

X-ray emission spectra and electronic structure of charge transfer salts

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Charge transfer salts formed by linear chains of organic molecules BETS (bis(ethyleneditho)tetraselenafulvalene), BEDT-TTF (bis(ethyleneditho)-tetrathiafulvalene) and TMTSF (tetramethyltetraselenafulvalen) display a rich variety of electronic properties from magnetic insulators to superconductors depending on the nature of the donors or acceptors and their location in the crystal structure. 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 has been shown that one-dimensional conductors are not Fermi liquids like normal metals, but Luttinger or Luttinger-Emery liquids with distinct different physical properties. High-resolution angle-resolved photoemission spectra (ARPES) have shown a strong suppression of quasiparticle states near the chemical potential [1]. On the other hand a decrease in photoemission intensity near the Fermi level may 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.

We report soft x-ray fluorescence measurements for the charge transfer salts (TMTSF)₂PF₆, (BETS)₂FeBr₄ and (CPDT-STF)(TCNQ), carried out at Beamline 8.0 of the Advanced Light Source. Nonresonant carbon K α (2p \rightarrow 1s transition) X-ray emission spectra (XES) were recorded employing the soft X-ray fluorescence endstation [2]. Photons with an energy of 300 eV, well above the carbon K-edge, were used for excitation. The carbon K α spectra were obtained with an energy resolution of 0.3-0.4 eV.

Fig. 1 displays the carbon K α soft x-ray emission spectra (XES) [3]. A two-peak structure (labeled *a*, *b*) is found for all compounds. The same energy separation of peaks *a* and *b* in C K α (~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. Such low-energy subbands have been found in X-ray emission spectra of compounds and are attributed to ns-states of non-metal atoms. Therefore this subband can stem from the hybridization of carbon 2p-states of the BEDT-TTF molecule and 2s states of the oxalate layer [(H₃O)Fe(C₂O₄)₃] or from the nitrogen in benzonitrile

C_6H_5CN , which is due to hybridization between carbon π -metal electrons of donor (BEDT-TTF)-molecule and s-states of anion. The presence of an additional subband in carbon $K\alpha$ XES evidences strong cation-anion interaction in $(BEDT-TTF)_4[(H_3O)Fe(C_2O_4)_3]C_5H_5N$.

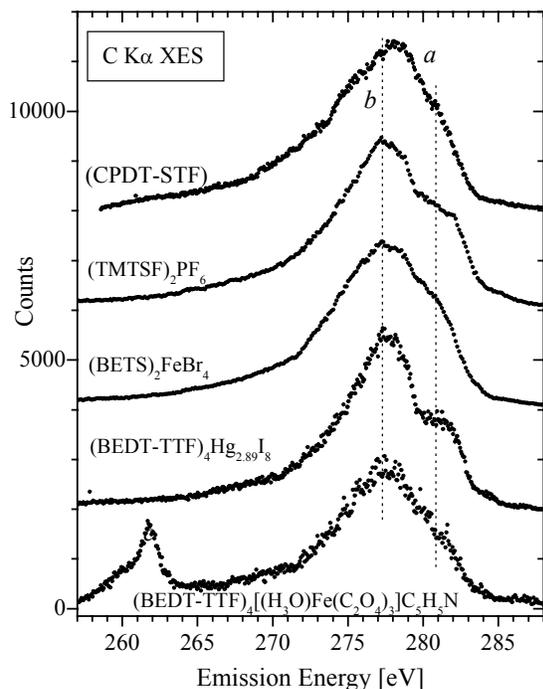


Fig. 1 C $K\alpha$ XES of charge transfer salts in the entire valence-band region

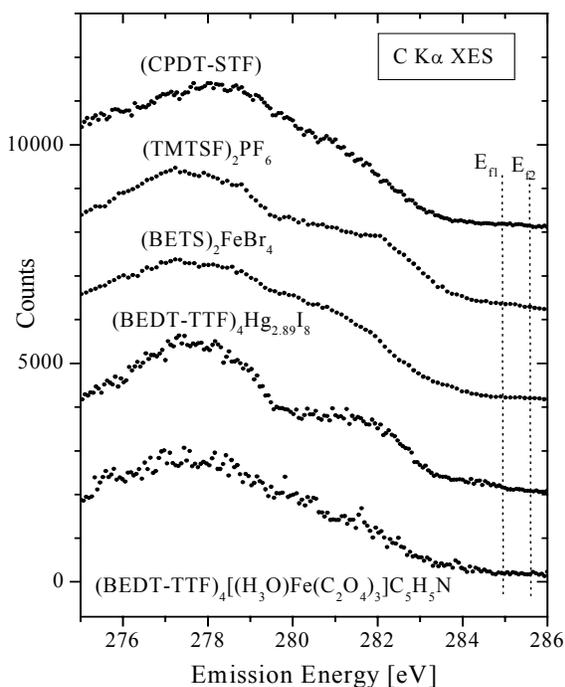


Fig. 2 C $K\alpha$ XES in the vicinity of the Fermi level.

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 [3]. 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. Fig. 2 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. All spectra show almost linear tails in the vicinity of the Fermi level (extending towards higher emission energies) and a suppression of the spectral weight at E_f . This pseudogap as well as the absence of a Fermi edge is incompatible with the usual spectroscopic behavior of normal 3D metals, which display Fermi-edges.

Our observations are in contrast to the conventional Fermi liquid picture of a metal where quasiparticle bands cross the Fermi level. We conclude that non-Fermi liquid features are observed in X-ray emission spectra of charge transfer salts. At the same time we point out that the decrease in spectral weight in the XES spectra stretches over almost 2 eV, which seems unreasonably large for Luttinger liquids. This value is even larger than the conduction bandwidths derived for organic CT salts (0.5 to 1 eV). This problem also exists in the non-Fermi liquid interpretation of the photoemission spectra.

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