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Correlation gap in the optical spectra of the two-dimensional organic metal $\mathbf{(BEDT\text{-}TTF)_4[Ni(dto)_2]}$

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Optical reflection measurements within the highly conducting (a,b) plane of the organic metal $(\text{BEDT-TTF})_4[\text{Ni(dto)}_2]$ reveal the gradual development of a sharp feature at around 200 cm^{-1} as the temperature is reduced below 150 K. Below this frequency a narrow Drude-like response is observed which accounts for the metallic behavior. Since de Haas–van Alphen oscillations at low temperatures confirm band structure calculations of bands crossing the Fermi energy, we assign the observed behavior to a two-dimensional metallic state in the proximity of a correlation induced metal-insulator transition.

Low-dimensional metals have attracted considerable interest recently due to observed deviations from the simple Fermi-liquid behavior. Although still under debate, the electronic properties of quasi-one-dimensional Bechgaard salts may be understood in terms of a Tomonaga-Luttinger liquid;[1–4] there exists only little agreement in the understanding of the quasi-two-dimensional systems like organic or high-temperature superconductors.[5]

The two-dimensional organic BEDT-TTF salts, where BEDT-TTF, abbreviated by ET, which stands for bisethylenedithio-tetrathiafulvalene, are widely studied for their superconducting properties (which are still heavily debated[6]); only a few investigations deal with the metallic state, which seems to be highly interesting because its vicinity to unconventional states like a Mott-Hubbard insulator or antiferromagnetism. Most of the systems consist of monovalent anions with each ET molecule donating half an electron. The new charge transfer complex based on the electron donor ET and the acceptor nickelbis(dithiooxalate) $[\text{Ni(dto)}_2]^{2-}$ was proven to be metallic down to low temperatures.[7] The aim of our investigation was twofold: first to understand why the material does not become superconducting although it is metallic down to very low temperatures; second to study the effect of electronic correlations in this prototypical two-dimensional metal. Here we report on the optical properties of $(\text{ET})_4[\text{Ni(dto)}_2]$ which strongly indicate that a correlation gap opens at low temperatures.

Single crystals of $(\text{ET})_4[\text{Ni(dto)}_2]$ grown by electrochemical methods were as large as $2\times3\times0.5\ \text{mm}^3$. The crystal structure consists of ET stacks along the a axis where the ethylene groups are highly ordered below 200 K as known from x-ray analysis. This resembles the β modification of the ET salts with one-dimensional stacks of ET molecules, in contrast to the κ phase where pairs of organic molecules are rotated by 90° with respect to each other.[6] Due to S–S contacts of the ET molecules in neighboring stacks, $(\text{ET})_4[\text{Ni(dto)}_2]$ forms a conducting (a,b) plane. These layers are separated along the c direction by sheets of the $[\text{Ni(dto)}_2]^{2-}$. Although the absolute value of the conductivity perpendicular to the planes is about one to two orders of magnitude smaller,[7] $(\text{ET})_4[\text{Ni(dto)}_2]$ exhibits a metal-like temperature dependence in all three directions (lower panel of Fig. 1), i.e., the conductivity increases like T^{-2} below 100 K.

Our samples were also characterized by electron spin resonance (ESR) experiments in the temperature range from 300 down to 4 K (Fig. 1) which yield an absolute value of the spin susceptibility of 6.4×10^{-4} emu/mole at room temperature. It decreases continuously by a factor of 3 when the temperature is lowered with the strongest reduction in the temperature range $150\ \text{K}>T>100\ \text{K}$ indicating that the density of states might be reduced. The ESR linewidth ΔH exhibits a maximum just below 100 K. This behavior is seen in all three directions. For $T<80$ K the drop of ΔH and the constant spin susceptibility are in qualitative agreement with Elliott's prediction for an isotropic metal. Internal fields lead to a pronounced anisotropy as reflected in the g values (not shown); they are basically independent of temperature: $g_a=2.0037$, $g_b=2.0048$, and $g_c=2.0110$.

