSOR with energy-tunable photons of 12-25 eV.

Figures 1(a) and 1(b) show a comparison of the ARPES intensity around the Brillouin-zone center measured in pristine FeSe and FeSe1-xTeX films, respectively. In pristine FeSe, highly dispersive hole band with the dominant Fe 3dxz/yz orbital character (blue) crosses the Fermi level (EF) and a relatively flat band with the Fe 3dxy orbital (red) is located well below EF. On the other hand, Se/Te substitution leads to an upward energy shift of the dxy band, resulting in the appearance of the dxz-orbital character at EF. The large electron mass of the dxy band enhances the density of states at EF, which is likely responsible for the Tc enhancement. We also determined the evolution of the electronic structure upon Se/S substitution, and compared the results with those on FeSe1-xTeX films to elucidate the mechanisms of nematicity and superconductivity as well as the origin of contrasting phase diagram between FeSe1-xSx and FeSe1-xTeX.

Fig. 1. (a) and (b) ARPES intensity plotted as a function of binding energy and wave vector measured in FeSe and FeSe1-xTeX films, respectively. Blue and red curves are a guide for the eyes to trace the dxz/yz and dxy band dispersions, respectively.

Elucidations of Electronic Structure and the Many-body Interactions of Organic Molecular Materials

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As the sustainability of our global resources and energy-harvesting rapidly becomes a central issue in navigating our technological advancements, the development of quantum devices made of organic molecular materials, characterized by their low fabrication cost using abundant elements and high biodegradability, is of paramount importance.

Among such organic molecular materials, single crystalline rubrene (C$_{42}$H$_{28}$) is known to exhibit exceptionally high carrier mobility (40 cm$^2$/V·s [1]) and is considered as a promising semiconductor material for the next-generation electronics.

However, despite the numerous superiorities mentioned above, what should be the most fundamental building blocks for the future development are still incomplete; that is, the understanding of the electronic structure and their interactions with phonons and molecular vibrations.

For the purpose of elucidating these aspects of organic materials, angle-resolved photoemission spectroscopy (ARPES) is a premier experimental technique, which can simultaneously reveal the energies and momenta of the transport carriers (i.e., electrons and holes). Indeed, ARPES has been extensively utilized for rubrene and unveiled, for instance, the existence of discernable band dispersions for HOMO-derived bands [2], and the band gap induced by the interactions of electrons with molecular vibrations, revealed in our recent work [3].

On the other hand, there remain numerous critical questions about this material that are yet to be answered, including whether or not there are two HOMO-derived bands (as theoretically predicted), and whether there exists an interplay between the modes of molecular vibrations and the directions of electron propagation.

In our attempt to give the answers to these questions, we have utilized the BL7U at UVSOR to perform the high-resolution ARPES experiments.

For elucidating the many-body interactions, we have utilized the low photon energy of $h \nu = 8.0$ eV to maximize the momentum resolution. From the data we have obtained (see Fig. 1), we observe a discernable difference in the magnitude of the band gap formed by the electronic interaction with the intramolecular vibrations at different locations of the Brillouin zone. This is likely a signature of anisotropy in the electron-molecular-vibration interactions in the rubrene crystal.

Further quantitative analyses are expected to give us the first opportunity to understand the interplay between the molecular vibrational modes and the direction of electron propagations in molecular crystals.

Furthermore, the ARPES data obtained at higher photon energy (see Fig. 2) show two different HOMO-derived bands which are degenerate at their maximum binding energy. These are in agreement with the calculated band structure and are expected to serve as a key for resolving the long-standing discrepancy between the theoretical predictions and experimental observations in rubrene band structure.

Fig. 1. ARPES second derivative plots obtained for (a) $k_x = 0$ Å$^{-1}$ (Γ-Y line) and (b) $k_x = 0.14$ Å$^{-1}$.

Fig. 2. ARPES plots for two HOMO-derived bands with (a, b) wider and (c) narrower dispersions. The dashed curves in (b), (c) are visual guides.

