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# Unusual electronic structure near $E_F$ in the organic superconductor $\kappa$-[bis(ethylenedithio)tetrathiafulvalene]$_2$Cu[N(CN)$_2$]Br

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We report on photoemission studies of the quasi-two-dimensional organic superconductor $\kappa$-[bis(ethylenedithio)tetrathiafulvalene]$_2$Cu[N(CN)$_2$]Br ($T_c$=11.6 K). Finite photoelectron-emission intensities were observed in the region close to the Fermi level ($E_F$). However, the spectral line shape displays a broad onset from the Fermi level with a near zero emission intensity at exactly $E_F$. This is in contrast to a sharp Fermi edge that is observed in most three- and two-dimensional metallic systems. The midpoint of the broad emission onset is shifted toward the higher binding-energy side by about 0.1 eV, resulting in an apparent "gap." Strong electron-electron correlations and the excitation of phonons corresponding to molecular-vibration modes are considered as possible explanations for this unusual spectral behavior. The possible existence of a one-dimensional-like open Fermi surface in this material is discussed.

Organic conductors, also called synthetic metals, are interesting in that often all or most of the constituent elements are nonmetallic elements. The organic superconductor $(TMTSF)_2PF_6$ (where TMTSF is tetramethyltetraselenafulvalene) ($T_c$=0.9 K) was discovered in 1980.[1] Since then, numerous other organic superconductors have been discovered. This field has attracted increasing interest because of the recent breakthroughs in finding new materials with higher $T_c$'s.[2]

The majority of organic superconductors, including the ones with highest $T_c$'s, are charge-transfer salts derived from the electron donor molecule BEDT-TTF, or ET [bis(ethylenedithio)tetrathiafulvalene].[2] The ET-based organic superconductors have many physical properties that are similar to those of high-$T_c$ cuprates. For example, they both have layered structures and highly anisotropic conductivities. While the high-$T_c$ cuprates has been extensively studied by photoemission technique and important advances were made, vigorous photoemission studies on organic superconductors are lacking.

We carried out photoemission studies on $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br ($T_c$=11.6 K), the compound that has the highest $T_c$ at ambient pressure among all radical-cation based organic superconductors. Efforts were made to study the electronic structure near the Fermi level ($E_F$) with accuracy by employing high-energy resolution (50 meV) and keeping the samples at low temperature (12 K) to reduce thermal broadening. The valence band exhibits several prominent features. Significant photoelectron-emission intensities are observed in the region close to $E_F$. However, the spectrum displays a broad onset from the Fermi level with emission intensity at exactly $E_F$ being near zero. This result is in contrast to a sharp Fermi edge observed in most of the three-dimensional (3D) and two-dimensional (2D) metallic systems, including the quasi-2D high-$T_c$ cuprates. Electron-electron and electron-phonon interactions are considered as the likely causes for the absence of a Fermi edge.

Single crystals of $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br were grown by use of the electrocrystallization method.[3] Samples are flake-shaped with a typical size of $1.5\times1.5\times0.2$ mm$^3$. The cleavage surface exposes the conducting $a$-$c$ plane. Photoemission experiments were carried out at the Argonne-Minnesota ERG-Seya beamline,[4] at the Synchrotron Radiation Center, Stoughton, Wisconsin. Photoelectrons were collected by a 50-mm hemispherical analyzer mounted on a goniometer. The analyzer has an acceptance angle of 2°. The combined energy resolution (electron and photon) ranges from 50 to 150 meV for the spectra shown in this paper. The residual pressure of the measurement chamber is less than $5\times10^{-11}$ Torr. Photoemission measurements were repeated on many samples and the results are reproducible.

The valence band spectrum of $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br measured at normal emission with $h\nu$=24 eV is shown in Fig. 1. The sample temperature is 12 K. Distinct features marked $A$–$H$ at approximately −9.5, −8.1, −7.3, −5.9, −3.8, −3.0, −1.6, and −0.6 eV binding energies can be observed. There is clearly a finite emission intensity in the region just below $E_F$, although the magnitude is quite small

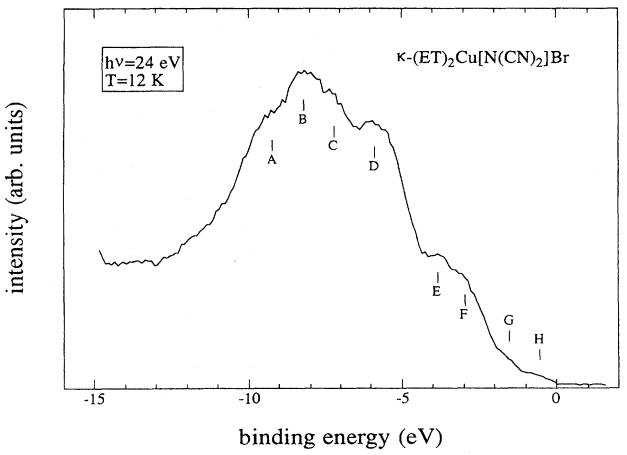


FIG. 1. Energy distribution curve (EDC) measured on $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br at normal emission with $h\nu$=24 eV.

