Collapse of Coherent Quasiparticle States in $\theta$-(BEDT-TTF)$_2$I$_3$ Observed by Optical Spectroscopy

K. Takenaka, M. Tamura, N. Tajima, and H. Takagi
RIKEN (The Institute of Physical and Chemical Research), Wako, Saitama 351-0198, Japan
CREST, Japan Science and Technology Agency, Kawaguchi, Saitama 332-0012 Japan

J. Nohara and S. Sugai
Department of Physics, Nagoya University, Nagoya 464-8602, Japan
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Optical conductivity measurements on the organic metal $\theta$-(BEDT-TTF)$_2$I$_3$ revealed that the system crosses over rapidly from a coherent quasiparticle state to an incoherent state with temperature. Despite the metallic temperature dependence of resistivity, a well-defined Drude peak at low temperatures turns into a far-infrared peak with temperature. The peak energy shifts to higher frequencies and, simultaneously, the spectral weight is transferred to high frequencies beyond the electron band width. These characteristics imply that $\theta$-(BEDT-TTF)$_2$I$_3$, so far believed to be a typical metal, is in fact a strongly correlated electron system with "bad-metal" character.

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At first glance, the transport properties of strongly correlated electron systems are not very different from those of ordinary metals at low enough temperatures $T$ because of the formation of coherent Landau quasiparticles. However, since the coherent quasiparticles are marginally formed in this class of compounds, coherence is rapidly diminished with increasing $T$ and the transport properties show qualitatively different behavior at high temperatures. The "bad-metal" behavior often observed in conducting transition-metal oxides is believed to represent such a crossover from coherent-to-incoherent states. In a class of transition-metal oxides near a Mott transition, such as VO$_2$ [1], V$_2$O$_3$ [2], La$_{2-x}$Sr$_x$CuO$_4$ [3], and La$_{2-x}$SrMnO$_4$ [4], the resistivity often shows a metal-like increase with $T$ well beyond the Ioffe-Regel-Mott (IRM) limit where the mean free path is as short as the Fermi wavelength. We do not see any signature of resistivity saturation around the IRM limit.

Incoherence is also identifiable via optical spectroscopy. Optical conductivity $\sigma(\omega)$ has a certain advantage over resistivity in that incoherence can be probed in the frequency $\omega$ domain. In $\sigma(\omega)$ of prototypical transition-metal oxides, we indeed observe incoherence as a deviation from the Drude behavior expected for simple metals. Even in the coherent regime at low temperatures, the Drude component often shows a pronounced slowly decaying (typically $\sigma \propto \omega^{-1}$) tail at high frequencies, compared with the expected $\omega^2$ decay, signaling coexistence of the incoherent transport. At high enough temperatures, we no longer observe Drude behavior and an almost $\omega$-independent feature dominates the low-$\omega$ $\sigma(\omega)$. It is not yet clear, however, how the Drude component evolves into the $\omega$-independent feature with increased incoherence. These unusual natures of transport and optical conductivity have been taken as a signature of the breakdown of the coherent quasiparticle states [5–9].

Most of the concepts described above were developed for transition-metal oxides in the aftermath of the discovery of high-$T_c$ cuprates. However, since these concepts must be generic to a variety of correlated systems, it should work in other systems including molecular conductors when the correlation dominates. Indeed, it now becomes clear that the molecular solids in many cases fall into the category of a strongly correlated electron system. To establish the universality of this incoherence concept, we have investigated a molecular conductor $\theta$-(BEDT-TTF)$_2$I$_3$ [7]. BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene (inset of Fig. 1). $\theta$-I$_3$ consists of alternating stacking of BEDT-TTF conduction layers and insulating ones of I$_3$ anions. In the conduction layer, the molecules are almost uniformly arranged to give a two-dimensional 3/4-filled band [10,11]. The resistivity of $\theta$-I$_3$ shows a metal-like increase over all the $T$ range from 1 K up to room temperature and any trace of density wave transition cannot be seen [10]. Quantum oscillations were observed in this molecular solid, which clearly indicates the presence of well-defined Landau quasiparticles at low enough temperatures [12]. From these observations, $\theta$-I$_3$ had been considered as a typical metal.

