

**Project Title:**

**Computational Studies of Muon Locations, Electronic Structures and Electron Transport in High-T<sub>c</sub> Superconductor, Organic, Organometallic and Biological Systems.**

**Name:**

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1. Background and purpose of the project, relationship of the project with other projects

One of the methods that able to provide information at such microscopic properties due to high sensitivity to local magnetic and electronic environments is muon spin rotation/ relaxation/ resonance ( $\mu$ SR) spectroscopy. The understanding of various events such as magnetism, hyperfine interactions, and electron transport can be gained. Positively charged anti-muon,  $\mu^+$  is commonly used by  $\mu$ SR spectroscopy as a dilute magnetic probe.  $\mu$ SR experiments give a measure of the microscopic field distribution at the interstitial sites where the muon stops inside the sample. Hence, the muon stopping sites is definitely important to determine electronic properties, for example, long-range magnetic ordering or localized magnetic moments.

However,  $\mu$ SR spectroscopy has a limitation on the determination of possible muon location. Therefore, Density Functional Theory (DFT) approach as a valuable strategy to assist  $\mu$ SR experiments interpretation can be used to tackle the limitations. In addition, the information on the muon stopping sites between microscopic theory and  $\mu$ SR data can ultimately be compared. Thus, a better understanding of the electronic structures of both

pure and muoniated systems of each target materials can be accomplished.

There are six different target materials that have been studied by each user in this project. The background study and characteristic interests of each target materials are elucidated separately as below:

i High-T<sub>c</sub> superconducting oxides ( $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ )

$\mu$ SR technique is a powerful approach to investigate the electronic structure of Cu-based high-T<sub>c</sub> superconducting oxides. To reveal muon positions inside  $\text{La}_2\text{CuO}_4$  (LCO) gives an important information to obtain a deeper understanding of the magnetically-ordered state of this system. However, the  $\mu$ SR results on LCO achieved in the early stage of high-T<sub>c</sub> history have not yet been fully explained due to the lack of unified method to determine exact position of muon. We are approaching this issue by using density functional theory technique with the additional Hubbard parameter (DFT+U) to obtain accurate position of the implanted muon and its comparison with the experimental  $\mu$ SR data.

In the current computational project, we have already determined the most possible position by considering the internal field comparisons between

our DFT data and  $\mu$ SR data. We also obtain the optimized U-value for the LCO system. Now, we extend our studies by considering several symmetric positions existing in LCO structure. This study could provide an information on how symmetric position affects our technique to optimize the U-values and provide a general information for many related cases which is governed by strong electronic interaction such as Mott-insulating systems.

### iii Organic magnets, $\lambda$ -(BETS)<sub>2</sub>GaCl<sub>4</sub> and relative compounds

The superconducting (SC) gap structure appearing in systems with single Fermi surface (FS) is generally described by single gap function with *s*- or *d*-wave symmetry. The organic superconductor  $\lambda$ -(BETS)<sub>2</sub>GaCl<sub>4</sub> [BETS=(CH)<sub>2</sub>S<sub>2</sub>Se<sub>2</sub>C<sub>6</sub>Se<sub>2</sub>S<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>] endeavors to examine a novel SC gap structure on the distorted single cylindrical FS. Using the positive muon spin rotation  $\mu$ SR experiment, we showed an example of the formation of the distorted SC nodal line. The nodal line has a narrower width than that of the traditional *d*-wave by the steepness factor of 4.6(2.1), and flat part with the maximum gap exists. We simply called this symmetry *h*-symmetry since the temperature dependence of the superfluid density was best fit using the absolute hyperbolic tangent function.

### iv Single and double strand 12mer synthetic DNA oligomers

Electron transport occurs in many important biological processes such as storage and consumption of energy, enzyme response, and DNA UV damage repair.  $\mu$ SR is an experimental technique that can be used to study electron transport phenomena in DNA at the microscopic level. The changes in the electron transport properties due to damages in DNA can be probed by using muon hyperfine interactions which are very sensitive to the changes in the electronic structure surrounding the muonium (Mu) trapping sites. To systematically study the effect of damages

on DNA to the behavior of electrons, it is, therefore, crucial to develop baseline data using DNA systems with known DNA sequences.

