Electronic structure of charge transfer salts

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Fluorescence carbon $K\alpha$ x-ray emission spectra (XES) of low-dimensional charge transfer salts [$(TMTSF)_2PF_6$, $(BETS)_2FeBr_4$, and (CPDT-STE) (TCNQ)] are presented. The Fermi energy positions are determined for these spectra using XPS binding energies of the C $1s$ core level. The absence of metallic Fermi edges in the carbon $K\alpha$ XES data is reminiscent of Luttinger-liquid behavior predicted for one-dimensional metals, but the observed suppression of spectral weight near the Fermi level occurs on a surprisingly large energy scale. An additional low-energy subband found in carbon $K\alpha$ XES of $(BEDT-TTF)_4[(H_3O)Fe(C_2O_4)_3]C_5H_5N$ is attributed to strong cation-anion interaction in this organic super-conductor.

Charge transfer salts formed by linear chains of organic molecules BETS [bis(ethyleneditho)tetraselenafulvalene] (Ref. 1), BEDT-TTF [bis(ethyleneditho)-tetrathiafulvalene] (Ref. 2), and TMTSF (tetramethyltetraselenafulvalene) (Ref. 3) display a rich variety of electronic properties from magnetic insulators to superconductors depending on the nature of the donors or acceptors and their arrangement in the crystal structure. Most of these compounds are 2:1 cation radical salts such as the D_2X systems $(TMTSF)_2X$, $(BETS)_2X$, and κ-$(BEDT-TTF)_2X$, where X stands for a monovalent anion (X^-). The average valence of the organic molecule becomes $+1/2$. The conducting properties are attributed to the π band with quarter filling. The on-site Coulomb interaction U should be relatively small in the organic system due to the large size of the constituent organic molecules. On the other hand, the transfer integrals t between the neighboring molecules are also strongly reduced in comparison with typical inorganic crystals, so that the ratio of U/t can reach values as large as in strongly correlated transition metal oxides.

Low dimensionality of charge transfer salts is of special interest due to the theoretical suggestion that the normal state of these systems may be unusual. It is shown that one-dimensional (1D) conductors are not Fermi liquids like normal metals, but Luttinger[4] or Luttinger-Emery[5] liquids with distinct physical properties. Instead of a discontinuity jump at the quasimomentum k equal to the Fermi momentum k_F, the one-electron distribution function displays a power-law singularity $n_k \approx n_F - C \, \mathrm{sgn}(k-k_F)|k-k_F|^\alpha$, $\alpha > 0$. Correspondingly, the spectral density $\rho(E)$ at the Fermi energy E_F behaves as $|E-E_F|^\alpha$ instead of displaying a metallic Fermi edge. Previous results do suggest this behavior for real quasi-1D or even 2D materials.[6] High-resolution angle-resolved photoemission spectra (ARPES) have shown strong suppression of quasiparticle states near the chemical potential.[7–11] On the other hand, a decrease in photoemission intensity near the Fermi level can also result from extrinsic changes in the electronic structure at the surface, reconstruction, off-stoichiometry, or degradation. Additional measurements using bulk sensitive spectral techniques such as x-ray emission spectroscopy are necessary to verify the validity of observations resulting from photoemission experiments.

In the present work we report soft x-ray fluorescence measurements for charge transfer salts $(TMTSF)_2PF_6$, $(BETS)_2FeBr_4$, and (CPDT-STF) (TCNQ) were carried out at Beamline 8.0 of the Advanced Light Source, Berkeley. Photoemission experiments [ultraviolet photoemission spectroscopy (UPS) and x-ray photoemission spectroscopy (XPS)] measurements of $(TMTSF)_2PF_6$ were performed at the University of Augsburg.

