Anomalous spin correlations and excitonic instability of interacting 2D Weyl fermions

Michihiro Hirata,1,2* Kyohi Ishikawa,2 Genki Matsuno,3 Akito Kobayashi,3 Kazuya Miyagawa,2 Masafumi Tamura,4 Claude Berthier,5 Kazushi Kanoda2*

The Coulomb interaction in systems of quasi-relativistic massless electrons has an unscreened long-range component at variance with conventional correlated metals. We used nuclear magnetic resonance (NMR) measurements to reveal unusual spin correlations of two-dimensional Weyl fermions in an organic material, causing a divergent increase of the Korringa ratio by a factor of 1000 upon cooling, in marked contrast to conventional metallic behavior. Combined with model calculations, we show that this divergence stems from an interaction-driven velocity renormalization that almost exclusively suppresses zero-momentum spin fluctuations. At low temperatures, the NMR relaxation rate shows an unexpected increase; numerical analyses show that this increase corresponds to internode excitonic fluctuations, a precursor to a transition from massless to massive quasiparticles.

Weyl fermions in solids are massless quasiparticles described by a linear energy-momentum dispersion relation that mimics the relativistic Weyl-Dirac theory (1). Their effective model is characterized by a pseudospin-½ degree of freedom whose projection onto the momentum, known as the chirality, produces unconventional charge (2, 3) and spin (4–7) responses. Here, we focus on a two-dimensional (2D) material and use the term Weyl fermions (WFs) to describe massless quasiparticles that obey the generalized Weyl Hamiltonian in 2D materials (4, 5, 7–10). In contrast to the short-range electronic correlations in ordinary metals, the Coulomb interaction among WFs has a long-range component that is unscreened at the band-crossing points, owing to the vanishing density of states at the Fermi energy $E_F$ (2). As a result, anomalous phenomena can occur, such as an upward renormalization of the electron velocity in graphene (1, 2, 11), in marked contrast to its suppression in conventional correlated materials. For strong coupling, characterized by a large value of $\alpha$ [the dimensionless coupling constant given by the ratio of the Coulomb potential to the electronic band (1)], theoretical studies have predicted an excitonic mass gap opening (or chiral symmetry breaking), which originates from the incipient instability of massless fermions as first discussed in high-energy physics (12) and more recently in the context of condensed matter (13, 14). However, experimental characterization of interacting WFs under strong coupling has remained limited because $\alpha$ has been found to be rather small in a range of materials (1, 2).

Here, by combining nuclear magnetic resonance (NMR) experiments and model calculations, we demonstrate the realization of a strongly coupled 2D WF system in the organic charge-transfer salt $\alpha$-I$_3$[α-(BEDT-TTF)$_2$I$_3$], where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene. $\alpha$-I$_3$ is a layered material comprising BEDT-TTF conducting layers and I$_3$ insulating layers (Fig. 1A). In the bulk of conducting layers, a ¾-filled system is realized in which a charge-ordered insulating phase caused by short-range electron correlations appears below 135 K (15–19). An application of hydrostatic pressure ($P$) increases the bandwidth and reduces the correlations, in turn suppressing charge order (Fig. 1B) (20). Above a threshold $P = 1.2$ GPa, transport measurements found a semiconducting behavior with a vanishingly small gap (15), which led to the predictions of a 2D WF phase with a pair of spin-degenerate tilted Dirac cones (8–10, 21) resulting from the presence of space and time inversion symmetries; the cones originate from BEDT-TTF molecular orbitals, and their nodes are fixed at $\mathbf{K}_\pm$ because of the ¾-filling of the electronic band. Experimentally, direct evidence for the cones has been found by recent NMR measurements (4) at a pressure of 2.3 GPa. Reflecting the low-symmetric crystal lattice that only possesses inversion symmetry, the band-crossing nodes are located away from high-symmetry points within the first Brillouin zone; in an extended region of the hopping parameter space, these nodes are stable to perturbations, such as pressure, that do not break space and time inversion symmetries (8–10).

The presence of WFs competing with charge order suggests a strong influence of electron-electron interactions on the nature of WFs (5, 7, 16, 19, 22). Indeed, the recent measurement of the Knight shift (4), probing the real part of the longitudinal static uniform susceptibility $\chi_0$ ($\mathbf{Q} = 0$, $\omega = 0$) (where $\mathbf{Q}$ is a wave number vector and $\omega$ is a frequency), found a logarithmic velocity enhancement caused by the long-range component of the interaction as well as a ferrimagnetic spin polarization by short-range correlations (7, 22), where opposing magnetic moments having unequal signs appear. These findings make $\alpha$-I$_3$ an ideal playground for investigating the effects of electron-electron interactions in WF materials. In addition,

