Observation of Mott Transition Coupled to Intramolecular Degrees of Freedom

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ABSTRACT

Quasi-two-dimensional (Q2D) organic conductors exhibit a variety of electronic phases such as Mott insulator, unconventional superconductivity, and quantum spin liquid, which have been intensely studied as emergences in strongly correlated electron systems. However, it remains unknown how the intramolecular degrees of freedom peculiar to organic materials are involved in the correlation-driven electronic states. Recently, the authors of this article and their colleagues have investigated the electrical and magnetic properties of the Q2D organic material β-(BDA-TTP)$_2$I$_3$ under pressure and found that molecular motions activated in the low-pressure Mott insulator phase are suppressed simultaneously with metallization by pressure. This indicates that the metal-insulator transition due to electron correlation is associated with the intramolecular degrees of freedom.

INTRODUCTION

Electrons in narrow-band systems strongly interact through Coulomb repulsive force, which leads to remarkable phenomena such as high-T_c superconductivity. Those systems, called strongly correlated electron systems, have been enthusiastically studied not only in inorganic materials but also in organic ones. Since organic materials are more flexible in structure than inorganic ones, pressure varies the strength of electron correlation through lattice contraction more significantly than in inorganic ones, leading to drastic changes in physical properties of organic materials. Another characteristic of organic materials is the intramolecular degrees of freedom at each lattice point of the crystal. Introducing such degrees of freedom to crystals is expected to be a key to producing new physical properties. However, despite intensive studies regarding the correlation effects on the charge and spin states, it is not well understood what role the intramolecular degrees of freedom will play in strongly correlated electron systems.

Physical Properties of β-(BDA-TTP)$_2$I$_3$

The organic conductor, β-(BDA-TTP)$_2$I$_3$, is a Q2D material, in which conducting layers comprised of BDA-TTP dimers and insulating I$_3$ layers are stacked alternately, and the conducting layer is regarded as a dimer-Mott system having one hole per one BDA-TTP dimer [1]. Thus, the conducting layer constitutes a half-filled band electron system, which undergoes a Mott transition under pressure in common with other dimer-Mott systems [2]. Notably, this material carries a peculiar molecular motion of trimethylene groups at the end of the BDA-TTP molecule, which lie out of the molecular plane (Fig. 1) and have vibrational degrees of freedom allowing "flapping motion" [3]. It had not been thought that the Mott metal-insulator transition in this system could be connected with the flapping motion.

Connection between the Mott transition and molecular motion

Recently, the authors have performed electrical resistivity and ^{1}H nuclear magnetic resonance (^{1}H-NMR) measurements to examine the electronic states and the molecular motion of β-(BDA-TTP)$_2$I$_3$ at several pressures in collaboration with researchers at the University of Tokyo and the University of Hyogo. The results revealed a clear association between the Mott transition and the intramolecular degrees of freedom. This work was published

in the September 2018 issue of the *Journal of the Physical Society of Japan* (JPSJ) [4].

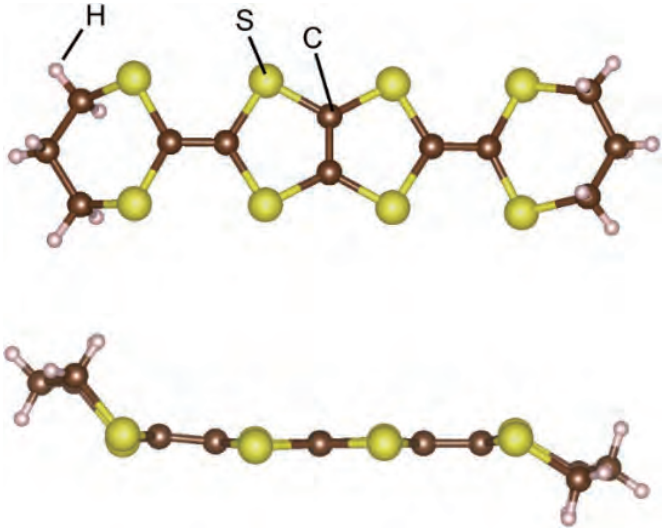

Fig. 1: Illustrations of a BDA-TTP molecule viewed from above (upper) and from the side (lower).