In previous project, the Mu hyperfine interactions at all possible Mu trapping sites in the four nucleobases and four nucleotides were investigated. The results show that the presence of a methyl group or a sugar phosphate group to the nucleic acid bases has a direct effect on the electronic structure of the system. The distortion test in the geometry of guanine nucleobase when Mu is added to the possible trapping sites was conducted. An analysis on the optimized muoniated systems structure was done to investigate whether the presence of Mu caused the guanine base ring to deviate from the planar shape.

In real, DNA consists of two polynucleotide chains twisted around each other in the form of a double helix. Each nucleotide units consist of nitrogenous bases and sugar phosphate backbone. The existence of sugar phosphate backbone and neighbouring bases can give effect to the electronic structure of the system. Accordingly, this calculation was extend using bigger cluster size with more bases so that the effect of neighbouring bases could be included.

Thus, in FY2021, 12mer single strand DNA with homogeneous nitrogenous bases was chosen as a model of this study. In this investigation, we performed DFT calculations to determine the geometry, electronic structure, and molecular properties, as well as Mu trapping sites, in 12mer ssG oligomer.

## 2. Specific usage status of the system and calculation method

Gaussian16 and Vienna Ab initio Simulation Package (VASP) software are two main ab initio quantum mechanical programs have been utilized in this group. The Gaussian program package is more suitable for the electronic structure studies of molecular systems because it employs the linear

combination of atomic orbital molecular orbital (LCAO-MO) technique. The VASP software, on the other hand, which has been used in the band theory calculations for solid systems as it employs pseudopotentials or the projector-augmented wave method and a plane wave basis set. In addition, the ADF software has also been used in our computational work to provide better results on the hyperfine coupling constant (HFCC). NAMD software is used for molecular dynamics simulation and it is noted for its parallel efficiency that is often used to stimulate large system. Next, NBO for Gaussian that is based on a method for optimally transforming wave function into localized form is also used in this project. MATLAB is a high-performance language for technical computing that integrates computation, visualization, and programming in an easy to use environment. Wannier90 also used in this project. It is an open source code for generating maximally localized Wannier functions and using them to compute advanced electronic materials with high efficiency and accuracy. It is proven that the HOKUSAI Great Wave supercomputer facility is crucial and extremely useful for our group research, particularly for the large-scale calculations due to the results obtained from the calculations by using all the resource units.

### 3. Result

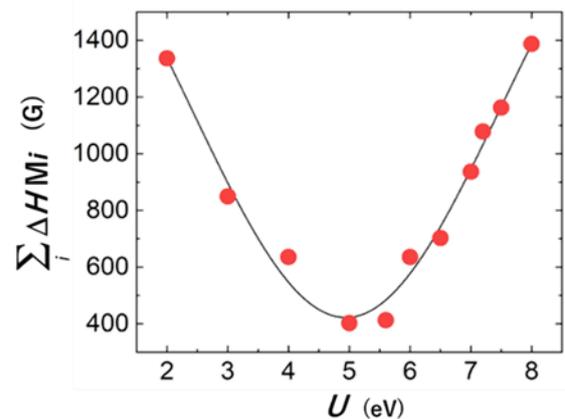
In section 1, a considerable amount of computational effort has been done in FY2021 on the different systems is described. The data from the computational studies is collected to assist the interpretation of  $\mu$ SR experiments. The results for each subproject are reported separately and are as follows:

#### i High-Tc superconducting oxides ( $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ )

To determine the optimized U-values we consider distributed-spin model and zero-point vibration

motion for each muon position to provides a realistic view on LCO system. By varying U value from 2 – 8 eV we estimate that the best U-value for LCO system is 4.87(4) eV as shown on Figure 1(a). This value U-value will produce an insulating gap of 1.24(1) eV.