It is widely accepted that cation (donor) π molecules provide the conductive properties of organic conductors. We have therefore measured x-ray emission spectra (XES) of carbon belonging to donor molecules (Fig. 1). For the analysis we have also used the results of our previous measurements of carbon $K\alpha$ XES of BEDT-TTF charge transfer salts $(BEDT-TTF)_4Hg_{2.89}Br_8$ and $(BEDT-TTF)_4[(H_3O)Fe(C_2O_4)_3]C_5H_5N$.[12]

Single crystals of these compounds used for our measurements were prepared under conditions described in Refs. 1, 13, and 14. All of these materials are organic conductors or superconductors (see Table I).

Nonresonant carbon $K\alpha$ ($2p \rightarrow 1s$ transition) x-ray emission spectra were recorded employing the soft x-ray fluorescence endstation.[15] Photons with an energy of 300 eV, well
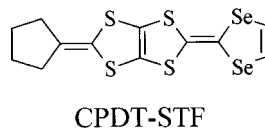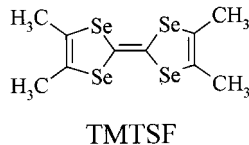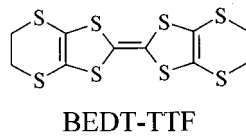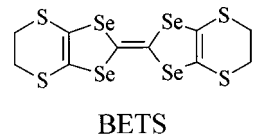
BETS

BEDT-TTF

TMTSF

CPDT-STF

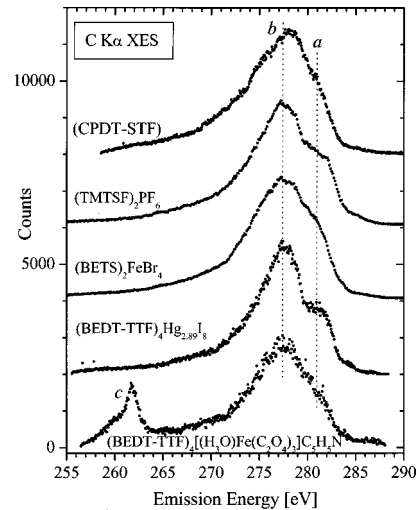FIG. 1. Chemical structure of donor molecules in charge transfer salts.

FIG. 2. C $K\alpha$ XES of charge transfer salts in the entire valence-band region.

The carbon $K\alpha$ soft x-ray emission spectra are presented in Fig. 2. A two-peak structure (labeled a-b) is found for all compounds. The same energy separation of peaks a and b in C $K\alpha$ (~2.8 eV) XES is found for all charge transfer salts indicating that the same structure of carbon π states in the valence band is present in all spectra. The low-energy subband c located around 258–263 eV is revealed only in C $K\alpha$ XES of $(BEDT-TTF)_4[(H_3O)Fe(C_2O_4)_3]C_5H_5N$ as well as in the spectra of other organic superconductors containing Fe and Cr oxalate layers $(BEDT-TTF)_4[(H_3O)Fe(C_2O_4)_3]C_6H_5CN$ and $(BEDT-TTF)_4[(H_3O)Cr(C_2O_4)_3]C_6H_5CN$.[13] Such low-energy subbands have been found in x-ray emission spectra of different elements with nonmetals and are attributed to ns states of nonmetal atoms.[17] Therefore this subband can originate from the hybridization of carbon $2p$ states of BEDT-TTF molecule and oxygen $2s$ states of oxalate layer $[(H_3O)Fe(C_2O_4)_3]$ or nitrogen $2s$ states of benzonitrile C_6H_5CN, which is due to hybridization between π-metal electrons of donor (BEDT-TTF) molecules and s states of anions. On the other hand, this subband is absent in C $K\alpha$ XES of $(BEDT-TTF)_4Hg_{2.89}Br_8$ where the anionic layer does not consist of nitrogen or oxygen atoms. In most electron conduction models suggested for organic stack electrons, the anion influence is attributed mainly to an external Coulomb potential that may be eliminated for centrosymmetrical species. In the case of noncentrosymmetrical anions—as the anions in $[(H_3O)Cr(C_2O_4)_3]C_6H_5CN$—the structural ordering can strongly modify the nature of the electronic states. Therefore the presence of an additional subband in the carbon $K\alpha$ XES evidences a strong cation-anion interaction in $(BEDT-TTF)_4[(H_3O)Fe(C_2O_4)_3]C_5H_5N$. Some authors emphasize the possible role of anions in order to explain variations in the superconducting transition temperature T_c,[18] the effect of pressure on T_c and on Shubnikov–de Haas oscillations,[19] or anomalies in the resistivity as a function of temperature in κ salts.[20] It is worthwhile mentioning that anion-cation induction interactions in organic superconductors derived from Bechgaard salts have