![Fig. 1 Crystal structure and phase diagram of $\alpha$-(BEDT-TTF)$_2$I$_3$. (A) Side view of the crystal structure. The conducting BEDT-TTF layers are separated by nonmagnetic insulating layers of I$_3$. Inset: BEDT-TTF molecular structure, with selectively introduced $^{13}$C isotopes indicated by arrows. (B) Pressure-temperature phase diagram of $\alpha$-(BEDT-TTF)$_2$I$_3$ (adapted from (4)). The dashed line indicates the first-order transition line, which was derived from the resistivity measurements in (20).](Image)
at high temperatures, α-I₃ moves into a conventional 2D metal-like regime (4), reflecting the flatness of the density of states (DOS) above |Eₚ – E₀| ≈ 12 meV (∼150 K) (where E₀ is a threshold up to which the DOS is linear in energy; see insets of Fig. 2A) (8, 27). By varying the experimental energy scale (i.e., temperature), one can thus explore the electronic properties of 2D WFs at low T as compared to the metal-like state at high T.

To gain a deeper knowledge of the electron-electron interactions, we measured the 13C-NMR spin-lattice relaxation rate divided by temperature (1/T¹T), which probes the Q average of the imaginary part of the transverse dynamic spin susceptibility Im χ(ω) (where ω lies in the MHz region) (23–25). Figure 2A presents the temperature dependence of 1/T¹T and the squared Knight shift K² (4) in the WF state of α-I₃ (at 2.3 GPa), measured on the 13C nuclei at the center of BEDT-TTF molecules. A magnetic field of 6 T was applied parallel to the 2D conducting layers for NMR measurements (26.) Both quantities are approximately flat above 150 K and decrease notably upon cooling below this temperature. In standard metals with a DOS constant in energy, the quantity 1/(T¹T²) is constant upon cooling; this is known as the Korringa law (23–25). In contrast, in a Dirac cone system, both 1/T¹T and K² rapidly drop upon cooling, reflecting the vanishingly small DOS around E₀ (27). The overall behavior in Fig. 2A points to a crossover from a Korringa-like metal to a gapless state below 150 K, in line with the predicted DOS profile (insets of Fig. 2A).

To see the nature of the interaction in a standard metal, it is useful to study the behavior of the so-called Korringa ratio, K = 1/(T¹T²S₀βK²), which measures the strength of the short-range electron correlations (24, 25). Here, S₀ = (∝kβ/ħ) (γₐ/γₐ)² (where γₐ is the nuclear gyromagnetic ratio, γₑ is the electron gyromagnetic ratio, kβ is the Boltzmann constant, and β is the reduced Planck constant) and β is a form factor representing the anisotropy of the nuclear hyperfine interaction. The action of K is on the order of unity and does not considerably vary with T in weakly correlated systems, whereas a sizable deviation from unity appears in strongly correlated metals, with K > 1 signifying enhanced antiferromagnetic spin fluctuations and K < 1 signifying enhanced ferromagnetic spin fluctuations (24, 25). Figure 2B shows the temperature dependence of K obtained from the data in Fig. 2A using the value of β previously reported at ambient pressure in α-I₃ (28), which is approximately independent of temperature and pressure (4, 26). Above 150 K, a T-independent behavior with a size of K ∼ 3 is seen, such as has been observed in the typical 2D organic metals (BEDT-TTF)₂I₃ (29) and a-(BEDT-TTF)₂Cu(NCS)₂ (30). This corroborates the 2D metallic picture at high T with moderate short-range correlations.

In contrast, a breakdown of the Korringa law sets in below 150 K, and an increase of K by several orders of magnitude appears with decreasing temperature, leading to K ∼ 10⁻³ at 10 K. The notable increase of K directly originates from the distinct 7 dependence of K² and 1/T¹T (Fig. 2A).

