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NMR Studies of Massless Dirac Fermions in the Quasi-Two-Dimensional Organic Conductor α-(BEDT-TTF)$_2$I$_3$

（擬二次元有機伝導体 α-(BEDT-TTF)$_2$I$_3$ におけるゼロ質量ディラックフェルミオンの NMR 研究）

Abstract

1. Introduction

This thesis explores the electronic structure of the quasi-two-dimensional (Q2D) massless-Dirac-fermion system realized in the layered organic conductor α-(BEDT-TTF)$_2$I$_3$ (α-I$_3$; Fig. 1) under hydrostatic pressures. Our study has been motivated by the ideality and uniqueness of α-I$_3$ for the unprecedented exploration of local electronic properties relevant to the tilted Dirac cone with strong electron-electron interactions by means of nuclear magnetic resonance (NMR), which is an excellent probe to resolve density of states with a high real-space resolution.

α-I$_3$ is known as a strongly correlated metal which undergoes a metal-insulator (M-I) transition with charge ordering at low pressures due to strong electron-electron Coulomb repulsions.[1] The M-I transition is suppressed by applying hydrostatic pressures, and disappears at P_C of ca. 1.5GPa,[2] above which an electronic phase with linear dispersion near the Fermi level – massless Dirac fermion (MDF) – is emergent at low temperatures,[3] in analogy with monolayer carbon atoms; graphene. MDFs of α-I$_3$ have three outstanding features distinguished from other MDF systems. First, the massless Dirac cones are tilted and locate at general points in momentum space (k_D and $-k_D$; Fig. 2), while those in graphene are isotropic and locate at high-symmetric K and K' points. Secondly, owing to the narrow bandwidth, strong electron correlations are present in α-I$_3$, as evidenced by charge ordering at low pressures. Finally, α-I$_3$ is a bulk material that affords us a rare opportunity to observe MDFs microscopically with bulk measurements such as NMR. All of these features, hence, make α-I$_3$ a distinctive system in which electronic properties of MDFs can be explored by NMR techniques in association with electron correlation effects, which have been hard to perform in other MDF systems including graphene. A leitmotif in this thesis is thus to reveal detailed local electronic structures of MDFs in α-I$_3$ with the use of ^{13}C NMR.

The thesis is divided into two parts; the first two sections (Sec. 3.1 and 3.2 in the following) present our microscopic ^{13}C-NMR studies of MDFs in the presence of an in-plane magnetic field (i.e., electron spins are polarized but the kinetic energy is not quenched). We have uncovered that the electronic state in α-I$_3$ is indescribable by a simple band structure without electron correlations over a wide temperature range; interaction-enhanced susceptibility and NMR relaxa-

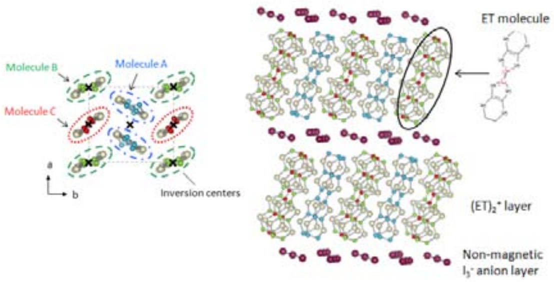

Fig. 1 Crystal structure of α-I_3. (ET = BEDT-TTF)

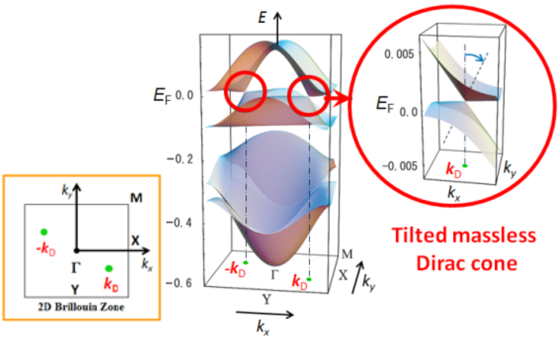

Fig. 2 Tilted Dirac cone in α-I_3 under pressure.[3]

tion rate T_1^{-1} at high energies, and/or reshaped Dirac cones with the reduced density of states (DOS) near the Dirac point are emergent. In the next section (Sec. 3.3), we present the NMR results of the zero-mode Landau level (z-mLL) generated at the Dirac point under perpendicular magnetic fields. Owing to the high sensitivities of NMR to the DOS near the Fermi level, we have been able to make accurate measurements of the zero-mode Landau quantization both by NMR shift and relaxation rate T_1^{-1} measurements. All of these results open up new possibilities in the field of MDFs, especially the explorations of strongly correlated MDFs and its spin and valley symmetry breakings by NMR spectroscopy.

