Bandwidth Tuning Triggers Interplay of Charge Order and Superconductivity in Two-Dimensional Organic Materials

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We observe charge-order fluctuations in the quasi-two-dimensional organic superconductor $\beta''-(BEDT-TTF)_2SF_5CH_2CF_2SO_3$, both by means of vibrational spectroscopy, locally probing the fluctuating charge order, and by investigating the in-plane dynamical response by infrared reflectance spectroscopy. The decrease of the effective electronic interaction in an isostructural metal suppresses both charge-order fluctuations and superconductivity, pointing to their interplay. We compare the results of our experiments with calculations on the extended Hubbard model.

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From a naive point of view, superconducting and ordered insulating states are incompatible. This is true, for example, for the competition of charge-density waves and superconductivity [1], or stripes in cuprates [2,3]. However, experimental and theoretical studies on materials with strong electronic correlations suggest that *fluctuations* of an ordered state may mediate superconductivity. Prime candidates for this mechanism are magnetic order in heavy fermions [4,5] and high-temperature superconductors [6], incommensurate charge-density waves in dichalcogenides [7], or fluctuating charge order in quasi-two-dimensional organic conductors [8–14].

In bis-(ethylenedithio)tetrathiafulvalene (BEDT-TTF)-based 1/4-filled conductors the ground state can be tuned by modifying effective electronic correlations via changing the bandwidth [15,16] [Fig. 1(a)]: A charge-ordered insulating state is observed when the effective Coulomb repulsion is large enough [16–20], while compounds with weaker effective electronic correlations are metallic [21]. In the metallic state close to the metal-insulator phase boundary, charge fluctuations are observed [9,20,22], while the response of coherent carriers is still present. These experimental results are in agreement with calculations of the extended Hubbard model. It is the minimum model that can describe a metal-insulator transition in quasi-two-dimensional molecular conductors with a 1/4-filled conduction band [7]. It takes into account the effective on-site U/t and intersite V/t Coulomb repulsion, where t is the hopping integral related to the bandwidth. This model predicts that fluctuations of checkerboard charge order (CO) can act as an attractive interaction of quasiparticles forming Cooper pairs and can lead to a superconducting state [8,23]. In this Letter we present experimental evidence for bandwidth-tuned CO fluctuations in the normal state of a β'' family of quasi-2D organic conductors. We see an unambiguous relation between the presence of CO fluctuations and superconductivity and discuss its origin.

The materials studied are layered compounds, where a slightly anisotropic quasi-two-dimensional conducting electronic system of the (ab) plane is created by the overlap of the neighboring BEDT-TTF molecules [24] [Fig. 1(b)]. The bandwidth is tuned by changing the size of the anion, by so-called "chemical pressure." $\beta''-(BEDT-TTF)_2SF_5CH_2CF_2SO_3$ (called β''-SC later on) [25] becomes superconducting at $T_c \approx 5$ K [inset of Fig. 2(a)] and was suggested as an ideal model to investigate the interplay between CO and superconductivity in a 1/4-filled system [8]. In the isostructural compound $\beta''-(BEDT-TTF)_2SO_3CHFSF_5$ (called β''-M) the effective Coulomb repulsion between electrons is reduced by chemical pressure [24,26], and the compound is metallic.

The molecular structure of conducting layers of BEDT-TTF salts gives us a unique opportunity to locally probe the charge distribution between the lattice sites by IR reflectance. We follow a temperature dependence of the

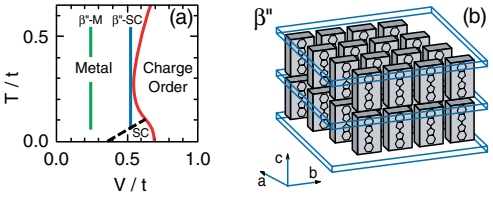

FIG. 1 (color online). (a) Phase diagram for the 1/4-filled organic conductors calculated by the extended Hubbard model. The dashed line is for superconductivity, schematically based on Ref. [8]. The solid lines show the approximate positions of the studied compounds in the phase diagram. (b) A schematic view of a 3D structure of the layered BEDT-TTF-based crystals, with the rectangles marking the BEDT-TTF molecules.

