Coherent particle response of two-dimensional organic conductors upon crossing the Mott transition

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Abstract. The two-dimensional organic charge-transfer salt κ-(BEDT-TTF)₂Cu[N(CN)₂]BrₓCl₁₋ₓ is tuned across the metal-insulator transition by varying the Br content. Temperature dependent measurements of the optical conductivity yield information on the electrodynamics of the half-filled correlated electron system. At room temperature a broad incoherent response is observed with no clear Drude peak. As the temperature drops below 50 K, an energy gap develops in the Cl-rich samples which grows to approximately 1000 cm⁻¹ for T → 0. With increasing Br concentration spectral weight shifts into the gap region and eventually fills it up completely. A Drude-like component develops due to the coherent quasiparticles.

1. Introduction
One of the most intriguing phenomena in condensed-matter physics is the transition from a metal to an insulator driven by electronic correlations [1]. Organic conductors are superior models to study certain effects of electron-electron interaction since their properties can be easily tuned by physical/chemical pressure which gives access to the bandwidth-controlled Mott transition [2].

Infrared measurements on the family κ-(BEDT-TTF)₂Cu[N(CN)₂]BrₓCl₁₋ₓ (x = 0, 0.4, 0.73, 0.85, and 0.9) reveal significant deviations from the simple Drude behavior found in conventional metals. At ambient temperature, the frequency dependent conductivity σ₁(ω) is dominated by a broad absorption band located at finite frequencies around 2000 - 3500 cm⁻¹. Down to T = 50 K, no clear Drude peak is present although the crystals are moderate conductors. By gradual substitution of Cl by the isovalent Br in the anion layers, a cross-over is observed from a Mott insulator with antiferromagnetic ground state (Cl-compound) to a Fermi liquid, which undergoes a superconducting transition at Tc = 12 K (Br-compound). The low-temperature optical conductivity develops a coherent quasiparticle contribution, and the spectral weight shifts to low frequencies as the Br content x increases [3, 4].

2. Results and Analysis
Our aim is to investigate the influence of electronic correlations on the electrodynamics of the two-dimensional electron gas; thus we have to disentangle the various contributions to the optical spectra [5]. The localized charge carriers (mid-infrared peak and env-coupled features) are satisfactorily described using the cluster model [6]. After subtracting these contributions from the original experimental data, we obtain the itinerant-charge-carriers response plotted in Fig. 1.
Figure 1. Optical conductivity due to itinerant charge carriers after the contributions from localized excitations are subtracted. The frames (a) - (e) show spectra of $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br$_x$Cl$_{1-x}$ with different Br concentrations $x$ at various temperatures as indicated.

3. Discussion

The pristine $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl crystals show typical signatures of a Mott insulator with an energy gap which gradually grows as the temperature drops below 50 K (Fig. 2a). If we choose the frequency $\Delta$ for which the spectral weight drops below $\int_0^{\Delta} \sigma_1(\omega) d\omega = 50000$ $\Omega^{-1}$cm$^{-2}$ (in SI units) as a gap, we obtain $\Delta = 520$ cm$^{-1}$ as the 50-K gap value. For $T \to 0$, we extrapolate to $900$ cm$^{-1}$ and $1000$ cm$^{-1}$ when $E \parallel a$ and $c$-axes, respectively.

The behavior completely differs when Cl is increasingly substituted by Br in the anions as seen by the low-temperature conductivity plotted in Fig. 2b. Here the optical gap is gradually filled in by spectral weight from higher energies. For large $x$, a strong Drude contribution develops which resembles the metallic state. The observed behavior does not differ qualitatively between the two orientations which confirms the two-dimensional nature of the system in any regard.

These two scenarios are interpreted in such a way, that for increasing temperature the carriers in $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl are less localized and eventually become mobile because the correlated ground state fades. The gap decreases continuously with rising temperature as expected from a mean-field transition. On the other hand, changing the Br content varies the bandwidth $W = 10t$ and therefore the relative Coulomb repulsion $U/t$. This is a first-order transition for which the density of states at the Fermi level is supposed to rise abruptly to a finite value [7]. Compared to a conventional metal, however, the density of states is reduced over a certain energy range due to strong electronic interactions. Nevertheless, as the Br concentration increases, itinerant carriers are added and show up as spectral weight at low frequencies. Eventually the coherent quasiparticles form a Drude-like zero-frequency peak.

The zero-frequency mode, which develops in $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br$_x$Cl$_{1-x}$ at high Br content and low temperatures, corresponds to the coherent quasiparticle response expected for a Fermi liquid. In order to get some information about the strength of this contribution, we have to separate the quasi-free electrons from those which are excited across the Mott-Hubbard gap. Since in the range between 500 and 800 cm$^{-1}$ the optical conductivity is minimum for any...
our observations, summarized in Fig. 1: At ambient temperatures some incoherent background at elevated temperatures only a flat background is seen. This prediction is in full accord with there is a narrow Drude-like contribution and some broad feature at higher frequencies, while in the low-temperature conductivity the gap \( \kappa \) typically condenses as the temperature decreases due to the increase of the effective mass \( m^* \). In strongly correlated electron systems, like heavy fermions, the spectral weight of the zero-frequency contribution typically condenses as the temperature decreases due to the increase of the effective mass \( m^* \). For \( \kappa-(BEDT-TTF)_2Cu[N(CN)_2]Br \) by integration up to \( \omega_c = 500 \text{ cm}^{-1} \) for the electric field parallel to \( c \) direction. The inset shows these data normalized to the entire spectral weight integrated up to 3500 cm\(^{-1}\).

