論文題目　　　NMR Study of Electronic States in the Multi-Orbital

Organic Conductor M(tmdt)$_2$
（多軌道系有機導体M(tmdt)$_2$の電子状態に関するNMR研究）

氏　　名　　　高木　里奈

1. Introduction

Orbital degrees of freedom are among sources to give novel physical properties to strongly correlated electron systems. A family of M(tmdt)$_2$ is a candidate for the multi-orbital correlated electron systems.

In M(tmdt)$_2$, each *M* compounds possess different ground states. When *M* is replaced with Ni or Pt, the compounds are paramagnetic metals, while the replacement with Au leads to an antiferromagnetic metal [1][2]. Moreover, the *M* = Cu compound becomes an antiferromagnetic Mott insulator, which indicates that electron correlation is strong in M(tmdt)$_2$ [3].

It is considered that the different orbital states are responsible for the various conducting and magnetic states in M(tmdt)$_2$. The first-principles calculations predict that the molecular orbitals near the Fermi level consist of *pdσ*-orbital in a metallic ion *M* and the surrounding S atoms and *pπ*-orbitals in tmdt, where tmdt denotes trimethylenetetrathiafulvalenedithiolate. The energy-level difference between the *pdσ* and *pπ*-orbitals depends on *M*; that is, we can tune the orbital-degeneracy by replacing *M*.

The first-principle band calculations describe the *M* = Cu salt as a *pdσ*-orbital system, and the *M* = Ni
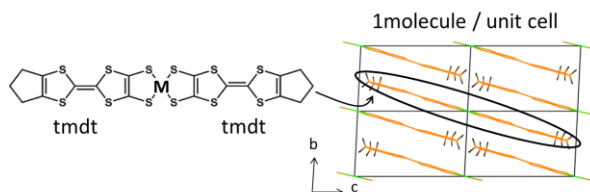

Fig. 1 Molecule and crystal structure of M(tmdt)$_2$.

and Pt salts as $p\pi$-orbital systems, which are consistent with the experimental results of the three compounds. However, it is not the case for M = Au. About the antiferromagnetic transition at T_N = 110 K, the calculation suggests a possible Fermi-surface instability into a spin-density-wave (SDW) in the tmdt conduction band formed by the $p\pi$-orbitals [4]. However, this SDW scenario has some difficulties in explaining the experimental results, which imply a large localized moment below T_N and the absence of anomaly in conductivity at T_N. The disagreement seems to require reconsideration of the electronic state in Au(tmdt)$_2$, taking the multi-orbital character and/or the strong electron correlation into account.

In this thesis, we seek for a systematic view of the electronic states in the isostructural compounds M(tmdt)$_2$ (M = Cu, Au, Ni and Pt) related to the orbital-degeneracy and the electronic correlation, and explore the novel physical properties under pressure. Though the variation of the orbital states by replacing M is suggested by the first-principles calculations, it is necessary to study it experimentally. In order to know the orbital states responsible for the conducting and magnetic properties, we performed ^{13}C nuclear magnetic resonance (NMR) measurements on each M compound (Part 1).

Because organic conductors are highly compressible, it is expected that applying pressure varies the band-width and/or modulates the orbital hybridization in M(tmdt)$_2$. Not only replacing M but also applying pressure can lead to different electronic states. In order to investigate the pressure-induced physical properties, we performed ^{1}H and ^{13}C NMR measurements under hydrostatic pressure (Part 2)

2. Results and Discussions

Part 1: Variation of orbital-degeneracy in M(tmdt)$_2$

In order to clarify experimentally the orbital states of M(tmdt)$_2$, we measured ^{13}C NMR spectra of the M = Cu, Au and Ni salts. As a reference, we also measured the neutral solid of tmdt. As shown in Fig. 2 (left), the spectra of the powdered samples at room temperature vary depending on M, implying a difference in the orbital nature. Considering that the M = Cu salt is $pd\sigma$-orbital system and the M = Ni salt is $p\pi$-orbital system, we propose that both $p\pi$ and $pd\sigma$-orbitals contribute to the physical properties in the M = Au salt from the spectral shift analyses. This is the first experimental study probing the orbital states in M(tmdt)$_2$. It becomes clear that we need to take the multi-orbital character into account and construct a new model to understand the electronic state in Au(tmdt)$_2$.
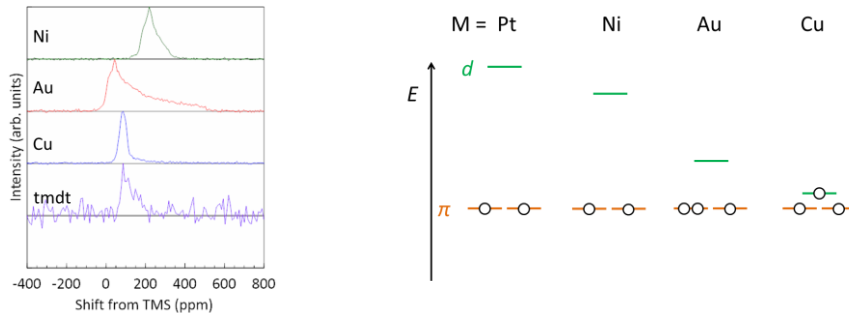

Fig. 2 ^{13}C-NMR spectra of M(tmdt)$_2$ (M = Cu, Au, Ni) and the neutral solid of tmdt (left), and schematic molecular orbital near Fermi level suggested by the first-principles calculations [4] (right).

Part2: Electronic states under pressure

We performed ^{13}C NMR measurements on the M = Ni and Pt compounds. At ambient pressure, both compounds showed the temperature-independent NMR relaxation rates, $1/T_1T$, which was consistent with the paramagnetic metallic states. We also measured $1/T_1T$ of Pt(tmdt)$_2$ under hydrostatic pressure and found the absolute values of $1/T_1T$ decreased with increasing pressure, indicating that the band-width was broadened by applying pressure.

However, [13]C $1/T_1T$ shows an enhancement below approximately 50 K and [1]H $1/T_1T$ shows a more pronounced increase in the whole temperatures below 300 K [5]. The ^{1}H is located in the terminal of tmdt, whereas ^{13}C is at the middle of tmdt; so, the interaction between a nuclear spin and a conducting electron is much smaller at the ^{1}H site than at the ^{13}C site. It is likely that the ^{1}H NMR probes the molecular dynamics common in M(tmdt)$_2$ more sensitively than the electronic spin dynamics. It is reasonable that the molecular dynamics contribution to $1/T_1T$ becomes appreciable in ^{13}C NMR only at low temperature, where the relaxation to the conducting electron becomes smaller. The molecular dynamics possibly originate from the softness of organic materials. However, such dynamics as observed in M(tmdt)$_2$ is remarkable in that it keeps activated even at very low temperatures.

The structure of M(tmdt)$_2$ (M = Cu, Au, Ni, and Pt) is planar, but the first-principles calculations indicated that the increase of the total energy by twisting tmdt ligands around the central metallic atoms is so small that it is possible to thermally excite the twisting motion even at a few Kelvin [4]. This scenario is consistent with X-ray diffraction experiments, which implies the large vibration of the S atoms in the tmdt ligands [6].

We also performed ^{1}H NMR measurements under hydrostatic pressure for Au(tmdt)$_2$ and Cu(tmdt)$_2$, which undergo antiferromagnetic transitions at 110 K and 13 K, respectively, at ambient pressure. We observed sudden disappearances of the antiferromagnetic transition and drastic changes in the temperature profile of the relaxation rates under pressure for both compounds (Fig. 3).