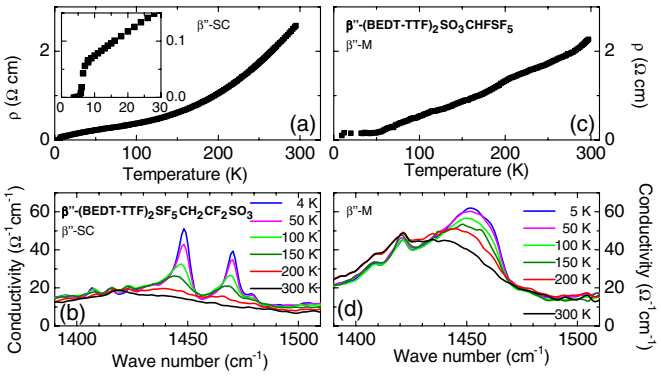

FIG. 2 (color online). Temperature-dependent dc resistivity in the conducting plane of (a) β''-SC and (c) β''-M. Optical conductivity perpendicular to the conducting layers in the region of $B_{1u}(\nu_{27})$ BEDT-TTF vibration is shown: (b) β''-SC, a band of $B_{1u}(\nu_{27})$ splits into two components at 1448 and 1470 cm^{-1} as the temperature decreases; (c) β''-M, $B_{1u}(\nu_{27})$ vibration of BEDT-TTF is a single wide band at all temperatures, showing the frequency of 1452 cm^{-1} at 10 K.

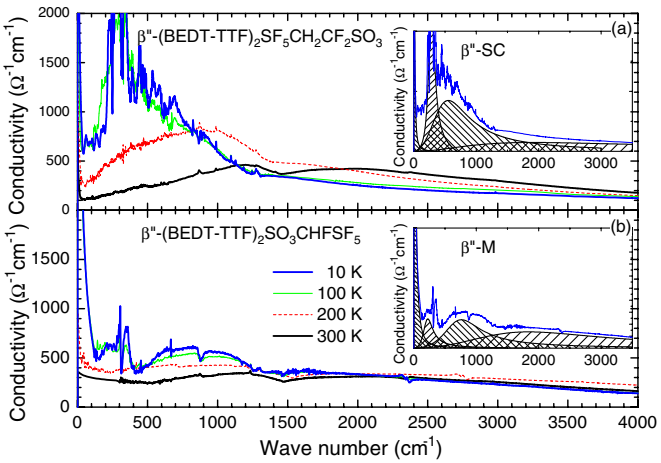

FIG. 3 (color online). In-plane conductivity ($E \parallel b$) of (a) β''-SC and (b) β''-M at different temperatures. The insets show conductivity spectra at 10 K with the results of the Drude-Lorentz fit and marked electronic bands, as discussed in the text. The spectra in the perpendicular direction show the same electronic features.

sensitive to site charge $B_{1u}(\nu_{27})$ vibrational mode of BEDT-TTF molecules, observed in the out-of-plane IR spectra [14,27]. This temperature dependence, compared to the in-plane temperature-dependent dc conductivity, gives a spectacular result which is presented in Fig. 2. At room temperature both compounds show a wide single line of $B_{1u}(\nu_{27})$ vibration. The band stays wide but single for the β''-M in the whole temperature range. When the effective correlations increase in the case of β''-SC, the spectra show a splitting $\Delta\nu = 22$ cm^{-1} of this charge sensitive vibration at temperatures below 200 K. No changes in any other vibrational feature occur, and our x-ray studies at $T = 300$, 123, and 20 K give evidence that the symmetry of the unit cell of β''-SC does not change with temperature. The observed splitting suggests that the system is tuned into a state with a charge disproportionation $\Delta\rho \approx 0.2e$ between neighboring lattice sites [27]. Nevertheless, the compound stays metallic with only a slight change in the slope of dc resistivity temperature dependence below 200 K [28]. We interpret this result as the formation of a weak fluctuating CO. The analysis of the width of the vibrational bands suggests a characteristic time of charge fluctuations between the sites of not less than 10^{-12} s [29]. β''-SC with fluctuating CO shows superconductivity with $T_c = 5$ K, while β''-M with $\Delta\rho$ below $0.1e$ stays metallic.