In this work, the transport and optical properties of $\theta$-I$_3$ were investigated. In marked contrast with the conventional wisdom, the results are in striking parallel with the bad-metal behavior of correlated transition-metal oxides, implying that $\theta$-I$_3$ is a strongly correlated electron system in which the electronic coherence is barely formed. We indeed observed a well-defined crossover to an incoherent state with a minute increase of $T$. This establishes common physics over chemically different classes of conductors. Furthermore, by closely inspecting the $T$ dependence of $\sigma(\omega)$, we were able to disclose the evolution of coherence as a function of $T$ in the $\omega$ domain.
The single crystals of $\theta$-I$_3$ were grown by an electrochemical technique. Near-normal incident polarized reflectivity spectra $R(\omega)$ were measured on a flat and shiny as-grown $ac$ plane of 0.5 mm $\times$ 0.5 mm in size, using a Fourier-type interferometer (0.01–2.2 eV) and a grating spectrometer (1.2–6 eV). The crystal size was sufficient for optical measurements when we used microscopes designed for infrared (IR) and visible-ultraviolet spectrometers. As a reference mirror, we used an evaporated Au (far to near-IR regions) and Ag (visible region) film on a glass plate. In order to cancel out the diffraction effect of IR light, we used an Au mirror of the same size as the sample for the far-IR region. Optical conductivity was deduced from $R(\omega)$ via Kramers-Kronig (KK) transformation. The Hagen-Rubens formula below 10 meV and $R \propto \omega^{-4}$ above 6 eV were assumed in the analysis. We confirmed that $\sigma(\omega)$ in the range 0.03–2 eV was not affected by the detailed extrapolation procedures to the low and high $\omega$ limits. At low frequencies 10–30 meV, the absolute value is slightly (at most 3%) affected by the extrapolation procedure but $\omega$ dependence of $\sigma$ does not change qualitatively. We measured $R(\omega)$ at each $T$ only below 1.6 eV. Above 1.6 eV we used $R(\omega)$ data taken at 295 K for all the temperatures. The present data agree reasonably with previous work [11] over the same range (16–295 K, 0.09–3 eV).

In Fig. 1, the $T$-dependent resistivity $\rho(T)$ of $\theta$-I$_3$ is shown. The resistivity shows a monotonous increase and we do not observe any anomalies indicative of a phase transition or any tendency for resistivity saturation. At first glance, it looks like typical behavior of a metal, but the analysis of magnitude immediately tells us that this system shows a typical bad-metal behavior at high temperatures. In the two-dimensional limit, the IRM limit resistivity $\rho_{\text{IRM}}$ is simply expressed by $(h/e^2)d$ [3], which yields $\rho_{\text{IRM}} = 4.4\, \text{m}\Omega\, \text{cm}$ for interlayer distance $d = 17\, \text{Å}$ [11]. As clearly seen from Fig. 1, the magnitude of resistivity exceeds $\rho_{\text{IRM}}$ already at 50 K, indicating the incoherent transport dominates over most of the $T$ range measured. The $\omega$ and $T$ dependence of the optical conductivity is indeed consistent with a dominant incoherent transport except for the lowest $T$.

The reflectivity spectra are summarized in Fig. 2. A free-carrier plasma edge at 0.7 eV for $E \parallel a$ and 0.4 eV for $E \parallel c$ can be clearly seen. The edge positions are different between the two polarizations, which can be ascribed to the anisotropic band structure within the plane [11,12]. The qualitative features are identical between the two polarizations. The signature of incoherence can be identified in Fig. 2. In ordinary metals, the edge is steep and the reflectivity below the edge is already close to 1. In contrast, $\theta$-I$_3$ shows rather gradual increase below the edge and the reflectivity is rather suppressed in the far-IR region. This suppression becomes more and more significant with increasing $T$. For example, at 295 K, both $R_a$ and $R_c$ are still only 75%–80% even at the lowest $\omega$ (10 meV). This low reflectivity represents the absence of a Drude peak in $\sigma(\omega)$, as is argued later. Here we examine the spectra along the most conductive $a$ polarization as a representative. Figure 3 shows the $\sigma(\omega)$ spectra obtained from the reflectivity shown in Fig. 2. Three features are observed. The most important one is the low energy Drude-like component. The broad structure at 0.2–0.4 eV is attributed to interband transitions that become IR active due to weak dimerization [11,13]. A peak structure at 0.15 eV is due to an electron-molecular-vibration mode $\nu_3$ [14]. In BEDT-

![FIG. 1](image-url) Typical $ac$ plane resistivity of $\theta$-(BEDT-TTF)$_2$I$_3$. Inset displays the structure of a BEDT-TTF molecule.

![FIG. 2](image-url) Optical reflectivity of $\theta$-(BEDT-TTF)$_2$I$_3$; (a) $E \parallel a$ and (b) $E \parallel c$. Inset: Magnified spectra below 0.2 eV. Dashed lines represent the extrapolation for a KK analysis.
TTF salts are commonly observed and are often much more pronounced.

Focusing on the low energy Drude-like contribution, we immediately notice an unconventional $T$ dependence. In the spectrum at 4 K, a conventional Drude-like response centered at $\omega = 0$ is observed. This is accompanied by a long tail as observed in many strongly correlated transition-metal oxides, which already suggest that incoherence should be invoked as a key ingredient. At 100 K, surprisingly, the Drude response is absent and instead is characterized by a far-IR peak centered at about 0.05 eV.