2. Experimental

Single crystals of α-I_3 are prepared by conventional electrochemical method, whereby the central carbon sites in ET molecules are selectively enriched by ^{13}C isotopes (nuclear spin I = 1/2) with 99% concentration for ^{13}C-NMR measurements (Fig. 1 right). NMR spectra are obtained by the Fourier transformation of spin-echo signals. Spin-lattice relaxation rate T_1^{-1} is determined by the saturation and recovery method. Hydrostatic pressures of ca. 2.0GPa are applied to the sample with BeCu/NiCrAl clump-type pressure cell and the Daphne oil 7373 as the pressure medium. Low field measurements are done using a superconducting split-pair magnet with fields up to 6T (Sec. 3.1 – 3.3), while high field measurements up to 15T are done with another magnet (Sec. 3.3).

3. Results and Discussions

3.1 High-pressure NMR characterization of massless Dirac fermions (MDFs) under in-plane field

We first measured site-averaged NMR local electron spin susceptibility χ_s (determined by Knight shift K; Fig. 3A) and nuclear spin-lattice relaxation rate T_1^{-1} (Fig. 3B) under an in-plane field of 6T at 2.3GPa. We found that power-law behaviors expected in uncorrelated MDF collapse above ca. 30K, accompanied by large enhancements with downward convex behaviors in both K and T_1^{-1} which are not predicted by theoretical calculations without electron-electron correlations.[4] We further explored the molecule-site dependence of χ_s and T_1^{-1} at three nonequivalent molecular sites in the unit cell (i.e., A, B, and C; Fig. 1 left) and confirmed a large spin-density disproportionation in both

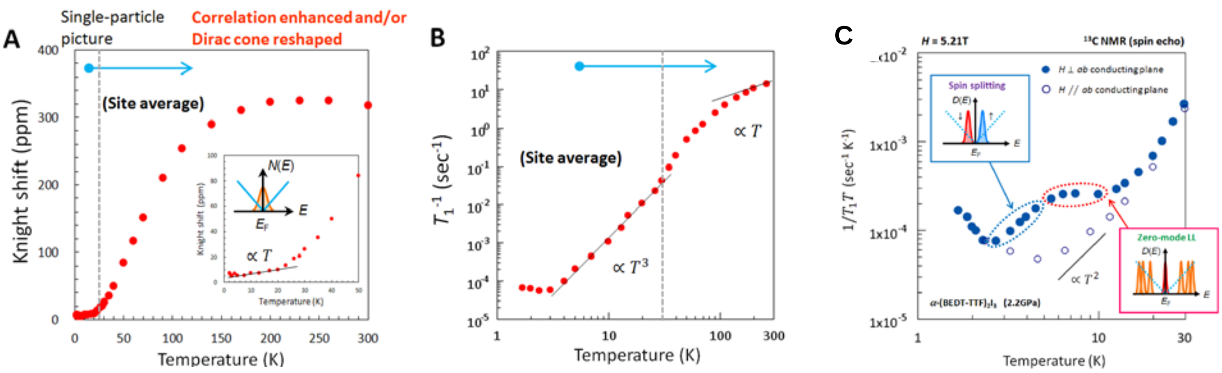

Fig. 3: Knight shift K and spin-lattice relaxation rate T_1^{-1} under in-plane magnetic field (6T) at 2.3GPa (A, B). Spin-lattice relaxation rate T_1^{-1} under in-plane and perpendicular filed geometries (5.2T) at 2.2GPa. (C)