In crystalline solids, NMR probes local magnetic fields at nuclear sites in the crystals. Among physical quantities available in NMR measurements, the nuclear spin-lattice relaxation rate detects the fluctuations of the local magnetic field in a frequency band of MHz range. A source of the fluctuations of the internal fields is from the dynamics of electron spins around the nuclei. For example, near an antiferromagnetic transition point, the dynamics of electron spins slow down so that the fluctuations have a large spectral weight in the MHz frequency range, and the relaxation rate is enhanced. Indeed, in β-(BDA-TTP)$_2$I$_3$, the relaxation rate forms a sharp peak at the antiferromagnetic transition temperature, 30 K, in the Mott insulator phase at low pressures (upper panel in Fig. 2). On the other hand, the relaxation rate also captures molecular motion, which is another source for local-field fluctuations at nuclear sites. This is because the nuclear spins of atoms in motion create fluctuating dipole magnetic fields at nuclear sites that are used as probes. The collaborative team observed an anomalous enhancement in the relaxation rate above the antiferromagnetic transition temperature in the low-pressure Mott insulator region (Fig. 2). This temperature dependence well obeys the Bloembergen, Purcell, and Pound equation that describes molecular motion [5], and thus it was concluded that the enhancement in the relaxation rate is due to the flapping motion of the molecules. Surprisingly, however, the relaxation enhancement abruptly disappeared under pressure, indicating a sudden suppression of the molecular motion. To further investigate this drastic change of molecular dynamics, the collaborative team measured electrical resistivity under pressure and found that the Mott insulator-to-metal transition has an extraordinarily strong first-order character and coincides with the suppression of the molecular motion (lower panel in Fig. 2). The behavior of the electrical resistivity also implies a large structural change at the Mott transition. Thus, it is considered that the suppression of the molecular motion and a concomitant structural change by pressure increase intermolecular transfer integrals and promote the metallization.

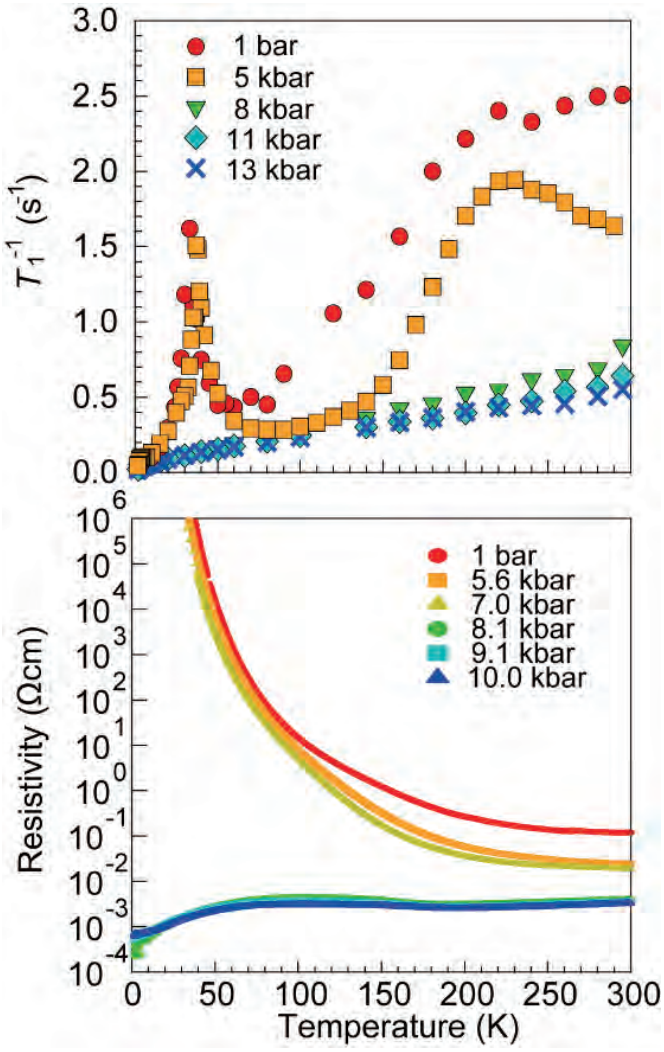

Fig. 2: Temperature dependences of ^{1}H nuclear spin-lattice relaxation rate (upper panel) and electrical resistivity (lower panel) under pressure.

These results show the link between the Mott transition and molecular motion. Since many organic materials

have such intramolecular degrees of freedom, further novel properties with electronic and molecular degrees of freedom mutually entangled are expected to be developed.

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References

[1] H. Aizawa, K. Kuroki, and J. Yamada, Phys. Rev. B 92, 155108 (2015).
[2] K. Kanoda, J. Phys. Soc. Jpn. 75, 051007 (2006).
[3] J. Yamada and H. Akutsu, Crystals 2, 812 (2012).
[4] R. Takehara, K. Nakada, K. Miyagawa, T. Kadoya, J. Yamada, and K. Kanoda, J. Phys. Soc. Jpn. 87, 094707 (2018).
[5] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948).

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