The Fermi surface of $(\text{ET})_4[\text{Ni(dto)}_2]$ as obtained by band-structure calculations[7] (inset of Fig. 1) is similar to that of $\alpha\text{-(ET)}_2(\text{KHg(SCN)}_4)$ and to the typical Fermi surface observed in the κ phase of ET salts. It consists of a two-dimensional hole pocket (α-orbit) which covers about 14% of the first Brillouin zone; as well as one-dimensional open trajectories with a flat dispersion which are less than half filled. These calculations are fully confirmed by Shubnikov-de Haas and de Haas-van Alphen (dHvA) experiments at low temperatures.[7]

The polarized optical reflectivity $R(\omega)$ of $(\text{ET})_4[\text{Ni(dto)}_2]$ was measured at $5\ \text{K}<T<300\ \text{K}$ for the electric field parallel to the a and to the b axes. Using two Fourier-transform spectrometers and a quasioptical submillimeter spectrometer we covered the spectral range from 20 cm^{-1} up to 8000 cm^{-1}. We combined all results on $R(\omega)$, and after using appropriate low-frequency (Hagen-Rubens) and high-frequency (ω^{-2} decay) extrapolations finally performed a Kramers-Kronig analysis to obtain the optical conductivity $\sigma(\omega)$ and dielectric constant spectra.

The frequency dependence of the reflectivity and the corresponding conductivity are displayed in Fig. 2 for both polarizations of the highly conducting plane. For the b direction

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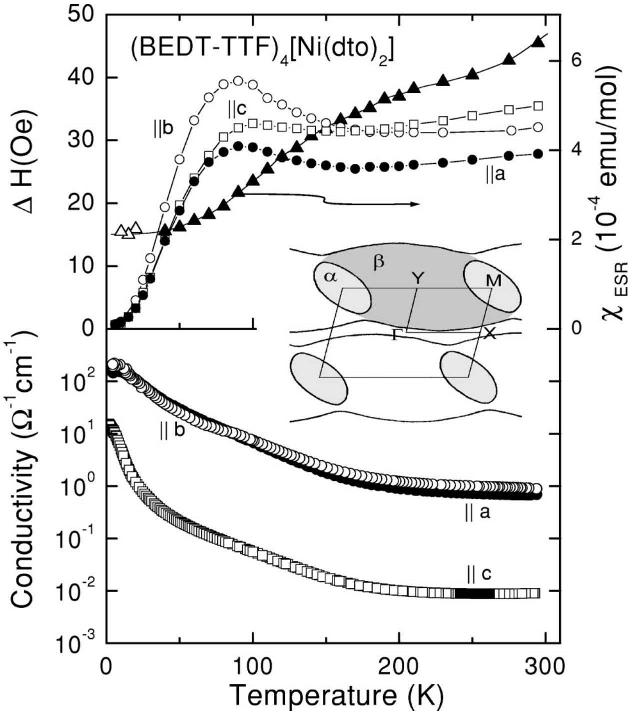

FIG. 1. Upper frame: the ESR linewidth ΔH of $(\mathrm{BEDT\text{-}TTF})_4[\mathrm{Ni(dto)}_2]$ as a function of temperature for the magnetic field oriented in the three different directions as indicated. The solid triangles (corresponding to the right axis) show the temperature dependence of the spin susceptibility obtained from the integrated ESR intensity; the open triangles for $T<20$ K (for the high-conductivity values) are evaluated by the skin-effect corrected Dyson-shaped ESR signal. Lower frame: the temperature dependence of the electrical conductivity of $(\mathrm{BEDT\text{-}TTF})_4[\mathrm{Ni(dto)}_2]$ along the three crystal axes. The inset shows a cut through the Fermi surface (after Ref. 7). The areas shaded light gray correspond to the α orbit, the dark gray area is the β orbit.

the plasma edge is located at somewhat higher frequencies as compared to the a direction. In both directions no simple Drude response is observed. As the temperature is reduced below 150 K, pronounced features develop in the low-frequency domain: a dip in $R(\omega)$ with a corresponding mode in $\sigma(\omega)$ around 200 cm^{-1}, which we ascribe to excitations across a gap. As discussed below, we assign the origin of this gap to correlation effects. Below this gap, a narrow Drude-like peak appears at low temperatures. The position of the maximum is the same for both axes and does not change with temperature. The intensity (oscillator strength) increases linearly by about a factor of 10 when going from 150 to 50 K and stays constant below.

We now discuss possible scenarios for the understanding of our experimental results. The major challenge is to reconcile two aspects of the experimental data. On one hand, the observed quantum oscillations[7] are in excellent agreement with calculations of the electronic band structure which do not take into account correlation effects. On the other hand, the optical conductivity shows signs of a gap. This situation stands in contrast to other materials such as $(\mathrm{ET})_2\mathrm{AuBr}_2$ which also exhibits a low-temperature gap in the conductivity spectrum at 130 cm^{-1}, the origin being assigned to a spin-density-wave ground state.[8] This magnetic instability, originating from nesting properties of the one-dimensional parts of the Fermi surface, leads to a correlation-induced reconstruction of the Fermi surface topology which does not match band-structure calculations. This has been confirmed by dHvA experiments.[9] In the case of $(\mathrm{ET})_4[\mathrm{Ni(dto)}_2]$ no indication of magnetic ordering was found at low temperatures, hence the formation of a spin-density wave can definitely be ruled out. In particular the g value does not show any shift in this range of temperature which would indicate the development of an internal magnetic field.[10] No x-ray study of $(\mathrm{ET})_4[\mathrm{Ni(dto)}_2]$ has been performed at $T<200$ K which would give a clear answer to whether a charge-density-wave ground state is present. However, we do not observe an abrupt change in any physical quantity and therefore we do not expect an increase in size of the cell as reported in typical charge-density-wave systems.[11] Furthermore, such transitions should show up in the Fermi surface topology.

Given the above, the most natural way of understanding the experimental data is in terms of a metallic state in the proximity of a quantum phase transition which partially or totally gaps the Fermi surface. The feature in $\sigma(\omega)$ at 200 cm^{-1} is interpreted as a precursor effect of this transition. As one approaches the transition (by changing the relevant microscopic parameters) spectral weight will be transferred from the Drude response to frequencies above the charge gap. The question is then: what is the nature of this transition and which microscopic parameter controls it?

To illustrate this idea, we consider one-dimensional organics such as $(\mathrm{TMTSF})_2\mathrm{PF}_6$. Along the chains the optical conductivity has very similar features to those of $(\mathrm{ET})_4[\mathrm{Ni(dto)}_2]$: a gap feature at 200 cm^{-1} with a small Drude peak containing 1% of the spectral weight. The Bechgaard salts consist of quarter-filled chains which are insulating at low temperature due to umklapp processes[2,12] and/or the combination of dimerization and strong Coulomb interaction.[13] The metallic behavior is attributed to interchain hopping which effectively warps the one-dimensional Fermi surface thus leading to doping away form the ideal quarter-filled case. In this picture, the conductivity spectrum corresponds to that of a metallic state in the proximity of a metal-insulator transition, the control parameter being the (dimensionality driven) doping away from quarter-filling.[4] The Fermi-surface of the $(\mathrm{ET})_4[\mathrm{Ni(dto)}_2]$ material has one-dimensional features; however, interchain hopping is a sizable fraction of the intrachain hopping, which explains the nearly isotropic dc conductivity within the (a,b) plane. Although tempting, an interpretation of the data in terms of strongly coupled chains seems out of reach.

Since the conductivity of $(\mathrm{ET})_4[\mathrm{Ni(dto)}_2]$ is roughly isotropic in the (a,b) plane it is appropriate to start with a two-dimensional model. The unit cell contains four ET molecules each donating half an electron to the acceptor. Band-structure calculations reveal two conduction bands. In comparison to the energy scale of the gap, the other two bands lie well below the Fermi energy and we will omit them. In real space this leads to a model with two s orbitals per unit cell each orbital accommodating one hole, i.e., half filling. The reduction to a two-band model may be explicitly carried out by noting that there is one hopping matrix element between the ET molecules (of approximately 0.269 eV) which dominates, thus defining a dimer. Each unit cell contains a pair of