For WFs in 2D systems, the conduction and valence bands touch at E₀, giving rise to a pair of spin-degenerate nodes at ±k₀, that are not topologically protected, and lack of conventional screening causes the Coulomb interaction to remain long-ranged (I, 2). An in-plane magnetic field lifts the spin degeneracy and causes the Zeeman splitting of the up- and down-spin nodes. The electronic excitations at low temperature appear exclusively around these four nodes; the excitations can be categorized into two processes that are characterized by contrasting momentum transfers (Q), Cₐ (0, 0) and Cₐ (0, 0) (30). The bare Coulomb coupling constant, α = e²/ε₀ε₀ is estimated to be ~8 by using ε = 30 and v = 2.4 × 10⁴ m/s as determined from fitting K (4), where ε is the elementary charge, e is the permittivity, and v is the electron velocity (26). The RG calculation can properly trace the observed excess suppression of K² with respect to 1/T¹T and hence the divergent increase of K upon cooling (Fig. 3, A and B). The contrasting temperature dependence of K² and 1/T¹T can be accounted for by the T-driven RG flow of the coupling constant (fig. S1) and the resultant upward velocity renormalization, which only suppresses the Q = 0 response. Thus, the uniform part of the static susceptibility Re χ(Q → 0, 0)
Fig. 3. Renormalization group simulations. (A) Calculated temperature dependence of 1/T, T and K2 at 6 T for double tilted Dirac cones with the velocity renormalization introduced by the self-energy correction: RG techniques within the leading-order large-N expansion were used (4). The Coulomb coupling is chosen as a = 0 (dashed line) and a = 8.4 (solid line) determined from fitting the K data (4, 26). Inset: The calculated 1/T, T in the electron-hole channel (interband excitations across Ek, dash-dotted line) and the electron-electron channel (within the same band; dashed line) for the process C0,2k0 (a = 8.4). (B) Calculated K as a function of temperature for double cones with and without the tilt and self-energy correction. The tilt becomes more irrelevant at low energies by RG flow (4). (C) Double tilted Dirac cones in α, 1.5 for α = 0 (gray cones) and a = 8.4 (green reshaped cones). Two nodes appear at ±k0, where the conduction band (CB) and the valence band (VB) touch at Ek. Relevant excitation processes at low temperature (C0,0 and C0,2k0) are indicated by arrows. Electron Zeeman splitting is considered in the calculations but omitted in this illustration because it has only minor impact on the results (see text). (D and E) Calculated wave vector Q dependence of the transverse (κ⊥) and longitudinal (κ∥) spin susceptibilities for double tilted cones with the self-energy correction (a = 8.4). The direction of Q is set along the line connecting the two nodes. The calculated profiles of Im χ, (D) and Re χ (E) at 25 K (blue) and 5 K (red) are shown. The inset of (D) shows the corresponding 3D plot of Im χ, on the Qx-Qy plane. Note that the Qx = 0 term in Re χ corresponds to K, whereas the Q-summed Im χ amounts to 1/T, T, a.u., arbitrary units.

\( a \) and \( b \), probing \( C_{Q,0} \), is directly affected (Fig. 3E), leading to a continuous drop of \( K^2 \) upon cooling \((4, 7)\). Conversely, the Q-summed Im \( \chi \)(Q, a) \((\propto 1/T, T)\), probing the sum of \( C_{Q,0} \) and \( C_{Q,2k0} \), is affected less; the process \( C_{Q,0} \) dies off upon cooling by renormalization, whereas the process \( C_{Q,2k0} \) in particular in the interband electron-hole channel (inset of Fig. 3A), diminishes less and becomes prevailing at low T (Fig. 3D), causing moderate T dependence. Note that the effect of the Zeeman splitting, which would induce a saturation of 1/T, T and K by field-induced pockets (Fig. S2), is negligible, as the renormalization drastically suppresses the DOS at \( E_F \) (Fig. S3) (26). Furthermore, the tilt of the cone has a very small effect (Fig. 3B). These considerations demonstrate that the divergent increase of K is a hallmark of general 2D WFs either tilted or vertical, which is directly promoted by the renormalization.

A similar violation of the Korrina law also appears in conventional half-filled correlated metals near a Mott transition, where an increase of K, up to at most 10 upon cooling is reported (23). Its origin is, however, the growing finite-Q components of \( \chi \)(Q, a) that push up 1/T, T but keep \( K \) intact, which can be clearly differentiated from the present case where the enhancement of K is driven by the suppressed Q = 0 term.

Surprisingly, 1/T, T shows an additional upturn below 3 K and increases by a factor of 2 toward 1.7 K (Fig. 4A). [Note that K is vanishingly small in this T range (4) and is difficult to use for quantitative analyses (26).] Given the sharp nature of this upturn, it is likely that slow spin dynamics emerge at low energies. Although the T-driven RG flow (Fig. S1) reduces the Coulomb coupling \( a \) toward lower temperatures, its value remains rather large in the present temperature range: \( a \approx 2.0 \) at 5 K. Considering this sizable value, the upturn suggests emergent spin fluctuations associated with the incipient instability of gapless fermions that is driven by the Coulomb interaction.

In the presence of the Coulomb force that preserves its long-range nature, theoretical studies in 2D WF systems have revealed an electronic instability favoring excitonic pair formations (32). Above a critical value for the Coulomb coupling \( a \approx 1 \), this leads to an excitonic transition accompanied by mass acquisition (2, 33), akin to the chiral symmetry breaking that has been intensively studied in the relativistic high-energy theory (32). To examine the influence of this instability, we calculated \( \chi(Q, a) \) according to the
ladder approximation (fig. S4) with the tilted Weyl Hamiltonian and evaluated the excitonic gap function at mean-field level, taking into account the velocity renormalization (26). We confirmed that the spin-triplet even-parity pairing gap function at mean-field level, taking into account. The Coulomb coupling of instability (solid line) is used. Inset: The corresponding eigenvalue at $Q=0$ (dotted line), whereas there is no instability in the $C_Q$-0 process (dashed line) (26).