Based on the experimental studies including our NMR results, we discuss the electronic states of these compounds under pressure from the viewpoint of multi-orbitals. We consider that the antiferromagnetic moment of Au(tmdt)$_2$ is located at the $pd\sigma$-orbital as in Cu(tmdt)$_2$; whereas the $p\pi$ electrons contribute to the metallic conduction even below T_N. Applying pressure increases the band-width and induces a Mott
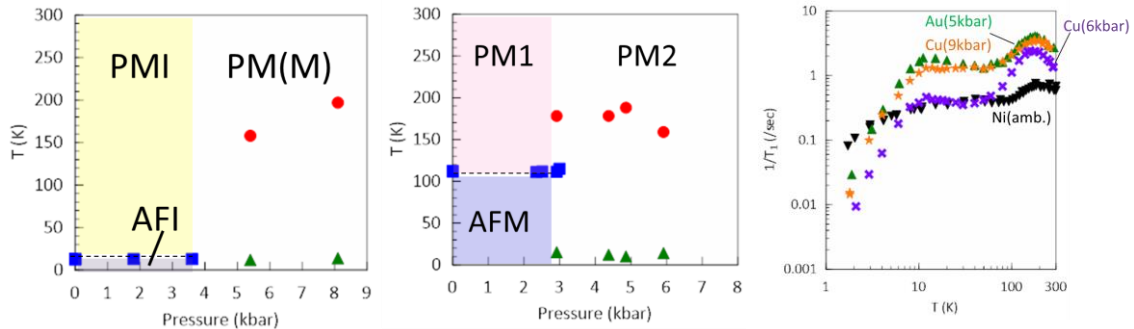

Fig. 3 Pressure-temperature phase diagram of Cu(tmdt)$_2$ (left) and Au(tmdt)$_2$ (center), and ^{13}C-NMR relaxation rates of M=Au and Cu in high pressure regions and M=Ni at ambient pressure (right).

transition on the $pd\sigma$-orbital, which resulted in the disappearance of the antiferromagnetic transitions in both M = Au and Cu salts.

About the change of the ^{1}H NMR relaxation rates under pressure variation, we point out that the molecular dynamics were induced or enhanced by pressure for the M = Au and Cu salts. In comparison with the M = Ni and Pt salts, the relaxation rates in the M = Au and Cu salts in the high pressure region were larger in magnitude but similar in temperature dependence in that two broad peaks appear (the right panel of Fig. 3). It is suggested that the molecular dynamics observed at ambient pressure was enhanced and/or changed under pressure.

A change in the electronic states in the $pd\sigma$-orbital can trigger not only the disappearance of the antiferromagnetic transition but also the enhancement of the molecular dynamics under pressure. It is considered that the twisted configuration of the molecule is stabilized with the increase in the electron occupation in the $pd\sigma$-orbital because of the energy gain by lowering the crystal field symmetry around d-orbital in M. The molecular dynamics might be influenced by the exchange of electrons between different orbitals. With the increase of the band-width, the hybridization of the $p\pi$ and $pd\sigma$-orbitals would change. If the averaged electron occupation of the $pd\sigma$-orbital increased above the pressure where the antiferromagnetic moments in $pd\sigma$-orbital disappeared, a change in the molecular dynamics could associate with the transition in the electronic state. This would explain why the change in the molecular dynamics contribution to the relaxation rates simultaneously occurred with the disappearance of the antiferromagnetic transitions in the M = Au and Cu salts.

3. Conclusions

We performed NMR measurements on the multi-orbital organic conductor $M(tmdt)_2$. It was experimentally evidenced that the orbital degeneracy can be varied by replacing metallic ion M and the band-width is widened by applying hydrostatic pressure in $M(tmdt)_2$.

We observed sudden disappearances of the antiferromagnetic transitions by hydrostatic pressure in $Au(tmdt)_2$ and $Cu(tmdt)_2$. We proposed that the origin could be changes in the electronic states of the $pd\sigma$-orbitals and concomitantly tmdt orbitals in both compounds. We found the characteristic molecular dynamics in $M(tmdt)_2$ possibly enhanced and/or changed under pressure. It is suggested that the characteristic pressure-induced molecular dynamics would be the cooperative product of the softness of the molecule and the orbital degree of freedom in $M(tmdt)_2$.

4. References

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