Dirac-cone and Saddle-point Energy Bands in a Kagome Superconductor $AV_3Sb_5$

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Kagome lattice is an excellent playground to study the physics intertwining electron correlation and non-trivial topology, owing to its peculiar band structure. Theoretical studies on the kagome lattice predict the formation of nearly flat band, Dirac-cone band, and saddle point van Hove singularity. When either of these bands is placed near the Fermi level ($E_F$), various unusual properties would be realized, e.g., Weyl magnet, density wave orders, charge fractionalization, and superconductivity.

Recently, a new family of kagome-lattice materials $AV_3Sb_5$ ($A = K$, Rb, and Cs) has been discovered. $AV_3Sb_5$ shows superconductivity with the superconducting transition temperature $T_c$ of 0.93–2.5 K, providing a rare opportunity to study superconducting properties in the kagome lattice. $AV_3Sb_5$ also exhibits a charge-density wave (CDW) transition at $T_{CDW} = 78–103$ K, possibly accompanied with time-reversal symmetry breaking. To understand the origin of these exotic properties, experimental investigations of electronic states are of crucial importance [1].

In this study, we performed low-energy angle-resolved photoemission spectroscopy (ARPES) study of KV$_3$Sb$_5$ and studied the electronic states with a high momentum resolution, which enables us to determine momentum dependence of the CDW gap.

High-quality single crystals of KV$_3$Sb$_5$ were grown by the self-flux method. ARPES measurements were performed by using a MBS-A1 spectrometer at BL7U in UVSOR. Clean surfaces of the samples were obtained by cleavage in an ultrahigh vacuum.

Figure 1 shows the ARPES intensity measured along the $\Gamma K M$ high-symmetry line of bulk hexagonal Brillouin zone. One can identify an electron pocket centered at the $\Gamma$ point. This band is attributed to the $5p$ band of Sb atoms. One can also recognize linear dispersions that produce multiple Dirac points near the K point. These bands are attributed to the kagome-lattice band with mainly V-3d$_x$ character. One of the Dirac-cone band (indicated by red arrow) shows a flattening with approaching the M point and forms a saddle-point dispersion. Upon decreasing the temperature below $T_{CDW}$, we found an opening of the CDW gap on V-derived bands. Our detailed momentum-dependent study demonstrates the largest gap opening on the saddle-point band at the M point as well as the absence of clear gap opening on the Sb-derived band. Our observations suggest that the scattering between the saddle-point bands and resultant large gap opening stabilizes CDW, and Sb-derived parabolic band at the $\Gamma$ point is likely responsible for the superconductivity that coexists with CDW.

Fig. 1. ARPES intensity plotted as a function of binding energy and wave vector measured in KV$_3$Sb$_5$.

Angle-resolved Photoemission Study of TPP[FePc(CN)₂]₂

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Molecular conductors are known to exhibit a variety of properties ranging from magnetism to superconductivity, depending on the addition of inorganic elements or the combination of cationic and anionic molecules. In particular, axially substituted metal phthalocyanine (MPC, M = metal) molecules have attracted attentions because of their unique physical properties such as a giant negative magnetoresistance effect [1]. Though their anomalous properties have been expected to originate from strong π-d interactions, being similar with those in strongly correlated transition metal, the electronic structure of this system has never been reported yet. In this study, we have investigated the electronic structure of axially-substituted quasi-one-dimensional (Q1D) molecular conductor TPP[FePc(CN)₂]₂ single crystal by using angle-resolved photoemission spectroscopy (ARPES).

ARPES measurements were performed at the UVSOR-III BL7U. Data were acquired with hν = 40 eV at T = 10 K. Measurement axis was set along 1D conducting axis (/c). Needle-shaped single-crystals (typical size < 1 × 0.1 × 0.1 mm³) were cleaved in situ along (110) plane. The relation between the cleavage plane and conducting axis is shown in Fig. 1. To minimize photoirradiation damage photon flux was sufficiently reduced during all measurements.