of them, C > A > B, which can be basically explained by a novel site-band correspondence inherent to the tilted Dirac cone;[4] the B site probes the steep slope of the tilted Dirac cone with a small DOS, while C site does its gentle slope with a large DOS, and A site is in between them. The temperature profiles of χ_s are different on B and C sites. Moreover, spin fluctuations, evaluated via the Korringa ratio $\mathcal{K} \sim (T_1TK^2)^{-1}$, show site-specific temperature dependence. These results suggest that electron correlations develop in a strongly momentum-dependent manner in momentum space. The overall results imply that, owing to the intense electron correlations, the DOS might be pushed up at a high energy scale well above the Dirac point (akin to the usual Stoner enhancement), whereas it is pushed down at low energies close to the Dirac point, giving rise to the downward convex behaviors in χ_s and T_1^{-1}. These findings, in turn, leads to a new explanation for MDF picture residing in the proximity of a correlation-induced charge ordered phase.

3.2 Ambient-pressure NMR characterization of conducting state under in-plane field

In this section, the ambient-pressure conducting phase above the M-I transition temperature was investigated by ^{13}C NMR under an in-plane magnetic field of 6T,[5] finding that susceptibility, relaxation rate, and Korringa ratio exhibit basically the same site-dependent characteristics as observed at high pressures. From these results, we demonstrate that, contrary to common beliefs, this phase can be well understood on the basis of tilted-Dirac-cone picture that has been originally validated only under high pressures, providing a unified view of conducting phases in α-I_3.

3.3 Zero-mode Landau level (z-mLL) observed by NMR

Here, we observed orientation dependence of spin-lattice relaxation rate T_1^{-1} in the plane normal to the 2D conducting layer under 5.2T at 2.2GPa. A clear difference is found between in-plane and normal-plane geometries in $(T_1T)^{-1}$ at low temperatures (Fig. 3C), indicating a spectral-density shift toward the Fermi level under the normal field condition. Together with the orientation dependence of $(T_1T)^{-1}$ at several field geometries, we argue that these results provide an evidence of z-mLL, inherited from the massless Dirac cone, and its spin splitting effect.

To extend the study of the z-mLL to higher fields, we measured spin-lattice relaxation rate T_1^{-1} with a strong magnetic field of 15T applied normal to the conducting plane at 2.2GPa. We find a large enhancement in $(T_1T)^{-1}$ from that in 5.2T with a similar plateau-like structure followed by a sharp drop around 10K, indicating an increase in DOS at the Fermi level probably due to increased LL degeneracy. Moreover, we observed a signature of spontaneous symmetry breaking in low-temperature NMR spectra that is not observed at 5.2T. The result may be relevant to the theoretical studies predicting a symmetry breakage driven by the strong electron-electron interactions in MDF systems; [6] the valley-degeneracy of z-mLL might split at these intense fields, accompanied by an inversion symmetry breaking. As a whole, these results are the first direct observation of the z-mLL by NMR, and demonstrate the potential availability of NMR for investigations of symmetry breakages relevant to spin and valley degeneracy splitting in MDF systems.

4. Conclusion

This thesis presents a comprehensive exploration of massless Dirac fermions in α-(BEDT-TTF)$_2$I$_3$ under hydrostatic pressures, with ^{13}C-NMR spectroscopy. Under an in-plane field (Sec. 3.1), we reveal that the local spin susceptibility χ_s and nuclear relaxation rate T_1^{-1} both exhibit large enhancements, with downward convex behaviors, from the theoretical values without electron correlations. These results indicate that a simple Dirac-cone picture without electron-electron interactions collapses over a wide temperature range, possibly implying that the Dirac cone is largely reshaped by intense correlations. The conducting phase at ambient pressure (Sec. 3.2) is also revealed to be well understood by the Dirac-cone picture with strong electron correlations similar to the high-pressure phase, contrary to common beliefs. Under out-of-plane magnetic fields (Sec. 3.3), we observe clear signatures of the zero-mode Landau level generated at the Fermi level, characteristic of massless Dirac fermions, and its spin and, possibly, valley degeneracy splitting by NMR spectra and T_1^{-1} measurements. All of these results indicate that NMR can be used as an excellent probe to explore the electronic structures near the Dirac point in a massless-Dirac-fermion system with strong electron correlation effects.

5. Reference

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