Br concentration at lower temperatures (Fig. 1), we have picked \( \omega_c = 500 \text{ cm}^{-1} \) as a possible cut-off frequency for evaluation of the spectral weight \( D(T, x) \) [8]:

\[
D(\omega_c) = \int_0^{\omega_c} \sigma_1(\omega) \, d\omega = \frac{ne^2}{4\pi m^*},
\]

where \( n \) and \( m^* \) are the effective carrier density and mass, respectively. The temperature dependences of \( D(\omega_c = 500 \text{ cm}^{-1}, T) \) are plotted in Fig. 3 for the various values of \( x \). The overall behavior is very similar for the two polarizations of the electric field, only the absolute values are greater for \( E \parallel c \). In all cases, the intensity of the low-frequency contribution increases when lowering \( T \) down to 50 K, but then it drops significantly when the \( x = 0 \) and 0.4 samples enter the insulating state and the Mott-Hubbard gap opens. For \( \kappa-(BEDT-TTF)_2Cu[N(CN)_2]Br_{0.73}Cl_{0.27} \) this downturn is observed only for the lowest temperature; no clear gap-structure is found, but a slight decrease of spectral weight. The metallic sample, on the other hand, exhibit a steady increase of the Drude peak as the temperature is reduced.

For a conventional metal the spectral weight does not change with temperature: with increasing \( \sigma_1(T) \) the Drude peak just becomes narrower as scattering freezes out when \( T \) drops. In strongly correlated electron systems, like heavy fermions, the spectral weight of the zero-frequency contribution typically condenses as the temperature decreases due to the increase of the effective mass \( m^*(T) \). At a metal-insulator transition (caused by electronic correlations or other reasons) the Drude spectral weight abruptly vanishes \( D(T) \rightarrow 0 \).

The situation is somewhat different in the metallic state of correlated two-dimensional electron systems; as pointed out by Merino and coworkers [9, 4], for temperatures well below \( T_{coh} \) there is a narrow Drude-like contribution and some broad feature at higher frequencies, while at elevated temperatures only a flat background is seen. This prediction is in full accord with our observations, summarized in Fig. 1: At ambient temperatures some incoherent background

\[\text{Figure 2. Development of the optical gap in the conductivity spectra of } \kappa-(BEDT-TTF)_2Cu[N(CN)_2]Br_\perp \text{Cl}_{1-x} \text{ for } E \parallel c. \] (a) For decreasing temperature the low-temperature conductivity the gap in \( \kappa-(BEDT-TTF)_2Cu[N(CN)_2]Cl \) becomes larger. (b) With increasing Br doping spectral weight is moved in the gap region.

\[\text{Figure 3. Temperature dependence of the spectral weight of the conduction electrons in } \kappa-(BEDT-TTF)_2Cu[N(CN)_2]Br_\perp \text{Cl}_{1-x} \text{ by integration up to } \omega_c = 500 \text{ cm}^{-1} \text{ for the electric field parallel to } c \text{ direction.} \] In all cases, the intensity of the low-frequency contribution increases when lowering \( T \) down to 50 K, but then it drops significantly when the \( x = 0 \) and 0.4 samples enter the insulating state and the Mott-Hubbard gap opens. For \( \kappa-(BEDT-TTF)_2Cu[N(CN)_2]Br_{0.73}Cl_{0.27} \) this downturn is observed only for the lowest temperature; no clear gap-structure is found, but a slight decrease of spectral weight. The metallic sample, on the other hand, exhibit a steady increase of the Drude peak as the temperature is reduced.
Relative Drude weight $D/D_0$ is present for all compositions under investigation. The spectral weight rises in a similar way by about a factor of two when going from room temperature to $T \approx 100$ K. The behavior significantly forks as $T < 90$ K. The opening of the energy gap in the Mott insulating state below 50 K causes a reduction of $D$ for $x = 0$ and 0.4; it can be extrapolated to zero when $T \to 0$ as seen in Fig. 3. For $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br$_{0.73}$Cl$_{0.27}$ a moderate increase down to $T = 20$ K seems to indicate the build-up of a coherent state, probably governed by thermal fluctuations since it starts to level off for very low temperatures ($T = 5$ K). For higher Br content ($x = 0.85$ and 0.9), the spectral weight $D(T)$ increases continuously for all temperatures.

From the simplest linear interpolation, two regimes can be identified as illustrated in Fig. 4. Only for $x > 0.7$ a coherent quasiparticle response is found at low temperatures, which rapidly grows in weight as the Br content increases, i.e. the relative strength of the Coulomb interaction $U/t$ decreases. The ratio $D/D_0$, where $D_0$ is the total spectral weight of the correlated carriers (here $x = 1$, which is the metallic Br compound), should exhibit a jump at $(U/t)_c$ in the range of 0.1 to 0.3.[9] The limited number of Br concentrations $x$ available for our study does not allow to give a definite value for $D/D_0$ at the critical point, but it might well fall within this range. Since the phase transition at the critical $(U/t)_c$ is first order, Bulla et al. [7] predicted that the abrupt change of the Drude weight $D(x)$ even shows some hystereses, which might be checked by a continuous variation of the external pressure.

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Figure 4. Change of the low-temperature Drude spectral weight $D(x, T = 20$ K) (with respect to the total spectral weight of correlated carriers $D_0$) when the (chemical) pressure increases, i.e. with growing $x$ in $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br$_x$Cl$_{1-x}$. The linear fits (solid lines) help to identify the Mott insulator and metallic regimes with a boundary around $x_c = 0.7$. 

\begin{figure}[h]
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\caption{Change of the low-temperature Drude spectral weight $D(x, T = 20$ K) (with respect to the total spectral weight of correlated carriers $D_0$) when the (chemical) pressure increases, i.e. with growing $x$ in $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br$_x$Cl$_{1-x}$. The linear fits (solid lines) help to identify the Mott insulator and metallic regimes with a boundary around $x_c = 0.7$.}
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