Now we also consider several symmetric positions existing in LCO structure, from our supercell calculation, the electrostatic potential describes 4 symmetric position exist in M1 and M2 positions as shown in the Figure 1(b). From the iso-volume shown in the figure, we can see immediately that for each M1 or M2 position it has 3 different symmetric position for each octahedron (two isovolumes, with two symmetric positions for each isovolume). Our initial results on 1 of the symmetric position for M1 shows slight discrepancies ( $\sim 3\%$ ) with the initial calculated internal field data. In order to reveal more information about this discrepancy we need to extend our calculation for all symmetric positions to observe possible effect of symmetric positions on internal field calculation and finally our U-optimization methods.



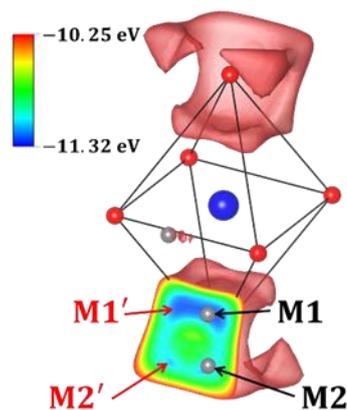


Figure 1. (a) Optimization of U-values in terms of absolute difference between  $\mu$ SR and DFT results. (b) Symmetric position of M1 and M2

### iii Organic magnets, $\lambda$ -(BETS) $_2$ GaCl $_4$ and relative compounds

To understand the origin of  $h$  symmetry, the anisotropy of the dimer lattice in  $\lambda$ -(BETS) $_2$ GaCl $_4$  is the plausible mediation of the  $h$ -wave Cooper pairing. We see it as an alternation of two sublattices in the  $a$ -direction which are anisotropic triangular with the ratio of the next nearest and nearest neighbor transfer integral is  $t'/t = 0.8$  and frustrated squared with  $t'/t = 0.2$ , shown in Figure 2(a), determined from our DFT calculation.

The DFT calculation were performed within the Kohn-Sham approach using the projector augmented-waves (PAW) formalism in Vienna Ab-initio Simulation Package (VASP) program. The exchange-correlation function generalized gradient approximation, GGA-PW91, was used. The ground-state densities were calculated by adopting value of the crystal axis obtained experimentally, using  $4 \times 4 \times 4$   $k$ -point sampling, ultrasoft pseudopotentials and plane-wave densities. The maximally localized Wannier orbital in the BETS molecule (molecule model) and BETS dimer (dimer model) were constructing using the implemented wannier90 package.

The typical  $\mu^+$  are bounded to the negative charge sites which might affect the measurements of the

local vortex field. To get the information about the anisotropy lattice including  $\mu^+$ , we calculate the band structure and transfer integral lattice after including  $\mu^+$ . The  $\mu^+$  site position is at  $x = 0.675$ ,  $y = 0.605$ ,  $z = 0.915$  in regard of the unit cell. The calculation result I summarized in table 1. This result is published in Ref. 4.

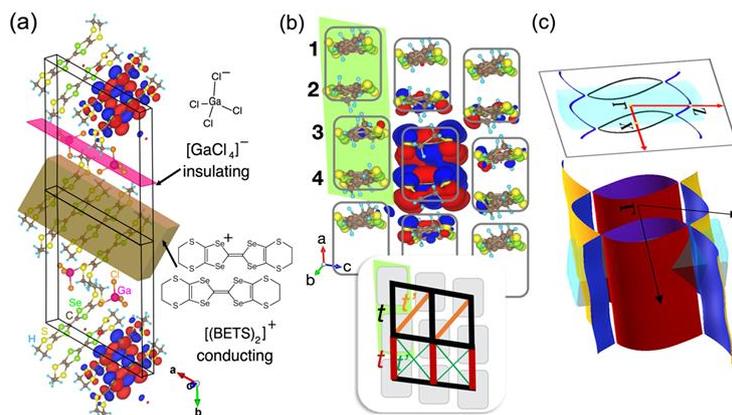


Figure 2. (a) Crystal structure of  $\lambda$ -(BETS) $_2$ GaCl $_4$ . Magenta and brown layers are  $[\text{GaCl}_4]^-$  insulating and  $[\text{((CH}_2)_2\text{S}_2\text{Se}_2\text{C}_6\text{Se}_2\text{S}_2(\text{CH}_2)_2)]_2^+$  conducting layers, respectively. (b) Conducting plane of  $\lambda$ -(BETS) $_2$ GaCl $_4$ . Cyan area is the unit cell. BETS molecule 1–2 and 3–4 form a dimer. The blue and red lobes indicate the maximally localized Wannier orbital of the  $\pi$  orbital on the BETS dimer (positive: blue, negative: red). In the inset, the first (second) nearest neighbors' transfer integrals are indicated by black  $t$  (orange  $t'$ ), with  $t'/t = 0.8$ . Another sublattice with the red  $t$ , cyan  $t'$ , and  $t'/t = 0.2$  alternates in the  $a$ -direction. (c) The 3D Fermi surface estimated from the DFT calculation.

	tag	$t^H$ [S4]	$t_{Fe}^H$ [S8]	$t_{Fe}^H$ [S9]	$t_{ij}^{DFT}$ [S7]	$t_{ij}^{DFT}$	$t_{ij}^{DFT+\mu^+}$
Molecule model (4-band)	$t_A$	238	747	336	233	235	214
	$t_B$	-98	-302	-183	-131	-129	-144
	$t_C$	-58	-279	-148	-138	-137	-146
	$t_P$	13	3	28	15	15	9
	$t_Q$	31	189	93	59	59	66
	$t_r$	37	237	130	63	64	56
	$t_s$	-48	-176	-171	-82	-81	-76
	$t_s$	-4	-33	-26	-17	-16	-29
Dimer approximation					$t_{\mu\nu}^{DFT}$	$t_{ij}^{DFT+\mu^+}$	
Dimer model (2-band)	$t_c$	41	215	126	69	64	58
	$t_{d1}$	24	88	86	41	52	-59
	$t_{d2}$	2	17	13	9	13	-17
	$t_{d3}$	29	140	74	69	76	-59
	$t_{d4}$	49	151	96	66	64	-84
	$t_e$	—	—	—	—	-17	14
	$t_f$	—	—	—	—	—	75

Table 2. Transfer integrals of  $\lambda$ -(BETS)<sub>2</sub>GaCl<sub>4</sub>. The superscript, H, indicates the extended Huckel method results and the subscript, Fe, represents the results of  $\lambda$ -(BETS)<sub>2</sub>FeCl<sub>4</sub>. Column-4 shows the current work on the molecule model, consistent with S7 in the table or Ref. H. Aizawa, et al., JPSJ 87 093701 (2018). The value of transfers integrals is in the unit of meV.

#### iv Single and double strand 12mer synthetic DNA oligomers

Structure of 12mer ssG Oligomer. The optimized geometrical structure of the 12mer ssG oligomer is shown in Figure 3. The total energy of the optimized structure is -476,790 eV, which is 54 eV lower than the total energy of the initial unoptimized structure. All 12 pyrimidine-imidazole rings maintain their planar characteristic after the geometry optimization procedure. The length and width of the optimized structure are 38.7 and 18.2 Å.

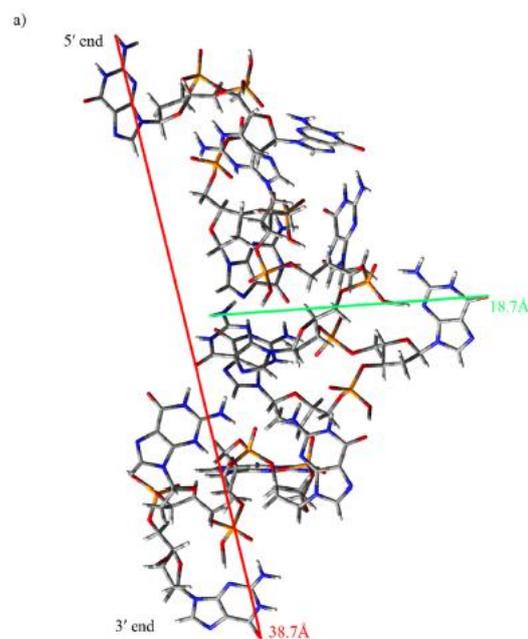


Figure 3. Shape and dimensions of the 12mer ssG oligomer optimized structure. The red and green lines represent the length and width, respectively.

The calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of 12mer ssG oligomers are -5.36 and -2.05 eV, leading to a HOMO-LUMO energy gap of 3.31 eV. The surface plots of the frontier molecular orbitals of the 12mer ssG oligomer are shown in Figure 4, where red and green isosurfaces represent positive and negative values. Both HOMO and LUMO are spread over 50% of the molecular length, indicating a significant delocalization.

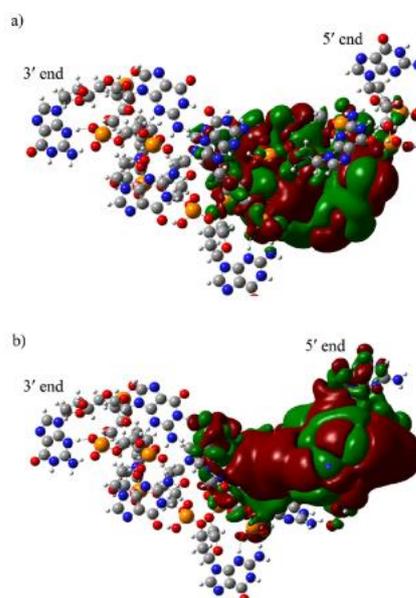


Figure 4. Surface plot of the 12mer ssG oligomer frontier molecular orbitals: (a) HOMO and (b) LUMO.

There are eight Mu sites at each base of the 12 bases: C2, C4, C5, C6, C8, N3, N7, and O6. Thus, the total number of possible Mu trapping sites in 12mer ssG oligomer that were investigated in this work is 96. Figure 5 shows the scatter plot of the relative energies and muon HFCCs of all 96 Mu sites in the 12mer ssG oligomer. Among the 96 sites, C8-G-B5 has the lowest total energy, which is  $-476,804.997$  eV. Relative energy of other Mu sites was calculated by subtracting the total energy of C8-G-B5 Mu sites from their respective total energy. Among C8, C8-G-B7 has the highest relative energy which is  $0.207$  eV. The calculated average Mu-C bond distance for C8 sites is  $1.099$  Å and with an average bond order of  $0.88$ , indicating a single covalent bond between Mu and the carbon atom. The charge on Mu at C8 sites calculated using the natural population analysis (NPA) method is about  $0.26$ . The calculated muon HFCCs at C8 sites range from  $384.6$  MHz (C8-G-B9) to  $481.1$  MHz (C8-G-B6). Based on the theoretically predicted ALC- $\mu$ SR resonance for the 12mer ssG, the positions where resonance signals should appear are in the range of  $1.419$  to  $1.775$  T.

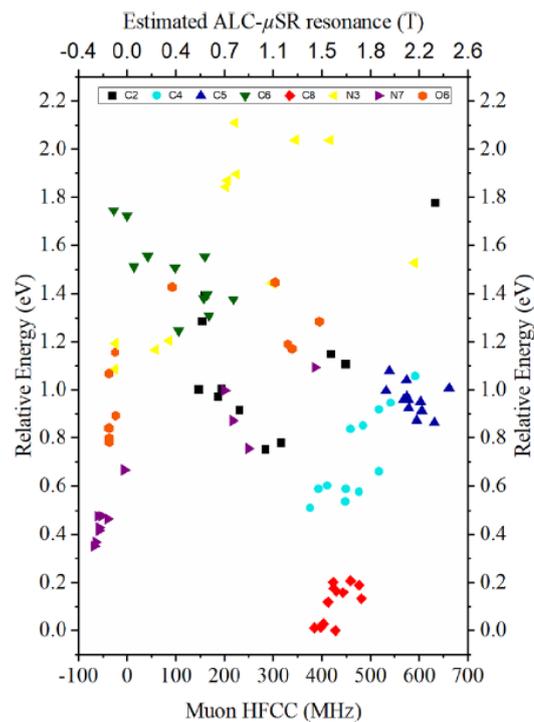


Figure 5. Scatter plot of relative energies and muon HFCCs of 12mer ssG oligomer Mu trapping sites. The relative energy is taken with respect to the Mu trapping site that has the lowest total energy.