Apart from the 2D WF picture discussed so far, let us briefly examine other possible mechanisms that can contribute to $1/T_1 T$ and $K$. Relaxation of the nuclear magnetization into paramagnetic impurities is one such example, which is, however, unlikely in the clean organic salt $\alpha_1$-$\mathrm{I_3}$ where extremely high mobilities exceeding $10^5$ cm$^2$ V$^{-1}$ s$^{-1}$ have been reported at low temperature (15). Indeed, even below 3 K, $1/T_1$ increases with decreasing temperature (fig. S7); this contradicts the impurity scenario, which would cause a leveling off of $1/T_1$ or an activation behavior ($\alpha_3$, $\alpha_5$). Relaxation caused by other (massive) electrons is another possibility, but this is also ruled out because it leads to a saturation of both $1/T_1 T$ and $K^2$ as in standard 2D metals, in contrast to the observations. Lastly, the orbital hyperfine interaction, which is predicted to give a divergent contribution in 3D topological Weyl semimetals (36), can be neglected in the weak spin-orbit 2D system $\alpha_1$-$\mathrm{I_3}$, as it plays an important role only in the strong spin-orbit 3D systems.

The anomalous spin dynamics whose signatures we found are a direct consequence of the chiral nature of the Weyl Hamiltonian (1, 10), which is common to various Weyl Dirac systems, regardless of dimensionality, pseudospin, or topology (1). Therefore, this physics would also apply to a range of 3D topological Weyl and Dirac semimetals if the contribution from ordinary electrons is sufficiently small. This work paves the way for the exploration of the rich physics of "strongly interacting WFs" in solids (2), which has until now mainly been discussed on a theoretical basis.

REFERENCES AND NOTES

26. See supplementary materials.

ACKNOWLEDGMENTS

We thank K. Nomura for critical discussions and reading of the manuscript; D. Basko for technical help with RG calculations; M. O. Goerbig for support and discussions; J. S. Kinyon for fruitful discussions; and H. Fukuyama, N. Nagaosa, H. Isoe, H. Kohno, Y. Suzumura, M. Ogata, T. Osada, C. Hotta, H. Yatsuoka, D. Liu, H. Nojiri, T. Kihara, H. Mukoda, M. Tokunaga, Y. Maeno, W. Li, M. Potemski, M.-H. Julien, H. Mayaffre, and M. Horvatic for helpful discussions and comments. Supported by MEXT/JSPS KAKENHI grants 20100002, 21105519, 24654014, 25220709, 15K05168, 15H02108, 17K05532 and 17K04330, JSPS Postdoctoral Fellowship for Research Abroad grant 66, 2013; the MEXT Global Center of Excellence Program at the University of Tokyo (Physical Sciences Frontier grant GO4); the Kurata Memorial Hitachi Science and Technology Foundation (G.M. and A.K.); and the Motizuki Fund of the Yukawa Memorial Foundation (H.I.). The data presented in this paper are available upon request to the first author.

SUPPLEMENTAL MATERIALS

www.sciencemag.org/content/358/6369/1403/suppl/DC1 Materials and Methods

Supplemental Text

Figs. 51 to 57

References (37–95)

27 April 2017; accepted 14 November 2017

10.1126/science.aar6351
Anomalous spin correlations and excitonic instability of interacting 2D Weyl fermions
Michihiro Hirata, Kyohi Ishikawa, Genki Matsuno, Akito Kobayashi, Kazuya Miyagawa, Masafumi Tamura, Claude Berthier and Kazushi Kanoda

Science 358 (6369), 1403-1406.
DOI: 10.1126/science.aan5351

Finding correlations in a Dirac-cone material
Researchers have long been on the lookout for signatures of electron-electron interactions in materials whose electrons have linear energy dispersions represented by Dirac cones, such as graphene. However, these effects have remained frustratingly small. Hirata et al. used nuclear magnetic resonance to study the layered organic material α-(BEDT-TTF)₂I₃, in which a phase featuring Dirac cones is known to be adjacent to one with enhanced electronic correlations. The unusual temperature dependence of spin-related properties in this material indicated strong correlations among the linearly dispersing electrons.

Science, this issue p. 1403

ARTICLE TOOLS http://science.sciencemag.org/content/358/6369/1403
SUPPLEMENTARY MATERIALS http://science.sciencemag.org/content/suppl/2017/12/13/358.6369.1403.DC1
REFERENCES This article cites 91 articles, 0 of which you can access for free
http://science.sciencemag.org/content/358/6369/1403#BIBL
PERMISSIONS http://www.sciencemag.org/help/reprints-and-permissions

Use of this article is subject to the Terms of Service