Figure 2 shows valence band ARPES spectra of TPP[FePc(CN)₂]₂ along the conducting axis. We have successfully observed several peak structures (A-G) from E₀ to 15 eV. Small background relative to peaks suggests the cleanliness of the cleaved surface. From the comparison of the ARPES spectra (Fig. 2) with the valence band structure image (Fig. 3), peak B around 4 eV seems to show symmetric intensity reduction together with sizable energy shift from Γ to Z point. In addition, systematic energy shift has also been recognized around 5-7 eV (blue dashed lines). On the other hand, the energy shift of the peaks cannot be observed at high-binding energy side (peaks E-G). We expect that the observed change of ARPES spectra originates from the energy dispersive feature on TPP[FePc(CN)₂]₂.

Fig. 1. Crystal structure of TPP[FePc(CN)₂]₂. Due to the existence of the axial CN ligands, Pc units form a one-dimensional chain along c axis, which corresponds to π conducting axis.

Fig. 2. Valence band ARPES spectra along the ΓZ line of TPP[FePc(CN)₂]₂. Blue and green dashed lines are guide for dispersive and non-dispersive features.

Fig. 3. Valence band structure along the ΓZ line of TPP[FePc(CN)₂]₂.

Relationship between Chemical Pressure Effect and Electronic Structure in $R_{1-x}Ce_xOBiS_2$ ($R$=Nd, La)

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BiCh$_2$ compounds are quasi-two-dimensional materials with a layered structure typically represented by the composition of $RO_{1-x}F_x$BiCh$_2$ ($R$=rare earth; Ch= S, Se). It can be doped electrons by replacing oxygen with fluorine atoms or by introducing mixed valence $R$ atoms such as Ce and Eu into $R$ sites. Electron-doped samples show superconductivity below 2-10 K. Several experimental and theoretical studies have indicated the possibility of unconventional superconducting mechanisms [1]. Since the superconducting transition temperature ($T_c$) is sensitive to the pressure applied to the BiCh$_2$ planes, the chemical pressure effects of many elemental substitutions have been intensively studied [1-3]. The chemical pressure effects are important for understanding the superconducting mechanism, although there are few systematic reports on the electronic structure. In $R_{1-x}Ce_xOBiS_2$, the ratio of Ce$^{4+}$ at the $R$ site is about 0.1-0.15 despite the composition, so the average ionic radius of the $R$ site can be controlled while keeping the electron doping level fixed [2,3]. Therefore, it is the best material for investigating the relationship between pressure and electronic structure in the BiCh$_2$ systems. In this study, angle-resolved photoemission spectroscopy (ARPES) measurements of $R_{1-x}Ce_xOBiS_2$ were performed to investigate the relationship between pressure and the electronic structure.

The measurements were performed using $R_{1-x}Ce_xOBiS_2$ ($R$=La, Nd; $x$=0.2-0.75) single crystals synthesized by the flux method [2,3]. ARPES measurements were performed at BL7U of UVSOR III, using 20 eV photons with an energy resolution of 15-20 meV. All samples were cleaved in situ on the (001) plane in an ultrahigh vacuum of less than 5×10$^{-9}$ Pa.