above the carbon K edge, were delivered to the endstation via the spherical grating monochromator. The carbon $K\alpha$ spectra were obtained with a 600-lines/mm, 10-m radius grating and energy resolution of 0.3–0.4 eV. A diffraction grating with 600 lines/mm and $R = 10$ m was used for these measurements.

In the present case of nonresonant excitation, the spectral shape of x-ray emission can be described with the emission decoupled from the excitation. According to the dipole selection rule $\Delta l = \pm 1$, the $1s$ core level hole in carbon atoms can only be filled by p-valence electrons. Therefore the intensity in nonresonant x-ray emission spectra of carbon maps the C $2p$ density at each particular atomic site. Since the final state of the x-ray emission process contains one hole in the valence band, XES spectra reflect the partial valence contribution to the single-particle spectral function.[16] XES is therefore a useful tool for the study of such highly correlated systems as charge transfer salts.

TABLE I. Description of the samples.

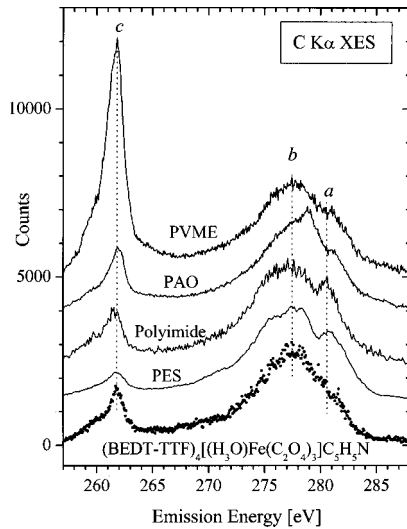| Sample	Electrical behavior
$(TMTSF)_2PF_6$	Superconducting at 12 kbar ($T_c = 0.9$ K)
κ-$(BETS)_2FeBr_4$	Antiferromagnetic metal (2.4 K$>$T$>$1 K), Superconducting ($T_c = 1.1$ K)
$(ET)_4Hg_{2.89}I_8$	Superconducting ($T_c = 4.3$ K)
$(ET)_2Cu[N(CN)_2]Br$	Superconducting ($T_c = 11.6$ K)
$(ET)_4[(H_3O)Fe(C_2O_4)_3]C_5H_5N$	MI transition at 116 K
(CPDT-STF) (TCNQ)	Metallic ($>$0.6 K)

FIG. 3. C $K\alpha$ XES of $(\text{BEDT-TTF})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3]\text{C}_5\text{H}_5\text{N}$ and reference organic compounds (polymers: PVME [poly(vinil methyl ether)], PAO [poly(aniline oligomer)] PES (poly-1,4-phenylene-ether-sulphone and polyimide)).

TABLE II. XPS binding energies of C $1s$ core level for charge transfer salts.

