Project Title:

DFT Calculation on Organic Conductors as Supports for Muon Spin Spectroscopy

Name:

○Dita Puspita Sari(1,2), Wan Nurfadhilah Binti Zaharim(3,2), Muhammad Redo Ramadhan(4,2), Irwan Ramli(5,2), Phantip Jaikaew(6,2), and Supparat Charoenphon(7,2)

Laboratory at RIKEN:

(1) Shibaura Institute of Technology, Japan

(2) Nuclear Structure Research Group, RIKEN Nishina Center, Japan

(3) Universiti Kebangsaan Malaysia, Malaysia

(4) UPN Veteran, Yogyakarta, Indonesia

(5) Universitas Cokroaminoto Palopo, Indonesia

(6) Chiang Mai University, Thailand

(7) Kasetsart University, Thailand

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

The hole-doped organic metal κ-(BEDT-TTF)$_4$Hg$_{2.89}$Br$_8$, δ=11% (κ-HgBr) and κ-(BEDT-TTF)4Hg2.78Cl8, δ=22% (κ-HgCl), where ET=(CH2)2S8C6S8(CH2)2, are exceptional carrier-doped metal among half-filled organics, beside ET dimers with spin-half (S =1/2) tend to arrange triangular lattice causing a geometrical frustration in two-dimensional organic systems. κ-HgBr is a superconductor below 4.3 K, while κ-HgCl transitions to the insulator at ambient pressure and becomes a superconductor above 0.5 GPa. The magnetic susceptibility behavior of κ-HgBr has a broad peak around 30 K and decreases towards base temperature. This is well modeled by a triangular lattice model with exchange interaction J = −140 K. By scaling it with its J; the susceptibility is quantitatively similar to that of quantum spin liquid insulator, κ-ET2Cu2(CN)3. Therefore, κ-HgBr has been discussed as a doped quantum spin liquid metal with a superconducting ground state [3]. κ-HgBr shows non-Fermi liquid (NFL) behavior evidenced by the linear temperature dependence of resistivity, ρ(T), and the 13C-NMR measurement in the field of 9.4 T suggesting that the strong antiferromagnetic spin fluctuations contribute to the origin of NFL [5]. The transverse field (TF) μ+SR measurement in the field of 6 T showed a deviation from the linearity of the susceptibility against the μ+ Knight shift K(χ) at temperatures below 50 K, unlike other κ-type FL organics, which have typically FL behavior. As for the κ-HgCl 13C-NMR study under pressure, it reported the appearance of inhomogeneous staggered fields or spin glass. However, since the NMR spectrum has an inhomogeneous broadening, it is an indistinctive indication of whether it is an inhomogeneous distribution of the hyperfine coupling constant A_{hf} or local magnetic field. Here, we measure Knight shift using μ+SR. We expect muon to have well-defined A_{hf}, as reported in the case of κ-HgBr. We performed similar high-TF μ+SR in κ-HgCl, maintaining the experimental condition as that for κ-HgBr [6]. We compare the K(χ) plot of both compounds based on the same analysis procedure and discuss the quantum criticality related paramagnetic metallic and superconducting states.

In order to determine the muon site, we performed Density Functional Theory (DFT) calculation using HOKUSAI within VASP software. This method is in parallel with the methods our group uses, such as project numbers RB230087, and RB230086.

2. Specific usage status of the system and calculation method

The crystal structure of κ-HgCl and κ-HgBr was obtained from the X-ray diffraction measurements.

The density functional theory (DFT) calculation was performed within the Kohn-Sham approach using the projector augmented-waves formalism in the commercial VASP program run in the cluster supercomputer HOKUSAI of RIKEN during the period of January-February and April-June 2024. The method to calculate muon site in organic conductors has been reported in detail previously [D. P. Sari, PRB 2021]. The exchange-correlation function generalized gradient approximation GGA-PW91 was used. The ground-state charge densities were calculated by adopting the value of the crystal axis determined by the X-ray diffraction measurement and by using the 6 × 5 × 2 *k*-point sampling, ultrasoft pseudopotentials, and plane-wave densities.

3. Result

Figure 1 shows the crystal structure of κ-HgCl and κ-HgBr obtained from the X-ray diffraction measurements with the result of the minimum electron density calculation. The most probable muon site is within the lowest potential energy in the range of −7.225 to −7.456 eV, within the blue-shaded area, as shown by the red circles in Fig. 1(b). This site is at (0.32, 0.94, 0.79) and (0.32, 1, 0.83) of the unit cell for κ-HgCl and κ-HgBr, respectively. Note that there are other possible muon sites spreading in between ET molecules. Furthermore, several tests of the point dipole field calculations were done between the muon and Cl, Hg, and S atoms as assumed localized spin. The total internal field probed by the muon is calculated by summing up all the dipole fields acting on the muon inside the Lorentz sphere around the muon within 50 Å, centering the muon to achieve the converged results for dipole calculations. For κ-HgCl the dipole field between muon and Cl site with spin as large as one μB set to be perpendicular to the conducting bc-plane is 279 G. The same calculation is performed for the Hg and S site yielding 142 and 2292 G. For κ-HgBr case, the calculations were repeated yielding dipole field between muon and Br, Hg, and S sites as 274, 141, and 2292 G.

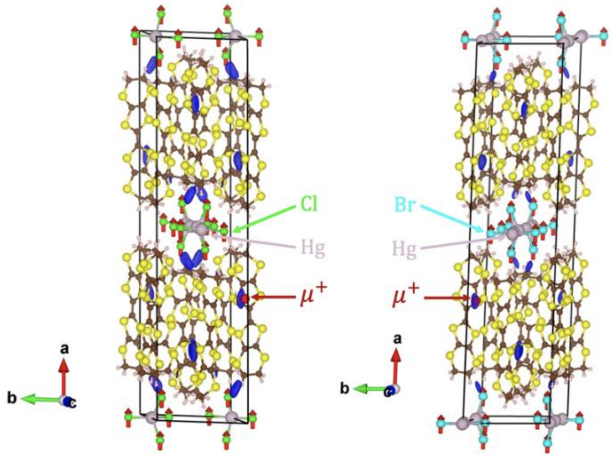

Figure 1. The electronic potential calculation with the blue shaded area indicates the minimum energy region for (left) κ-HgCl and (right) κ-HgBr. The red circle labeled as μ+ is the most probable muon site at (0.32, 0.94, 0.79) and (0.32, 1, 0.83) of the unit cell for κ-HgCl and κ-HgBr, respectively. The spin in the Cl atom parallel to the a-axis is assumed for one of the dipole field calculation tests.

4. Conclusion

In conclusion, the hyperfine coupling constant of κ-HgCl was estimated as A_{hf}(κ-HgCl) = 282 Oe/μB. This value is comparable with our calculation assuming a point dipole between the muon site, determined by the electronic potential calculation using density functional theory, and the localized spin at the Cl site. We need to continue the calculation using HOKUSAI since we will obtain more experimental data for the related samples.

5. Schedule and prospect for the future

Currently, we continue the calculation for the dipole field calculation, taking into account the distributed spins and muon zero-point energy. Several spin structures as a distributed spin will be included in the DFT calculation, and the method will be repeated to compare the calculated dipole field between muon and distributed spin with the muon hyperfine coupling constant A_{hf} obtained by the experiment.

Additionally, in January 2025, we got the muon beamtime to measure the muon Knight shift of κ-HgBr and κ-$ET_2Cu_2(CN)_3$. We will do the DFT calculation for the complementary of these experimental results.

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

Usage Report for Fiscal Year 2024

Fiscal Year 2024 List of Publications Resulting from the Use of the supercomputer

[Conference Proceedings]

1. D. P. Sari, Y. Cai, K. M. Kojima, I. Watanabe, H. Taniguchi, and Y. Ishii, "μ^+SR Knight shift of the hole-doped organic metal κ-$(ET)_4Hg_{3-\delta}Cl_8$, δ=22%, Interactions 245, 191 (2024)

[Oral presentation]

1. D. P. Sari, M. R. Ramadhan, I. Ramli, S. Charoenphon, Y. Ishii, H. Taniguchi, K. M. Kojima, I. Watanabe, "Possible unconventional spin freezing in κ-$(ET)_4Hg_{2.78}Cl_8$", presented in the JPS Autumn Meeting, held in Hokkaido University, Hokkaido, September 2024.
2. D. P. Sari, M. R. Ramadhan, I. Ramli, S. Charoenphon, Y. Ishii, H. Taniguchi, K. M. Kojima, I. Watanabe, "Origin of μ^+SR Knight shift in the hole-doped organic κ-ET-Mercury-Halide system κ-$(ET)_4Hg_{3-\delta}X_8$, X = Cl, Br", presented in the International Conference on Smart Materials and Nanotechnology (SMARTMAT@2024), held in Chiangmai, Thailand, November 2024.

Group discussions:

3. D. P. Sari, M. R. Ramadhan, I. Ramli, S. Charoenphon, Y. Ishii, H. Taniguchi, K. M. Kojima, I. Watanabe, "Possible unconventional spin freezing in κ-$(ET)_4Hg_{2.78}Cl_8$", presented in the University of Tokyo, Ogata-laboratory, Tokyo, September 2024.
4. D. P. Sari, M. R. Ramadhan, I. Ramli, S. Charoenphon, Y. Ishii, H. Taniguchi, K. M. Kojima, I. Watanabe, "Origin of μ^+SR Knight shift in the hole-doped organic κ-ET-Mercury-Halide system κ-$(ET)_4Hg_{3-\delta}X_8$, X = Cl, Br", presented in the JPARC Group Meeting, held online February 2024.

[Poster presentation]

1. Y. Someya, D. P. Sari, U. Widyaiswari, A. E. Putri, A. A. Firdaus, T. Takahashi, A. Koda, H. Taniguchi, I. Watanabe, and Y. Ishii, "Zero-field μ^+SR study of the hole-doped organic κ-ET-Mercury-Halide system κ-$(ET)_4Hg_{3-\delta}X_8$, X = Cl, Br", presented in the International JPARC Symposium held in Mito, Ibaraki, October 2024