Figures 1 (a) and (b) show the Fermi surfaces of Nd$_{0.7}Ce_{0.3}$OBiS$_2$ and La$_{0.75}Ce_{0.25}$OBiS$_2$, respectively, and (c) and (d) show the respective band dispersions. Nd$_{0.7}Ce_{0.3}$OBiS$_2$ is a superconductor with $T_c$ of ~5K, while La$_{0.75}Ce_{0.25}$OBiS$_2$ is non-superconductor at least above 1.5K. Nd$_{0.7}Ce_{0.3}$OBiS$_2$ and La$_{0.75}Ce_{0.25}$OBiS$_2$ have inner and outer electron pockets, respectively, centered at the X point. Nd$_{0.7}Ce_{0.3}$OBiS$_2$ is a relatively low-dimensional Fermi surface, with nested quadrilateral Fermi surfaces on both the inner and outer sides. On the other hand, La$_{0.75}Ce_{0.25}$OBiS$_2$ has an inner Fermi surface distorted into an elliptical shape extending in the Γ-X direction (perpendicular to X-M-X direction). The outer Fermi surface also seems to be distorted. The difference in the shape of the Fermi surface may be, to a first approximation, due to differences in electron doping levels rather than chemical pressure. In fact, the sizes of the Fermi surfaces are different and there is a difference of about 0.1 eV in the energy at the bottom of the band. Furthermore, their Fermi surface shapes are similar for $n$ = 0.125 and $n$ = 0.25 electron doping levels [4]. In this regard, it may be possible here that the nested Fermi surfaces are more favorable for achieving higher superconducting transition temperatures, given that Nd$_{0.7}Ce_{0.3}$OBiS$_2$ has a higher superconducting transition temperature. For a more comprehensive understanding, comparisons with other compositions of the material should be made.

Fig. 1 (a) and (b) Fermi surfaces, as well as (c) and (d) band dispersions along X-M lines, for Nd$_{0.7}Ce_{0.3}$OBiS$_2$ and La$_{0.75}Ce_{0.25}$OBiS$_2$, respectively.

Auger-free luminescence (AFL) is owing to the radiative transition between the valence band and the outermost core level. Generally, AFL is not efficient because the transition is competitive with the Auger process, which is generally a much faster process than that of AFL. In other words, efficient AFL has been observed in limited compounds such as alkaline- or alkaline-earth fluorides or CsCl-based compounds.

In recent years, we have developed fast scintillators exhibiting AFL on the basis of ternary CsCl-based compounds, such as Cs$_2$ZnCl$_4$ [1], CsCaCl$_3$ [2], and Cs$_2$BaCl$_4$ [3]. Fast scintillation decay within 2 ns has been achieved. The scintillation light yields of these compounds were less than 1,500 photons/MeV, which is significantly smaller than those of Ce-doped inorganic scintillators. Hence, we further investigated novel compounds based on CsCl. As an example of the further investigation, we have recently reported the photoluminescence and scintillation properties of Cs$_3$ZnCl$_5$ in comparison to those of Cs$_2$ZnCl$_4$ [4]. In the present report, we present the excitation spectra of Cs$_2$ZnCl$_4$ and Cs$_3$ZnCl$_5$, which clearly indicates that the emission was attributed to AFL.

Crystalline samples of Cs$_2$ZnCl$_4$ and Cs$_3$ZnCl$_5$ were used for the measurements. The measurements of the photoluminescence under irradiation with vacuum ultraviolet light were performed at BL7B of UVSOR at room temperature. The excitation wavelength between 50 to 200 nm was used for the measurements. The photoluminescence from the samples were observed with a CCD-based spectrometer via an optical fiber. The photoluminescence spectra with different excitation wavelengths were recorded. On the basis of the photoluminescence spectra, the excitation spectra were obtained.

To verify the origins of the emission bands at 260 and 310 nm of Cs$_2$ZnCl$_4$ and 240 and 290 nm of Cs$_3$ZnCl$_5$ crystals, we obtained the excitation spectra monitoring the wavelengths. Figures 1 and 2 present the excitation spectra. The excitation spectra of Cs$_2$ZnCl$_4$ are well consistent with those in a previous report [1]. A steep rise was observed in both excitation spectra at around 90 nm, which corresponds to the excitation of electrons at the outermost core level to the conduction band. Hence, based on the excitation spectra, the emission bands are attributed to AFL.

Fig. 1. Excitation spectra of Cs$_2$ZnCl$_4$ for monitored wavelengths of 260 and 310 nm [4]. Copyright (2020) The Japan Society of Applied Physics.