Compound	C $1s$ (eV)
$(\text{ET})_2\text{Cu}(\text{NCS})_2$	285.5[a]
DMTSA-BF_4	284.9[b]
$(\text{TMTSF})_2\text{PF}_6$	284.8[c]

[a]Reference 22.
[b]Reference 23.
[c]Reference 24

been evaluated within the framework of the valence-bond Hartree-Fock formalism, recently.[21] However, neither experimental nor theoretical studies have clearly established the role of the anions in the electronic properties of the organic salts. To our knowledge this is the first direct spectroscopic evidence of a cation-anion interaction in charge transfer salts. It is necessary to point out, however, that carbon $K\alpha$ measurements of κ-$(\text{BEDT-TTF})_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ and κ-$(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$ (Ref. 25) did not evidence these additional subbands, although anion-cation contacts are expected in these compounds as well.[26]

In order to verify the origin of this additional subband, we performed additional carbon $K\alpha$ measurements for some reference organic compounds. Those were the polymers PVME [poly(vinil methyl ether)], PAO [poly(aniline oligomer)], and PES poly-1,4-phenylene-ether-sulphone, having chemical structures $(—\text{CH}_2—\text{CH}(\text{OCH}_3)—)_n$, $\text{C}_6\text{H}_5—\text{NH}—\text{C}_6\text{H}_4—\text{NH}—\text{C}_6\text{H}_5$, and $\text{C}_6\text{H}_5—\text{O}—\text{C}_6\text{H}_4—\text{SO}_2—\text{H}$, respectively. The data are displayed in Fig. 3. The emission of these polymers as well as polyimide[27] and PES (poly-1,4-phenylene-ether-sulphone) (Ref. 28) also exhibits the low-energy feature labeled c at the same emission energy (262 eV) as found in the spectrum of $(\text{BEDT-TTF})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3]\text{C}_5\text{H}_5\text{N}$. In all these polymers nitrogen (PAO), oxygen (PVME and PES), or both nitrogen and oxygen (PI) is present. The assumption that this additional subband is displayed in carbon $K\alpha$ XES as a second order of oxygen $K\alpha$ XES with energy 524 eV is not correct since our measurements of O $K\alpha$ XES for PI (Ref. 27) show that the emission energy of intensity maximum is 527.3 eV, which is 3.7 eV higher than it would be expected. We finally attribute the origin of the feature labeled c in carbon $K\alpha$ XES of $(\text{BEDT-TTF})_4[(\text{H}_3\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3]\text{C}_5\text{H}_5\text{N}$ to nitrogen and oxygen $2s$ states of the anion layer which arise from C $2p$–N $2s$ and C $2p$–O $2s$ hybridization.

In order to examine the behavior of the carbon emission

features near the Fermi level, one would need XPS binding energies of the C $1s$ core levels. Unfortunately, such measurements have been performed, up to now, only for few charge transfer salts (see Table II). The binding energies vary between 0.2 and 0.7 eV, allowing us to estimate the position of the Fermi level in the carbon $K\alpha$ spectra displayed. Figure 4 shows carbon $K\alpha$ XES in the vicinity of the Fermi level. For carbon C $K\alpha$ XES two Fermi-level positions are indicated (E_{f1} and E_{f2}) which correspond to the lower and higher C $1s$ binding energies, respectively (see Table II). All spectra show almost linear tails in the vicinity of the Fermi level extending towards high emission energies and a suppression of the spectral weight at E_f. This pseudogap and the absence of the Fermi edge are incompatible with the usual spectroscopic behavior of normal 3D metals where the Fermi edges are definitely observed on spectral curves. Figure 5 shows a comparison of photo- and soft x-ray emission for carbon in $(\text{TMTSF})_2\text{PF}_6$ on a binding energy scale. Here C $K\alpha$ XES of $(\text{TMTSF})_2\text{PF}_6$ is converted to this scale using an XPS C $1s$ binding energy of 284.8 eV. Both spectra do not show metallic Fermi edges. Peaks 1 and 2, well resolved in UPS spectra, are smeared in C $K\alpha$ XES of $(\text{TMTSF})_2\text{PF}_6$ due to the limitation in energy resolution.