#### 4. Conclusion

##### i High-Tc superconducting oxides ( $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ )

We have successfully carried out DFT+U calculation with the exchange-correlation function of GGA PW91 to obtain accurate muon position and also precise U-value by considering both  $\mu$ SR experimental data and DFT theoretical data for LCO system. By utilizing distributed-spin model and the consideration of quantum behavior of muon, we observe that the optimized U-values is  $4.87(4)$  eV with the insulating gap of  $1.24(1)$  eV. This method could provide an accurate information of the electronic states in LCO and also a novel way to utilize  $\mu$ SR experimental data on many strongly correlated systems. Finally, we also consider the possible effects given by symmetric position to our methods to calculate internal field experienced by the implanted muon, in which slight difference of internal field is observed ( $\sim 3\%$ ). Further

investigation on this symmetric position is still required at this stage.

### iii Organic magnets, $\lambda$ -(BETS)<sub>2</sub>GaCl<sub>4</sub> and relative compounds

The band structure and transfer integral calculation including  $\mu+$  barely change the transfer integral lattice, although we assume one muon per unit cell in our calculation. Thus, the discussion about transfer integral lattice still holds. The origin of  $h$  symmetry might be the anisotropy of the dimer lattice in  $\lambda$ -(BETS)<sub>2</sub>GaCl<sub>4</sub> which is an alternation of two sublattices.

### iv Single and double strand 12mer synthetic DNA oligomers

In this investigation, we performed DFT calculations to determine the geometry, electronic structure, and molecular properties, as well as Mu trapping sites, in 12mer ssG oligomers. Our DFT computational study on the Mu stopping sites and the associated hyperfine interaction indicates that C8 sites are the most probable Mu trapping sites with muon HFCC ranges from 384.6 MHz to 481.1 MHz. If Mu centers are formed at all C8 sites in a 12mer ssG oligomer, a broad polarization dip would be observed in ALC- $\mu$ SR spectrum in the range of 1.419 to 1.775 T of the applied field.

## 5. Schedule and prospect for the future

### i High-T<sub>c</sub> superconducting oxides (La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub>)

Further investigation for each symmetric position is required. For the case of M1 and M2 have 4 symmetric positions, totaling on 8 different supercell calculations for each U-values. This will be our main focus and will be explained in detail on the next HOKUSAI project

### iii Organic magnets, $\lambda$ -(BETS)<sub>2</sub>GaCl<sub>4</sub> and relative

compounds

For the next plan, we would like to extend the calculation to the other sister compounds of the  $\lambda$ -(D)<sub>2</sub>GaCl<sub>4</sub> family with different cation such as STF, ET, or BEST. This family is recently attracting attention since it seemed to be an unconventional strongly correlated system with the superconducting (SC) state is near by the Antiferromagnetic (AF) state with the Mott transition. Although, in this system there is no such  $\pi$ - $d$  interaction like it has been in the  $\lambda$ -(D)<sub>2</sub>FeCl<sub>4</sub> family. The electronic structure by using first principal calculation in the  $\lambda$ -(D)<sub>2</sub>GaCl<sub>4</sub> have not yet been done so far. We have got the crystal structure data determined from X-ray diffraction experiment for the  $\lambda$ -(BEST)<sub>2</sub>GaCl<sub>4</sub>,  $\lambda$ -(ET)<sub>2</sub>GaCl<sub>4</sub>,  $\lambda$ -(STF)<sub>2</sub>GaCl<sub>4</sub>, for each compound and expect the systematic changing of the anisotropy of the lattice.

