Interplay of charge order and superconductivity in a ¼-filled quasi-2D organic conductor

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Strongly correlated electronic systems: closeness of an ordered state and superconductivity

3D: heavy fermions

2D: transitional metal oxides
organic conductors

HTSC
conductance band formed by Cu and O orbitals
comparatively simple electronic structure:
conductance band formed by molecular π-orbitals:

charge
spin
degrees of freedom
orbital
lattice

ordered state → metal
reached by doping

charge
spin
degrees of freedom
lattice
“intrasite”: intramolecular

ordered state → metal
reached by change of doping and
electron-electron correlations

Organic conductors
Crystal structure of BEDT-TTF-based 2D organic conductors:

- Anion layer: charge reservoir
- Cation layer: conducting layer

Low conductivity

High conductivity

Lattice site = one molecule

Anisotropy within the plane: \( \sigma_b / \sigma_c \sim 0.5 \)

Perpendicular to the plane: \( \sigma_b / \sigma_a \sim 10000 \)
band width depends on overlap integrals between the neighboring molecules: $W=8t$
$W$ is about 1eV for these compounds

- on-site ($U$) and intersite ($V$) electronic correlations: depend on the molecule
effective $U$ is about 0.5eV
strong influence of electron-electron correlations

- band filling depends on stoichiometry:
no additional disorder in the conducting layer
Quasi-two-dimensional organic conductors \((\text{BEDT-TTF})_2X\)

Proposed for \(\frac{1}{4}\) filled materials: calculations on the extended Hubbard model

\[ V / W \]

Tuning parameters:

- Electronic correlations (on-site \(U\), inter-site \(V\))
- Bandwidth \(W\)

J. Merino et al. PRL 87, 237002 (2001)
$\beta''$-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ : superconductor $T_c=5K$

- Simple quasi-2D electronic structure: bands are formed by overlap of $\pi$-orbitals of BEDT-TTF molecules
  - $\frac{1}{4}$ filled with holes
  - Ideal 2D metal
- In contrast to many similar materials, measured Fermi-surface is different from calculated one: no 1D sheets,
  - measured Fermi-surface is only $1/3$ of the calculated one

our optical study:

30-700 cm\(^{-1}\) Bruker113v+bolo 4.2 and 1.4 K
+ exchange gas cryostat down to 2 K

50-700 cm\(^{-1}\) Bruker66v+bolo4.2K
Coldfinger He flow cryostat
@ 300 and 150 K in-situ gold evaporation

MIR and NIR : Bruker66v + Microscope: measurements of
absolute reflectivity of surfaces down to 0.1-0.05 mm possible
Coldfinger cryostat down to 10 K

Submillimeter spectrometer 30-11 cm\(^{-1}\)
Exchange gas cryostat down to 1.8K

“Tesla” spectrometer 5-40 cm\(^{-1}\)
Down to 2.6 K, magnetic field up to 7 T
In collaboration with T. Room, Tallinn, Estonia
characterization of charge order by molecular spectroscopy:

\[ \nu_{27}(B_{1u}) \]

intramolecular vibration frequency linearly dependent on charge

\[ \Delta n \approx 0.2e \]

develops at about 150 K

- no corresponding feature in d.c. conductivity

In-plane conductivity: short range charge order

- Most of the spectral weight is in the MIR-band.
- MIR spectral weight shifts down on cooling, forming a band at 200 cm\(^{-1}\) below about 150 K.
- Drude-response is below 10% of spectral weight at 10 K.
In-plane conductivity: charge order fluctuations

band at 200 cm\(^{-1}\) gets well-shaped below 150 K, in the CO state

Calculation: extended Hubbard model square lattice T=0 K

band predicted to appear due to short range CO

“every quasi-particle carries localized spectral weight”

coherent carriers response

- A narrow coherent charge carriers response appears at T<200 K: typical for organic conductors

- Drude response is below 10% of spectral weight at 10 K

- The rest of the spectral weight is in the MIR-band: agreement with SdH data – only 1/3 of the predicted square of the FS was found.