To study the response of the quasi-two-dimensional conducting system, we perform IR reflectance measurements in the ab plane of high-quality single crystals ($3 \times 1.2 \times 0.15$ mm^3) in the frequency range 8–8000 cm^{-1} and temperature range 300–1.8 K by using Fourier-transform infrared spectroscopy and THz spectrometers. In Figs. 3, 4(a), and 4(b) we show the conductivity spectra obtained by a Kramers-Kronig transformation, using standard extrapolations [30]. These measurements cover the energy range of the conductance band formed by the overlap of the BEDT-TTF molecular orbitals [14]. For a metal we expect all the respectful spectral weight to be concentrated in a zero-frequency (Drude) peak of the conductivity spectrum. As in the case of many other materials with competing interactions [30,31], even in the metallic state the spectra do not contain only a Drude component (see Fig. 3). For both compounds at room temperature, most of the spectral weight is found in the wide features in the mid-infrared (MIR) with maxima at about 1000 and 2500 cm^{-1}. Upon cooling, the spectral weight shifts to low frequencies, and a Drude peak appears, as is typical for organic conductors [32–34].

The Drude spectral weight of β''-M does not change below 150 K, and respectively, the Drude plasma frequency Ω_p stays constant [see Fig. 4(c)]. In contrast, the Drude spectral weight of more correlated β''-SC grows on further cooling at the expense of the band at 2500 cm^{-1}. This reentrant behavior is suggested for a metal close to CO by the calculations on the extended Hubbard model: the phase border between CO and metal shifts to higher values of V at low temperatures; see Fig. 1(a). The estimated temperature of the reentrant behavior is $T = 0.2t$, which gives us 140 K with $t = 0.06$ eV, a typical value for these compounds.

At 10 K for the β''-M we observe a well-defined Drude-like peak below ≈ 200 cm^{-1}, a band at ≈ 700 cm^{-1} shifted down from 1000 cm^{-1}, and a wide band at 2500 cm^{-1} [see the inset in Fig. 3(b)]. A weak band at about 300 cm^{-1} might already be distinguished in the β''-M spectra. It becomes very intense for β''-SC and dominates the low-frequency response, while the Drude-like peak is extremely narrow and contains about 5% of the spectral weight [see the inset in Fig. 3(a)]. The 300 cm^{-1} band in the spectra of β''-SC starts to increase at temperatures where the charge disproportionation sets in.

The interpretation of experimental conductivity spectra for 1/4-filled organic conductors was based on the results of