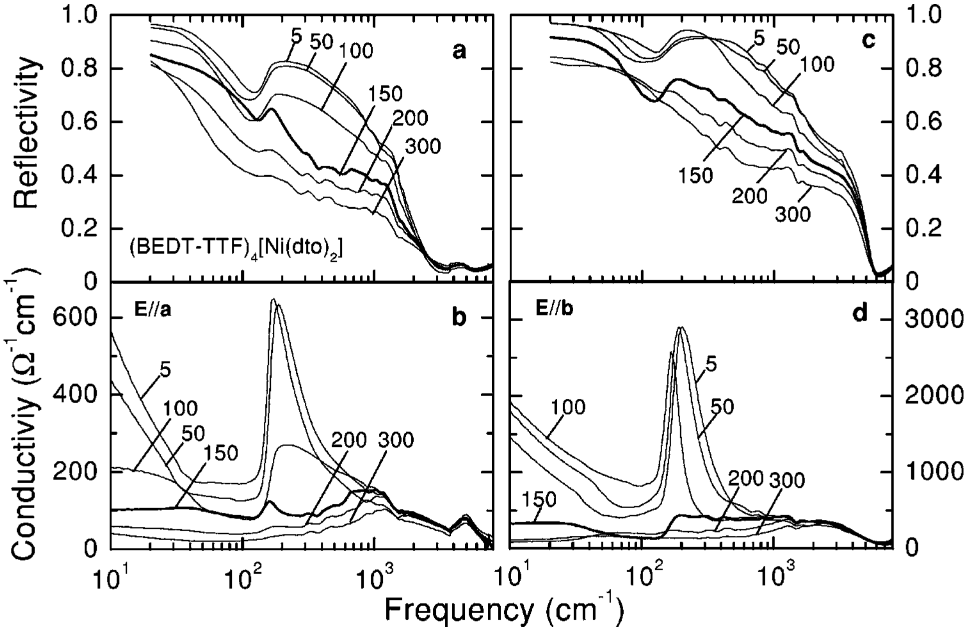

FIG. 2. (a) Frequency dependent reflectivity and (b) optical conductivity along the a direction of (BEDT-TTF)$_4$[Ni(dto)$_2$] for different temperatures as indicated. (c) and (d) show the reflectivity and conductivity, respectively, measured along the b direction for different temperatures. In both orientations a gap feature is clearly seen at around 200 cm^{-1}.

dimers, and the two conduction bands are well reproduced by considering only the antibonding combination of orbitals on the dimer. Matrix elements between dimers take the values 0.248 eV, 0.188 eV, 0.175 eV, 0.164 eV, 0.143 eV, 0.124 eV, and 0.055 eV. A similar mapping was carried out for the κ phase of the ET salts.[14]

Correlation effects are taken into account with a Hubbard U term which sets an energy cost U for doubly occupied s orbitals. Since we have precisely one hole per orbital large values of U lead to the localization of holes and hence a Mott insulating state.[15] The critical value of U_c at which the metal-insulator transition occurs depends sensitively upon details of the band structure. In particular, if nesting is present, as in the prototype single-band two-dimensional half-filled Hubbard model with nearest-neighbor hopping, $U_c = 0$ and the gap in a mean-field approach scales as $e^{-\sqrt{t/U}}$ where t is the hopping matrix element. On the other hand, when frustration is present thus prohibiting magnetic ordering, one expects U_c to be a sizable fraction of the bandwidth.

The antiferromagnetic insulating phase of the κ-phase salts is naturally described within the above approach if one chooses $U > U_c$. For the present material it is tempting to argue that $U < U_c$. This qualitatively explains the experimental data: the system remains metallic at arbitrary temperatures and no phase transition is present. Since the Mott transition is a mass divergent transition, one expects the Fermi surface to remain essentially unaltered as a function of $U < U_c$. As mentioned above this is consistent with the dHvA experiments.[7] An indication of the mass enhancement due to proximity of the Mott transition stems from the fact that in a and b directions respectively only 2% and 4% of the total spectral weight of the optical conductivity is contained in the narrow Drude-like mode. Comparing those values to the *large* Fermi surface observed by quantum oscillations infers an enhanced mass. We note that the above statements are based on the Brinkman-Rice[16] picture which is certainly correct in the limit of large dimensions. In lower dimensions its validity is debatable.

The major problem within the above approach is the small energy scale of the gap which is more than an order of magnitude smaller than the bandwidth. Approximate nesting properties of the Fermi surface will certainly reduce the value of the gap. A calculation of the spin and charge suceptibilities within the Hükel tight-binding model shows only slight enhancements at wave vectors corresponding to nesting of the one-dimensional portions of the Fermi surface.

Finally some remarks on the superconducting state which was not detected in (ET)$_4$[Ni(dto)$_2$] down to 0.06 K; the effect of the dimensionality is not clear yet, but it should be noted that the system is the least two-dimensional ET conductor. As argued above, in (ET)$_4$[Ni(dto)$_2$] the Coulomb repulsion is not strong enough to drive the system to a Mott insulator. Given the phase diagram of the κ phase as a function of pressure,[6] we can only speculate that reducing the pressure by chemical substitution will drive the system to a superconductor and ultimately to a Mott insulator. This would agree with superconductivity observed at quantum phase transitions in numerous systems.[5,17] We also predict a similar scenario in α-(ET)$_2$[KHg(SCN)$_4$]; optical investigations are in progress.

Thus we can conclude that the energy gap which develops in the optical conductivity at around 200 cm^{-1} for temperatures $T \leqslant 150$ K in both directions of the highly conducting (a,b) plane of (ET)$_4$[Ni(dto)$_2$] is due to electronic correlations. To reconcile the facts that the Fermi surface shows no correlation-induced gap and that there is no phase transition as the temperature is lowered, we have argued that the system is in the proximity of two-dimensional Mott metal-insulator transition. The narrow Drude-like contribution to the optical conductivity which is responsible for the metallic conductivity and quantum oscillations at low temperatures contains only a few percent of the spectral weight. The effective mass of these carriers has to be enhanced.

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