Fig. 2. Excitation spectra of Cs$_3$ZnCl$_5$ for monitored wavelengths of 240 and 290 nm [4]. Copyright (2020) The Japan Society of Applied Physics.

Investigation of Gamma-ray-irradiated Oxide Glasses for Deep Ultraviolet Detector with High Efficiency

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Vacuum ultraviolet (VUV) light is used in important technological applications such as photochemical processing, surface treatment, optical cleaning of semiconductor substrates, and sterilization. In particular, it has been suggested that non-contact sterilization, treatment, and processing could be advanced by using VUV in the current corona disaster. For such recent progress in VUV research and applications, it is necessary to develop detectors in the short wavelength range. In the development of VUV detectors, it is important to evaluate spectral characteristics in VUV region.

Previously, we have studied fluoride crystals, such as MgF$_2$ and CaF$_2$, for VUV optical devices [1,2]. Fluoride crystals are widely used in ultraviolet (UV) optics because of their wide band gaps. And also we have investigated fluoride glasses for VUV optical devices [3].

In addition, there are high expectations for material modification by gamma-ray irradiation. We have investigated the improvement of time resolution of scintillators such as ZnO by gamma-ray irradiation. Gamma-ray irradiation can be used as a post-processing step and is expected to improve the performance of various devices.

In our recent study, gamma-ray induced optical property changes in non-doped and Ce-doped lithium-rich oxide glasses are investigated [4]. However, optical properties of these material in VUV region has not been fully researched. Neutron measurements are important in fusion experiments, and lithium-rich oxide glasses are used as scintillator to detect neutrons. Evaluation of VUV characteristics of scintillator material is important to improve the performance of neutron detection. In high dose rate environment such as nuclear fusion experiment, optical materials are easily damaged. It is reported that Ce doping in the base material prevents degradation of optical materials.

In this study, we measured transmittance of gamma-ray-irradiated oxide glasses from VUV to visible region. We used a lithium borosilicate glass (LBS) and CeF$_3$-doped LBS. All glass samples were fabricated by the melt-quenching method [4]. To fabricate LBS, a mixture of high purity 99.99% boric acid (H$_3$BO$_3$), high purity silica (SiO$_2$) and lithium carbonate (Li$_2$CO$_3$) was melted at 1100 °C for 2 h under air atmosphere. Natural Li was used for all sample fabrication. The melted glass was quenched in air in a graphite mold and then annealed at 500 °C for 3 h. The CeF$_3$-LBS glasses were fabricated using similar precursors with the addition of CeF$_3$ powder. Precursors for Ce-doped samples were melted in an aluminum crucible for 3 h at 1200 °C and were quenched in air in a graphite mold, then subsequently annealed at 350 °C for 3 h. After fabrication, the non-doped glass samples were cut and polished into 10 mm × 10 mm flat plates with thicknesses ranging from 3.8 mm to 4.2 mm. The Ce-doped samples were cut and polished into 15 mm × 10 mm, with thickness ranging from 3.1 mm to 3.8 mm. The glass samples were irradiated with gamma rays carrying 1.17 and 1.33 MeV energies from a cobalt-60 ($^{60}$Co) source. The $^{60}$Co source was calibrated with water and had a dose rate of 36.82 Gy/h at a distance of 1.0 m. The samples were set approximately 10 cm away from the radiation source. The irradiation was performed at room temperature and in ambient atmosphere.

Figure 1 shows measured transmittance of gamma-ray-irradiated LBS and CeF$_3$-LBS. In both samples, high transmittance was measured even with VUV. Although Ce was not seen to have much of an effect in this measurement, it is expected to reduce the effect of gamma irradiation.

In the future, we will compare more detailed conditions and develop materials for high-efficiency deep-ultraviolet photodetectors.

![Fig. 1. Transmittance of gamma-ray-irradiated oxide glasses.](image-url)