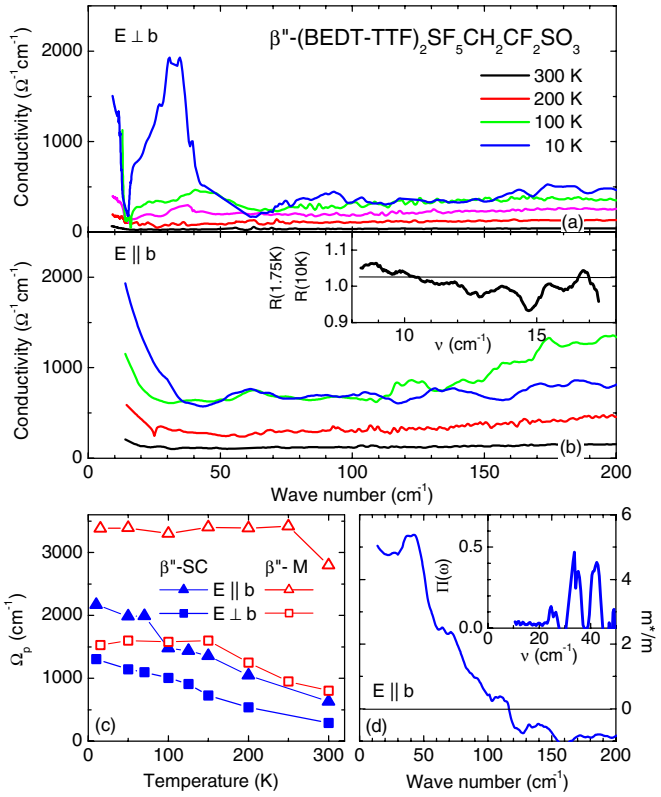

FIG. 4 (color online). (a) The conductivity in $E \perp b$ of β''-SC shows a narrow Drude contribution and the lattice mode at about 40 cm^{-1} coupled to charge carriers. (b) The conductivity in the $E \parallel b$ direction. The inset shows the opening of the superconducting gap at the ratio $R(1.75\ K)/R(10\ K)$. (c) Temperature dependence of Drude plasma frequency. Note the reentrant behavior. (d) The effective mass at 10 K calculated by the extended Drude analysis. The inset shows $\bar{\Pi}(\omega)$ at the lowest frequencies.

numerical solutions of the extended Hubbard model on a square lattice [9,23,32]. In a metallic state close to the charge order, where charge fluctuations are important, this theory expects to find three features in conductivity spectra: (i) a broad band in the MIR range which we associate with site-to-site transitions within a fluctuating CO pattern [this is a transition between ''Hubbard-like'' bands (see Figs. (8) and (9) in Ref. [23]], (ii) a Drude peak describing the coherent-carriers response, due to the narrow peak of density of states at Fermi energy, and (iii) a finite-frequency ''charge fluctuation band'' due to transitions between the density of states at Fermi energy and the Hubbard-like bands, observed for 1/4-filled organic conductors typically at 700–500 cm^{-1} [22,32]. The presence of the latter feature in the spectra proves that we observe CO fluctuations and not a separation between metallic and charge-ordered components. These three features can be well distinguished in the spectra of β''-M and β''-SC (Fig. 3).

The important and striking result of this work is an additional feature that appears at about 300 cm^{-1} and increases in intensity as it gets close to CO, when going from β''-M to β''-SC. In the metallic state with fluctuating CO in β''-SC the Drude peak gets extremely narrow and the band at 300 cm^{-1} very intense, while their spectral weights simultaneously increase upon cooling. This suggests an assignment of the band to the scattering of charge carriers on CO fluctuations near the CO phase. In the respective theoretical picture, close to CO and in the reentrant regime at $T < 0.2t$ [Fig. 1(a)], collective charge fluctuations are very soft [22,23]. The interaction between charge carriers and the respective bosonic low-energy plasmon modes leads to self-energy effects and electronic incoherent structures which manifest as a peak in the conductivity at $\omega \sim 0.6t$. However, the extremely high intensity of this feature at 300 cm^{-1} in β''-SC spectra is not reproduced by the calculations on the extended Hubbard model of Ref. [23].

An alternative theoretical approach proposes a description of the CO state that includes coupling to the lattice, resulting in a polaronic state [35]. This model deals with an ordering transition and charge disproportionation $\Delta\rho$ of above $0.5e$, and not a metallic state. Importantly, as a consequence of a strong coupling to the lattice, a CO electronic feature is extremely enhanced and a pseudogap is present in the metallic state. In accordance with this work, we suggest that polaronic effects enhance the low-energy band, and to fully describe the results, a coupling to the lattice should be taken into account in some more sophisticated model. This increasing importance of the coupling to the lattice in β''-SC can be explained by a large renormalization of the electron-phonon coupling due to CO fluctuations close to the transition [36].