 

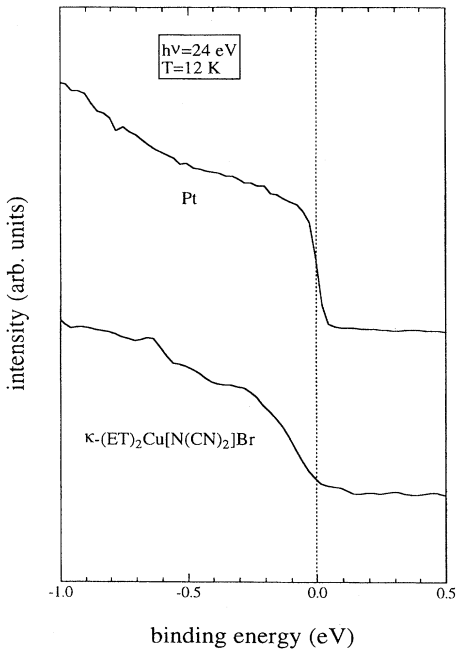


FIG. 2. EDC's measured on a platinum foil (upper curve) and on $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ (lower curve). Photons of 24 eV were used.

compared to the maximum of the valence band.

Note that our photoemission spectrometer is an angle-resolved one. However, the valence band spectrum does not show any noticeable change in either peak position or intensity, as the angle of the analyzer is changed. We note that the orthorhombic crystal structure of $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ has rather large unit cells ($a=12.871$ Å, $b=29.548$ Å, $c=8.466$ Å). Consequently the Brillouin zone in the reciprocal space is rather small. At $h\nu=24$ eV, the 2° angular acceptance angle of our analyzer translates to a momentum window of about $\frac{1}{3}$ of the $\Gamma$-$X$ and $\frac{1}{5}$ of the $\Gamma$-$Z$ lengths along the edges of the two-dimensional Brillouin zone. It is possible that the $k$ dependence of the spectral features might be obscured by the significant $k$ integration over the Brillouin zone due to this relatively large $k$ window.

Because $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ has a resistivity maximum at about 80 K (Ref. 2) (a phenomenon that is not completely understood), we also did measurements above 80 K. No spectral change in the valence band, including the region near $E_F$, is observed for different temperatures.

An energy distribution curve (EDC) measured with high-energy resolution (50 meV) for the narrow energy region near $E_F$ is shown as the lower curve in Fig. 2. Note that the emission intensity is almost zero at $E_F$. With increasing binding energy, the emission intensity gradually increases to a finite value. This spectral line shape is in contrast to a Fermi edge cut off by the Fermi distribution function that is normally observed in 3D and 2D metallic systems. For comparison, the EDC taken on a Pt foil is shown as the upper curve in Fig. 2. Note that the Fermi level falls at the midpoint of the leading edge. The width of the leading edge is determined by thermal broadening (i.e., the Fermi distribution function) and by the instrument resolution. The observation of a Fermi edge signifies the existence of a sharp Fermi surface and that electronic excitations consisting of infinitesimal energies are possible. In contrast, the spectrum of $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ has a broad onset with the midpoint shifted toward the higher binding-energy side by about 0.1 eV. It appears as if there is a "gap" of 0.1 eV.

The question then arises whether the absence of a Fermi edge is an intrinsic property of the bulk material or an artifact due to experimental limitations. One common concern for photoemission experiments is that they are surface sensitive. The probing depth is only about 10–20 Å. A natural question is, is it possible that the surface layer that photoemission is probing is an insulating layer? The structure of $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ consists of alternating layers of ET molecules and $Cu[N(CN)_2]Br$ polymeric anions. It is generally believed that electron conduction happens mainly in the ET layers. Cleaving the crystal usually results in the separation between the ET and the anion layer. In principle, the surface exposed by cleavage could have either the ET or the anion layer as the topmost layer. In reality, the cleaved surfaces probably have a combination of these two terminations. It is very unlikely that cleaved surfaces are always terminated with the anion layer. We also note that the anion layer is rather thin (nearly monatomic thick). Even when the top layer is an anion layer, the underlying cation layer should still be within the probing range of photoemission. Another possibility we should consider is the charge redistribution near the surface. Scanning tunneling microscopy (STM) and atomic force microscopy (AFM) studies on many ET-based salts show that the surface unit-cell parameters are in good agreement with those of the bulk.[5] STM studies on $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ and several other related salts indicate that the top cation layer is metallic.[6] From the above considerations, it appears unlikely that the absence of a Fermi edge is due to a surface region that is insulating.

Spectra were also measured using different photon energies ranging from 18 to 190 eV. In this photon energy range, the photoelectron scattering length would vary by approximately a factor of 2 according to the "universal curve" of the scattering length.[7] In all spectra, the line shapes near $E_F$ always show the absence of a metallic Fermi edge, although the spectral intensities immediately below $E_F$ show variations with photon energy. The intensity variations are probably due to atomic photoexcitation cross-section effects and will be discussed in more detail in a separate paper.

We also performed photoemission experiments on two other ET-based organic superconductors: $\kappa$-$(ET)_2Cu(NCS)_2$ ($T_c=10.4$ K) and $\beta$-$(ET)_2I_3$ ($T_c=1.4$ K).[8] The absence of a Fermi edge was observed on both compounds. Earlier photoemission studies on $\kappa$-$(ET)_2Cu(NCS)_2$ also reported very low emission intensity near $E_F$,[9] although the experiments were done with rather poor resolution. To the best of our knowledge, no observation of a sharp Fermi edge has been reported by any photoemission studies on the quasi-two-dimensional ET-based organic superconductors. The generality of this unusual spectral behavior in this group of materials calls for a more fundamental explanation.

It is known that the carrier concentration in these materials is very low. The room-temperature conductivity $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ is approximately 50 $(\Omega\,\mathrm{cm})^{-1}$.[2] This value is about four orders of magnitude lower than those of ordinary metals such as Cu. The low carrier concentration

can be easily understood by considering the crystal structures and the chemical stoichiometry of these compounds. In the $(ET)_2X$ salts, one electron is transferred from $(ET)_2$ to $X$ to form $(ET)_2^-X^+$ within a unit-cell volume of typically 900 Å$^3$. The very low carrier concentration may explain the overall low emission intensities in the vicinity of the Fermi level. However, it cannot explain the spectral behavior showing the absence of a Fermi edge, which is qualitatively different from what is observed in ordinary metals.

We note that very similar spectral behavior that shows the absence of a Fermi edge has been observed in many quasi-1D materials.[10–12] In a paper by Dardel *et al.*,[10] it is shown that the spectra from the quasi-1D $K_{0.3}MoO_3$ and $(TaSe_4)_2I$ do not have a Fermi edge while the spectrum of quasi-2D $TaSe_2$ has a distinct Fermi edge, just as in the 3D Rh. It is known that electron-electron correlations are strong in 1D materials. Luttinger-liquid theory,[13] a model that differs fundamentally from Fermi-liquid theory, is believed to be valid in 1D systems. It has been suggested that Luttinger-liquid theory might also be valid in 2D systems.[14] However, a normal Fermi edge is observed in most 2D metallic systems, including the high-$T_c$ cuprates which are widely considered exotic materials. The intriguing questions are the following: Could the ET-based organic superconductors be unique examples in which Luttinger-liquid theory could be applied to a 2D system? Or, could the electronic structure in these materials have a strong 1D character? A recent first-principles self-consistent electronic structure calculation for $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ suggests very narrow bands near $E_F$, indicating the importance of electron-electron correlations.[15] The same calculation gives a Fermi surface which consists of a closed hole pocket and several open electron channels. (An earlier calculation using the semiempirical extended Hückel tight-binding method predicted only closed Fermi surfaces.[16]) Such open Fermi surfaces are similar to the Fermi surface one would have for a quasi-1D material. Our photoemission results might be an indirect evidence for the existence of such Fermi surfaces.

No de Haas–van Alphen (dHvA) or Shubnikov–de Haas (SdH) experiments on $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ have been reported. However, SdH and dHvA experiments on $\kappa$-$(ET)_2Cu(NCS)_2$ and $\kappa$-$(ET)_2(NH)_4Hg(SCN)_4$ reported the observation of oscillations, indicating the existence of closed Fermi surfaces.[17–20] A SdH study on $\kappa$-$(ET)_2Cu(NCS)_2$ by Sasaki *et al.*[21] reported observations of both closed holelike and open electronlike Fermi surfaces. A recent positron annihilation experiment on $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ (Ref. 22) reports an indication of a Fermi surface which only partially resembles the prediction of the first-principles self-consistent calculation. The discrepancies were attributed to insufficient statistics in the positron experiment.[15]

Another possible explanation is the excitation of phonons. When trying to explain the absence of a Fermi edge in the spectrum of quasi-1D organic conductor TTF-TCNQ, Grobman *et al.*[11] postulated the following scenario: electrons near $E_F$ might be viewed as localized to individual molecules in the short time scale of the photoemission process; these localized states are subject to the creation of phonons corresponding to molecular vibration modes (Frank-Condon principle). This process would cause the spectrum to appear broadened and shifted toward higher binding energies. Such a scenario can also apply to the quasi-2D ET-based organic superconductors.

In summary, we performed photoemission experiments with high-energy resolution on the quasi-2D organic superconductor $\kappa$-$(ET)_2Cu[N(CN)_2]Br$. The valence band spectrum displays a broad onset near $E_F$ with the emission intensity at exactly $E_F$ being near zero. The midpoint of the leading onset is shifted toward the higher binding-energy side by about 0.1 eV, resulting in an apparent "gap." Strong electron-electron correlations and the excitation of phonons corresponding to molecular vibration modes are considered as possible explanations for this unusual spectral behavior. The possible existence of a 1D-like open Fermi surface in this material is discussed.

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