In ordinary metals, the Drude peak remains at a far-IR peak but to the higher energy region up to 1 eV or higher. Figure 4 shows the integrated SW defined as

$$N_{\text{eff}}(\omega) = \frac{2m_0V}{\pi e^2} \int_0^{\omega} \sigma(\omega')d\omega'$$

(m$_0$, bare-electron mass; $V \sim$ 847 Å$^3$ [11], volume per formula unit). $N_{\text{eff}}$ at 295 K is only 2/3 of $N_{\text{eff}}$ at 4 K in the range 0.2–1 eV, indicating that a substantial amount of SW is transferred to the energy range above 1 eV. Transfer of SW over such a wide energy range is reasonably ascribed to the electronic correlations, because the on-site Coulomb repulsion energy $U$ is typically of the order of eV for many correlated systems. Indeed, the drastic redistribution of SW over the eV scale as well as a finite-energy peak at high temperatures have been commonly observed for a wide variety of correlated bad metals [15], including ruthenates [16,17], cuprates [18–20], and manganites [21,22], as well as other molecular conductors [23–29]. This establishes empirically that the loss of coherence due to strong correlation effects manifests itself in $\sigma(\omega)$ in a universal manner for a surprisingly wide variety of systems from inorganics to organics. The present spectral features are relevant to the crossover from coherent-to-incoherent electronic excitations with $T$ suggested by the angle-resolved photoemission spectroscopy experiments on correlated systems [30].

It is now clear that the rapid loss of electronic coherence is associated with the strong suppression of the kinetic energy $E_K$ (or Drude weight) with $T$ [5–9]. We may...
draw a naive image based on the Gunnarsson argument [31]. In conventional metals, at high enough temperatures, the electronic coherence (or periodicity) is fully destroyed and the quasiparticle picture is no longer appropriate. $\sigma(\omega)$ is flat over an energy range of the band width $W$. $\sigma(0) \times W$ corresponds to the Drude weight, and $\sigma(\omega)$ is proportional to $|E_K|/W$, while $\Gamma/\sigma(0)$ equals the saturation resistivity $\rho_{sat}$. The resistivity saturation at the semiclassical IRM limit of a conventional bad metal such as Al5 is a consequence of the conservation of the Drude weight. In marked contrast, for correlated bad metals, $|E_K|$ and hence the Drude weight are suppressed rapidly with $T$ and the missing SW moves to higher energies beyond the band width. This decrease of kinetic energy (Drude weight) brings about electron incoherence, driving $\rho(T)$ in the incoherent regime higher than $\rho_{IRM}$. The above picture captures some of the important experimental findings, the metallic resistivity beyond $\rho_{IRM}$, the spectral weight transfer over a wide energy range, and the flat spectrum without the Drude peak at high temperatures.

Another important observation of this study is the finite-energy peak in $\sigma(\omega)$. With decreasing $T$, a finite-energy peak develops around 0.1 eV from the featureless flat spectrum and rapidly gains weight. The rapid increase of SW indicates that the peak originates from the strongly correlated charge carriers upon establishment of coherence. This finite-energy peak shifts to lower energy with decreasing $T$, and finally changes into a coherent Drude response centered at $\omega = 0$. It should be emphasized that $\theta$-I3 is away from any spin and charge density wave instability or strong dimerization and is therefore free from low energy SW redistribution across the energy gap.

It is not clear whether the presence of a peak at finite energy is purely electronic in origin [32]. Thermal expansion of the lattice is not a main origin of the incoherence because the electronic coherence is lost already at 50 K where the effect of thermal expansion is not large, although it may reduce the kinetic energy of the carriers to some extent at higher temperatures. The peak may be a consequence of interplay between the electronic correlations and some hidden excitation. Lattice and/or molecular vibrations may be candidates for such “hidden” excitations. At high temperatures, the carriers with substantially reduced coherence due to the correlations may be captured by the lattice or the molecules, giving rise to the finite-energy peak. On the process of kinetic energy increase with decreasing $T$, the carriers are delocalized into coherent quasiparticles and form a well-defined Drude component. A novel electron-lattice interaction, indeed, has been emerging as a new paradigm for correlated electron system including high-$T_c$ cuprates and it should be investigated as a key ingredient also for the coherent-to-incoherent crossover of a prototypical organic system $\theta$-I3.

In summary, the optical study demonstrates how electronic coherence is lost with $T$ in $\theta$-I3. The bad-metal behavior of the resistivity and the collapse of the Drude peak can be consistently explained in terms of a breakdown of the quasiparticle picture due to strong correlation. This work establishes that the phenomenology of the coherent-to-incoherent crossover is surprisingly universal among a variety of materials. On the process of losing coherence, we found that the Drude peak evolves into the $\sigma(\omega)$ peak at a finite $\omega$, which warrants further exploration.

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*Electronic address: k-takenaka@postman.riken.jp
†Also at Department of Advanced Materials Science, University of Tokyo, Kashiwa, Chiba 277-8561, Japan.
[32] A dynamical-mean-field-theory calculation of a Hubbard model at half filling [9] predicts a finite-energy peak of $\sigma(\omega)$ in the high-$T_c$ incoherent regime. The relation to the present finite-energy peak should be further explored.