The electron-phonon coupling is one reason for the increased intensity of a phonon mode at 30–40 cm^{-1} upon cooling. This mode is observed with $E \perp b$ [Fig. 4(a)] as charge disproportionation appears below 200 K. The lattice modes at these frequencies are vibrations that modulate the distance between the sites [37]. A mode involving a vibration of two neighboring lattice sites (BEDT-TTF molecules) will appear or increase its intensity in a CO state. While $\Delta\rho \approx 0.2e$ remains constant, the intensity of the 40 cm^{-1} mode increases upon cooling, together with the low-frequency electronic features, showing the strong coupling to the charge-carrier response. This agrees with an expected enhancement of the electron-phonon coupling near CO [36].

We obtain further information on electron-bosonic coupling from the extended Drude analysis and optical memory functions [31,38] for $E \parallel b$, where the zero-frequency peak in conductivity is wide enough to perform this analysis. An extended Drude model reveals the frequency dependence of the scattering rate and effective mass $\frac{m^*(\omega)}{m_b} = \frac{\Omega_p^2}{4\pi}\frac{\sigma_2}{\omega|\sigma|^2}$ [the latter is shown in Fig. 4(d)], where the plasma frequency Ω_p comes from the spectral weight of the Drude-like peak. The values of the effective mass are in good agreement with the value of $3.9m_e$ from specific heat measurements [39], while higher than $1.9m_e$ received from Shubnikov-de-Haas oscillations. Further, from our data we get an approximate value of $\bar{\Pi}(\omega)$ [40], the coupling of electrons to bosonic fluctuations: $\bar{\Pi}(\omega) \approx \frac{1}{2\pi}\frac{d^2}{d\omega^2}[\omega\frac{1}{\tau(\omega)}]$ (see [38] and references

therein) [inset in Fig. 4(d)]. The maxima in $\bar{\Pi}(\omega)$ around 40 cm^{-1} suggest the approximate frequencies of the coupled bosonic excitations, while the peak in conductivity in $E \perp b$ directly shows the coupling of charge carriers to the IR active 40 cm^{-1} feature. The phonons at about 40 cm^{-1} also give an important contribution to the specific heat of β''-SC [39].

Below $T_c = 5.4$ K we observe the opening of a superconducting gap [see inset in Fig. 4(b)], where at frequencies below $2\Delta \approx 12$ cm^{-1} the reflectivity jumps to 1 at $T = 1.8$ K. Importantly, we do not see any change in the charge disproportionation features while observing the superconducting gap in optics. The size of the superconducting gap $2\Delta(0) \approx 12\,cm^{-1}$ suggests weak coupling with $2\Delta/k_B T_c \approx 3.3$.

In conclusion, in this Letter we present a study of the bandwidth tuning of fluctuating charge order in quasi-two-dimensional 1/4-filled organic conductors. We directly estimate the charge disproportionation between the lattice sites by vibrational spectroscopy, and we detect spectra of the quasi-two-dimensional electronic system characteristic of charge-order fluctuations. We show that after an increase of effective correlations, both CO fluctuations and superconductivity appear in $\beta'' - (BEDT - TTF)_2SF_5CH_2CF_2SO_3$. The strong charge fluctuations affect the density of states and the Fermi surface. This explains the unexpected discrepancy found between the calculated and measured Fermi surfaces for $\beta'' - (BEDT - TTF)_2SF_5CH_2CF_2SO_3$ [41].

The MIR spectra of BEDT-TTF 1/4-filled salts, the β'' presented in this work, θ phases (for example, [19,42,43]), and α phases [32], are amazingly similar and are all well described by the extended Hubbard model (Ref. [21]) that takes into account only electronic correlations. However, this model cannot describe the high intensity of the band due to scattering of charge carriers on CO fluctuations for β''-SC; we suggest that the interaction with the lattice should be taken into account here.

Concerning the origin of superconductivity, the enhancement of electron-phonon coupling by CO fluctuations would also enhance superconducting pairing [36] near CO with respect to the pure electronic case [8]. This would put our results in agreement with previous calculations, showing the importance of both electron-phonon and electron-molecular vibrations coupling for superconductivity [44], but it would also explain the decisive role of charge-order fluctuations, proved by our work.

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