These observations are in contrast to the conventional Fermi-liquid picture of a metal where quasiparticle bands cross the Fermi level. Therefore one can conclude that non-
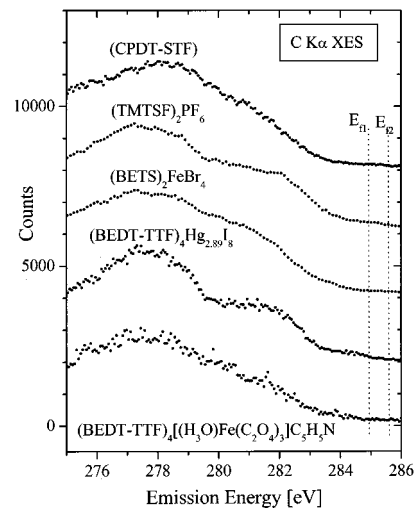

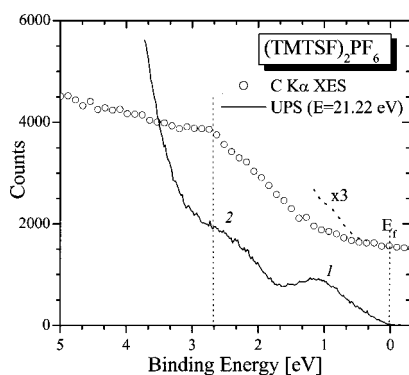FIG. 4. C $K\alpha$ XES of charge transfer salts in the vicinity of the Fermi level.

FIG. 5. Comparison of UPS and C $K\alpha$ XES valence-band spectra of $(TMTSF)_2PF_6$ near the Fermi energy on a binding energy scale. The UPS spectra are not corrected for an inelastic background, and the photon energy for the UPS spectrum is displayed.

Fermi-liquid features are observed in x-ray emission spectra of charge transfer salts. The accuracy of the data is not sufficient to obtain the exponent α but qualitatively one can conclude that it should be larger than 1 ($\alpha \gtrsim 1$). ARPES data for $(TMTSF)_2PF_6$ give an estimation $\alpha \cong 1.25$.[7] This is rather unusual since simple models deduce significantly smaller values for α. For example, the Hubbard model yields $0 < \alpha < 1/8$.[29] larger values of α are possibly a sign of the importance of long-range Coulomb interactions.[7] Recent numerical results[30] demonstrate that α can be larger than 1 in the spinless fermion model with competing nearest-neighbor- and next-nearest-neighbor interactions. However, we need to point out that the drop of spectral weight in the XES spectra stretches over almost 2 eV, which is larger than any reasonable energy scale expected for Luttinger liquid behavior. In fact, it is even larger than the conduction-band widths derived for organic CT salts (0.5–1 eV). This problem also exists in the non-Fermi-liquid interpretation of the photoemission spectra. The absence of spectral weight in the photoemission spectrum at the Fermi level of quasi-1D organic conductors could be related to a strong off stoichiometry in the surface of these compounds.[31]

To conclude, we have performed x-ray fluorescence measurements of charge transfer salts $(TMTSF)_2PF_6$, $(BETS)_2FeBr_4$, and $(CPDT-STF)(TCNQ)$. In all spectra the intensity near the Fermi level is suppressed. This cannot only be due to electron correlation effects, but also to high defect concentration in the surface of these materials. The additional low-energy subband found in carbon $K\alpha$ XES of $(BEDT-TTF)_4[(H_3O)Fe(C_2O_4)_3]C_5H_5N$ is attributed to a strong cation-anion interaction in charge transfer salts. The absence of quasiparticle features near the Fermi level is incompatible with a Fermi-liquid picture. An additional low-energy subband found in carbon $K\alpha$ XES of $(BEDT-TTF)_4[(H_3O)Fe(C_2O_4)_3]C_5H_5N$ can be attributed to a strong cation-anion interaction in charge transfer salts.

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