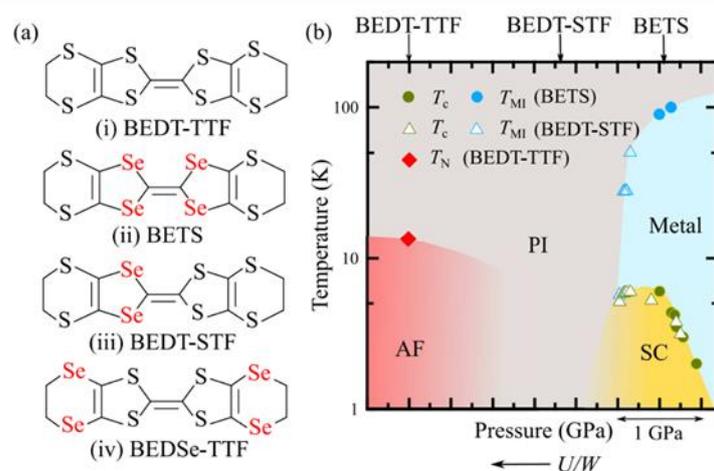


Figure 6. The P-T phase diagram of the  $\lambda$ -(D)<sub>2</sub>GaCl<sub>4</sub> family determined by the magnetic susceptibility, resistivity, and NMR, and  $\mu$ SR experiments. [Ref. 6]

### iv Single and double strand 12mer synthetic DNA oligomers

The optimized structure of 12mer ssG oligomer and the details information on the muoniated 12mer ssG oligomer have been obtained and published. Thus, in the next fiscal year, we would like to obtain the electronic structure of 12mer ssC, 12mer ssA, and 12mer ssT oligomers and the associate hyperfine interactions.

## Usage Report for Fiscal Year 2021

6. If no job was executed, specify the reason.

**Fiscal Year 2021 List of Publications Resulting from the Use of the supercomputer**

**[Paper accepted by a journal]**

1. Zaharim, W. N., Rozak, H., Sulaiman, S., Ahmad, S. N. A., Baseri, D. F. H., Mohd-Tajudin, S. S., ... & Watanabe, I. (2021). Density Functional Theory Investigation of Hyperfine Interaction in DNA Nucleobase and Nucleotide Muoniated Radicals. *Journal of the Physical Society of Japan*, *90*(4), 044301.
2. Zaharim, W. N., Ahmad, S. N., Sulaiman, S., Rozak, H., Hasan Baseri, D. F., Mohamad Rosli, N. A., ... & Watanabe, I. (2021). Density Functional Theory Study of 12mer Single-Strand Guanine Oligomer and Associated Muon Hyperfine Interaction. *ACS omega*, *6*(44), 29641-29650.
3. Watanabe, I., Sari, D.P., Ramadhan, R., Adiperdana, B., Shukri, S. 計算科学的手法による物質中におけるミュオン位置同定. *Journal of Computer Chemistry, Japan*, *19*(3), 115-123..
4. Sari, D. P., Asih, R., Hiraki, K. I., Nakano, T., Nozue, Y., Ishii, Y., ... & Watanabe, I. (2021). Distorted superconducting nodal line on a single Fermi surface in the anisotropic organic superconductor  $\lambda$ -(BETS) <sub>2</sub> GaCl <sub>4</sub>. *Physical Review B*, *104*(22), 224506.
5. Ito, A., Kobayashi, T., Sari, D. P., Watanabe, I., Saito, Y., Kawamoto, A., ... & Taniguchi, H. (2021). Antiferromagnetic ordering of organic Mott insulator  $\lambda$ -(BEDSe-TTF)<sub>2</sub>GaCl<sub>4</sub>. *arXiv preprint arXiv:2112.05972*.

**[Conference Proceedings]**

**[Oral presentation]**

1. Oral Presentation in International Conference Strongly Correlated Electron System 2020, "Distorted Superconducting Nodal Line on Single Fermi Surface in Anisotropic Organic Superconductor  $\lambda$ -(BETS)<sub>2</sub>GaCl<sub>4</sub>", Brazil, 1<sup>st</sup> of October 2021 (online)

**[Poster presentation]**

**[Others (Book, Press release, etc.)]**

1. Ramadhan, M.R., Ramli, I., Watanabe, I. Computational Physics Contribution on  $\mu$ SR studies. Sakura Science Program, Univ. Cokroaminoto Palopo, Indonesia, 2021.