- Spectral weight of the Drude-like response increases on cooling. At lowest temperatures it happens at the expense of the CO band.

- This is in contrast to stripes in HTcs and CDW/SC competition
Theoretical prediction: On cooling we “get away” from the charge ordered state.

Experiment: Spectral weight of coherent carriers increase.
Drude-like response shows a superconducting gap

\[ T_c = 5 \text{ K} \]

\[ 2\Delta = 12 \text{ cm}^{-1} \text{ at } 1.75 \text{ K.} \]

Submillimeter spectrometer
Stuttgart University

superconducting gap:
(M. Dressel, G. Gruner. Optical properties of solids)
Superconducting gap: temperature and field dependence

$\Delta = 12 \text{ cm}^{-1}$ at 3.6 K.

$T_c = 5 \text{ K}$

Collaboration with T. Rõõm, Tallinn, Estonia

$2\Delta = 12 \text{ cm}^{-1}$ at 3.6 K.
\( \beta''-(BEDT-TTF)_2SF_5CH_2CF_2SO_3 : \) superconductivity mediated by charge fluctuations?

- CO and SC conductivity co-exist but do not compete

- A SC with the highest \( T_c \) we studied + the most narrow Drude and the strongest CO-band observed

D.c. measurements show, that under pressure superconducting transition is suppressed above 10 kbar. The compound becomes metallic. CO suppressed?

our IR studies of chemical pressure:
CO suppressed, metallic behavior

Conclusions:

• Using vibrational spectroscopy we detect charge order in quasi-2D ¼ filled superconductor $\beta''$-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ at temperatures below 150 K.

• On cooling below 200 K a coherent carriers response and a band at 200 cm$^{-1}$ appear and increase on cooling. We assign the band at 200 cm$^{-1}$ to charge order fluctuations.

• Below $T_c=5K$ we see an opening of a superconducting gap. At $T=3.6$ K $2\Delta=12$ cm$^{-1}$. 
Reflectivity

$1/\tau(\omega)$

$\eta_{m_{\text{eff}}b}$

Frequency (cm$^{-1}$)

- 300 K
- 200 K
- 150 K
- 100 K
- 50 K
- 30 K
- 10 K
Wavenumber (cm$^{-1}$)

T=3.6 K

R$_S$(0T)/R(B)

R(T)/R(15K)

- 6 K
- 5 K
- 4 K
- 3 K
- 2.4 K

Wavenumber (cm$^{-1}$)
effective mass
Extended Drude analysis: scattering on charge order?

200 K above CO
30 K below CO

scattering rate goes linear with frequency: scattering of charge carriers on the CO?
Work is done thanks to:

Stefan Kaiser
Yaxiu Sun
Martin Dressel
John Schlueter
Toomas Room,
Molecular vibrations

Each site is a molecule: charge-dependent molecular vibrations can give information on the charge-redistribution in the charge-ordered state.

Raman: was used for charge order characterisation

Dependance of the modes frequency on the charge on BEDT-TTF:

\[ \nu_{3} = 1487.5 \text{ cm}^{-1} \]
\[ \nu_{2} = 1554.2 \text{ cm}^{-1} \]

IR active molecular vibrations are intensive only in \( E \perp \) conducting layers

\[ A(\nu_{3}) \]
\[ B_{1u}(\nu_{27}) \]
1/5-Filled System: $\beta''$- (BEDO-TTF)$_5$[CsHg(SCN)$_4$]$_2$

- More spectral weight in Drude part; at 300 K the pseudogap is at about 300 cm$^{-1}$ in both directions.

- With decreasing temperature the gap feature shifts to lower frequencies; the Drude component increases.

1/5 filling, $U = 20t$, different $V/t$

exact diagonalisation calculations on an extended Hubbard model

Drude peak for any $V$

D.c. measurements show, that under pressure superconducting transition is suppressed above 10 kbar.

Proposed for ¼ filled materials: