Coexistence of charge order and superconductivity in β″-(BEDT-TTF)$_{2}$SF$_{5}$CH$_{2}$CF$_{2}$SO$_{3}$

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In the all-organic paramagnetic correlated metal β''-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ spin fluctuations can be ruled out as glue to superconductivity below $T_c = 5.5$ K. Instead, we demonstrate the coupling of charge degrees of freedom to the superconducting state, which occurs adjacent to a charge-ordered insulating phase. Comparison to isostructural β''-(BEDT-TTF)$_2$SF$_5$RSO$_3$ compounds reveals that superconductivity is suppressed when the system is tuned away from the insulator towards the metal; enhanced charge imbalance, on the other hand, leads to an increase in T_c suggesting an involvement of charge fluctuations. By locally probing the charge disproportionation through the superconducting transition, we discover slight modifications of the Fano coupling constant and intensity at T_c indicating the effect of the paired electrons on the molecular vibrations.

I. INTRODUCTION

Interactions among conduction electrons in solids lead to peculiar physical properties, most pronounced in narrow-bandwidth and low-dimensional materials; prime example is the celebrated Mott metal-insulator transition in half-filled bands[1]. The genuine Mott transition down to lowest temperatures is best observed in quantum spin liquids, i.e. strongly frustrated lattices were magnetic order is suppressed[2,3]. With the discovery of high-T_c cuprates it was realized that antiferromagnetic Mott insulators can be driven towards superconductivity by charge carrier doping, and spin fluctuations are of superior importance as driving force[4]. Also in some organic charge-transfer salts the coexistence of antiferromagnetism and superconductivity is well established[5–7].

In quarter-filled materials, on the other hand, inter-site Coulomb repulsion V is the pivotal point, often leading to charge-order instabilities but no magnetic order. Unconventional superconductivity can appear here at the boundary between metal and insulator, as well. In first approximation the nearest-neighbor exchange vanishes for a checker-board charge pattern, suggesting charge fluctuations to mediate the attractive interaction between mutually repelling electrons[8–11].

Prototypical charge-ordered systems, such as VO$_2$ or α-(BEDT-TTF)$_2$I$_3$, undergo a sharp metal-insulator transition when the electrons become localized below a certain temperature T_{CO}[1,12,13]. In the molecular-based superconductor β''-(BEDT-TTF)$_2$SF$_5$-CH$_2$CF$_2$SO$_3$, however, V is not quite strong enough with respect to the bandwidth W[14]; hence the compound remains metallic despite considerable charge imbalance and correlation effects[15–17], as illustrated in Fig. 1(b). Detailed optical investigations of this charge-ordered metal reveal the presence of charge fluctuations[10,18] and our recent broadband study of the entire β''-(BEDT-TTF)$_2$-
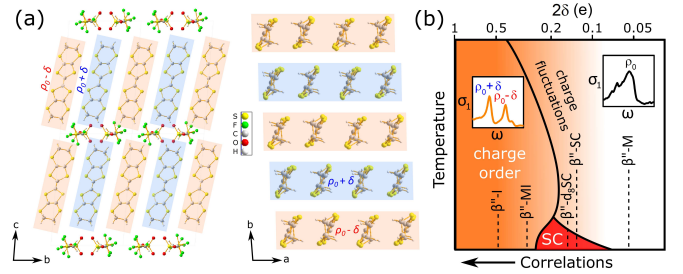

FIG. 1. (a) Molecular and crystal structure of the organic conductor β''-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ (β''-SC) where BEDT-TTF stands for bis-(ethylenedithio)tetrathiafulvalene. The stripe-like charge-order pattern is indicated by the blue and red background. (b) A generic phase diagram of 1/4-filled two-dimensional electron systems suggests[8] that the superconducting state is located right at the boundary of charge-ordered insulator and Fermi-liquid metal. We show the position of β''-SC and its fully-deuterated analogue β''-d$_8$SC, as well as β''-(BEDT-TTF)$_2$SF$_5$RSO$_3$ with slightly modified anions $R = $ CH$_2$, CHFCF$_2$ and CHF, called β''-I, β''-MI and β''-M, respectively[14]. The upper horizontal scale indicates the charge disproportionation 2δ determined in this work. The insets demonstrate that the splitting of the charge-sensitive vibrational modes is a measure of 2δ.

SF$_5$RSO$_3$ series clearly places the title compound close to the correlated insulating state[14].

Employing vibrational spectroscopy we establish charge imbalance as the order parameter guiding the metal-insulator transition in the phase diagram of quarter-filled β''-(BEDT-TTF)$_2$SF$_5$RSO$_3$. In order to examine the idea that charge-order fluctuations act as glue for unconventional superconductivity, we compare the title compound with its fully-deuterated analogue, where T_c is enhanced by 5%: concomitantly, charge disproportionation in fact increases. In the non-
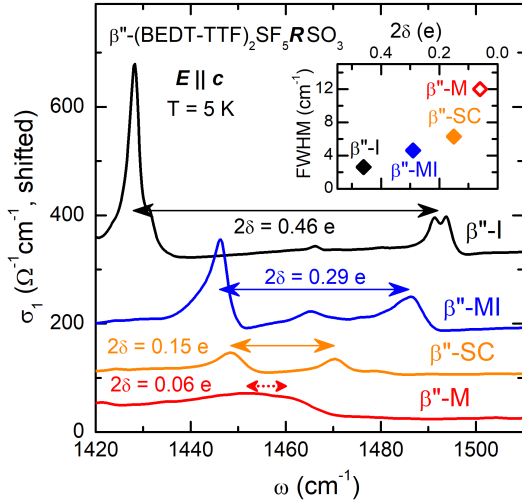
FIG. 2. The charge-sensitive vibrational band ν_{27} is compared for β''-(BEDT-TTF)$_2$SF$_5R$SO$_3$ with anions $R =$ CH$_2$, CHFCF$_2$, CH$_2$CF$_2$ and CHF, called β''-I, β''-MI β''-SC and β''-M, respectively. The charge disproportionation is largest for β''-I and reduces via β''-MI and β''-SC to a negligibly small number in β''-M[14]. Inset: As the splitting is reduced, the full-width at half-maximum (FWHM) continuously increases. The open symbol denotes that the value of β''-M bears significant inaccuracy as the peaks overlap due to small separation.

superconducting sister compounds, on the other hand, either insulating behavior prevails or charge order is absent in the metal. Furthermore, we observe that the charge response slightly alters when entering the superconducting state, suggesting a coupling of charge degrees of freedom and superconductivity.

II. MATERIALS AND EXPERIMENTS

Single crystals of the superconductor β''-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$, abbreviated β''-SC, and its counterpart with fully-deuterated donor molecules (β''-d$_8$SC), as well as the non-superconducting compounds with organic anions $R =$ CH$_2$ (β''-I), CHFCF$_2$ (β''-MI) and CHF (β''-M) have been synthesized by electrochemical methods[19–21]; the structure is depicted in Fig. 1(a). The optical experiments are conducted on the shiny bc-surfaces of up to 2 mm in size without further treatment. Furthermore, β''-SC single crystals were characterized by SQUID magnetometry and dc resistivity to verify the superconducting properties. Infrared reflectivity spectra are obtained by standard Fourier-transform spectroscopy with 1 cm^{-1} resolution. In order to achieve temperatures as low as $T = 2.9$ K, we use a helium bath cryostat with the sample immersed in helium exchange gas.

Girlando *et al.*[18] proposed the β''-(BEDT-TTF)$_2$-SF$_5R$SO$_3$ family as a prototype realization of the genuine phase diagram of 1/4-filled materials. Starting at the strongly correlated side, β''-I shows insulating transport

properties up to room temperature[20] followed by β''-MI which undergoes a metal-insulator transition at 170 K[21]; β''-SC ($T_c = 5.5$ K[19]) and β''-M exhibit metallic transport properties at all temperatures[10]. Here, electronic correlations V/W are driven by the inter-site Coulomb repulsion ($V \ll U$) rather than the on-site energy U in a Mott insulator at $1/2$ filling[14]. Previous dynamical mean-field theory calculations on the 1/4-filled extended Hubbard model suggested that pure charge fluctuations can stabilize d-wave superconductivity in the vicinity of the metal-insulator transition where correlation effects are most pronounced[8].

III. RESULTS

A. Charge disportionation as order parameter

To that end, we measured the out-of-plane ($E \parallel c$) optical conductivity in the low-temperature insulating state of β''-I and β''-MI and compare it in Fig. 2 to β''-SC and β''-M[14,17]. The ν_{27}(B$_{1u}$) vibration around 1460 cm^{-1} is known to be most sensitive to the charge on the molecule and is therefore commonly utilized as a local probe [22,23]. Indeed, the charge disproportionation 2δ determined from the splitting of the ν_{27} mode diminishes considerably in the order I–MI–SC–M, as summarized in Fig. 1(b). While previous notions were based on room-temperature values of 2δ in β''-I and β''-MI[18], here conclusive experimental evidence is provided for an increasing charge imbalance towards the insulating state, which is thus clearly identified as the order parameter. We also find that the vibrational features become more narrow as 2δ increases (Fig. 2 inset). According to the two-state jump model used to fit vibrational bands[18], the width is a measure of charge fluctuations, which clearly increases upon approaching the metallic side. Importantly, β''-SC is located between β''-MI and β''-M placing it close to the phase boundary between correlated metal and charge-ordered insulator. This unique position in the phase diagram combines appreciable charge disproportionation with significant charge fluctuations, fostering superconducting pairing.

Apart from strong correlation effects observed in the electrodynamic response[10,14], the inverse isotope shift constitutes further evidence for the unconventional nature of superconductivity in β''-SC: in the deuterated crystals the superconducting transition is enhanced by $\Delta T_c = 0.25$ K[24], opposite to the BCS prediction for phonon-mediated superconductivity[25]. In order to explore the relation between molecular site charge and superconductivity more deeply, we thoroughly compare the vibrational spectrum of β''-SC and β''-d$_8$SC in Fig. 3 and determine the molecular site charges. Evidently, those modes that include motions of the deuterium atoms are shifted significantly to lower frequencies due to the larger mass. We specifically identify CH$_2$ twisting and wagging vibrations below 1500 cm^{-1}, as well as C-H stretching
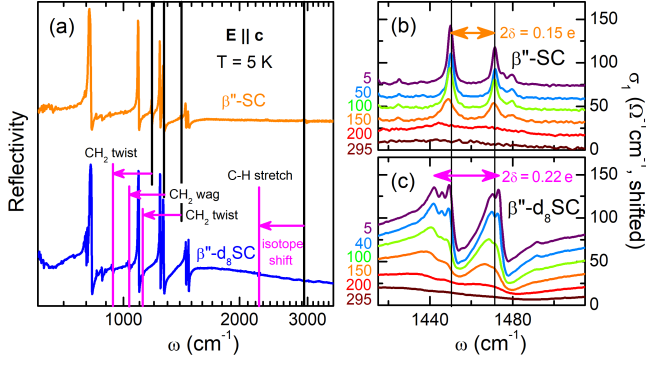
FIG. 3. (a) Comparison of the out-of-plane ($E \parallel c$) reflectivity spectra of d_8 and h_8 β''-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ yields pronounced red shifts of the CH$_2$ (twist, wag) and C-H (stretch) vibrations upon deuteration. The charge-sensitive ν_{27} mode around 1460 cm^{-1}, however, remains unaffected since it mainly involves the C=C bonds rather than hydrogen atoms. (b) Optical conductivity of β''-SC plotted in the range of the ν_{27} mode for various temperatures. (c) The splitting $\Delta\nu$ of the C=C vibrations is enlarged in β''-d_8SC, evidencing an increase of the charge disproportionation 2δ from 0.15e to 0.17e (average) and 0.22e (maximum peak separation). The additional fine structure of the modes indicates a more complex charge pattern. The concomitant enhancement of superconductivity by $\Delta T_c \approx 0.25$ K[24] nourishes the idea of charge fluctuations as the pairing glue of superconductivity in the vicinity of the metal-insulator transition.

around 2000–3000 cm^{-1}, all of which are red-shifted by 200 cm^{-1} or more. Seeing no residual h_8-resonance frequencies proves that the β''-d_8SC crystal is completely deuterated.

The strong ν_{27}(B$_{1u}$) mode around 1460 cm^{-1} mainly involves the C=C bonds and stays basically unaffected by hydrogen motions in the ethylene end group, in accord with Refs. 26 and 27. With lowering T to 5 K, the peak of the h_8-crystal splits by $\Delta\nu_{27} = 21$ cm^{-1} corresponding to a charge disproportionation $2\delta = 0.15e$; while for β''-d_8SC we extract a maximum splitting of 31 cm^{-1}, which amounts to $2\delta = 0.22e$. In addition several side bands occur, indicating inequivalent molecules and a generally more complex crystal structure. This may be the result of an enlarged supercell due to a non-trivial charge pattern. On average, the two broad trios of charge-rich and -poor sites are separated by 0.17e, which is considerably larger than in the h_8-compound.

From these observations we draw the clear conclusion that superconductivity is closely linked to the competition of the metallic and the charge-disproportionate insulating states close to the transition. While charge order is basically absent ($2\delta \leq 0.06e$) in the metallic compound β''-M[10,17], it strongly develops in the superconductor β''-SC and becomes even more pronounced in the deuterated crystal with a higher T_c; insulating behavior takes over in β''-MI and β''-I where 2δ is significantly larger[14,20,21].
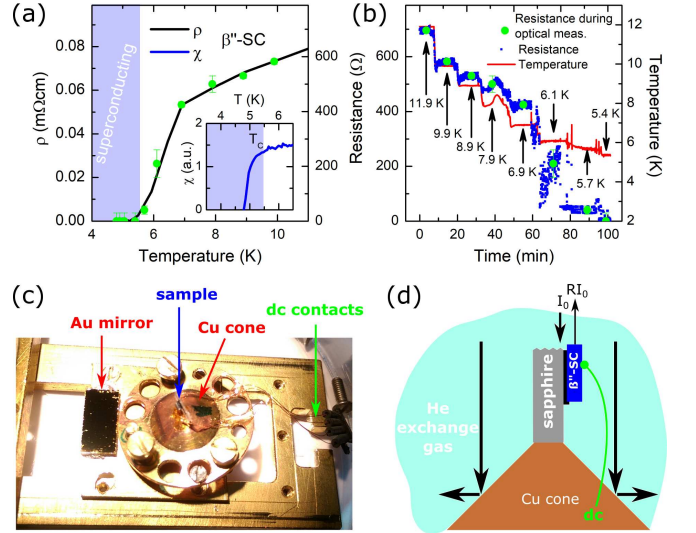

FIG. 4. (a) Temperature dependent resistivity and susceptibility of the β''-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ crystal used for optical experiments. Strong diamagnetic shielding below $T_c = 5.5$ K verifies the superconducting state. (b) Time evolution of the sample resistance (blue points, left scale) and corrected temperature (red curve, right scale) upon slowly cooling down. When a certain temperature value was sufficiently stabilized (plateau), the optical spectra are recorded (green dots). The last points are taken in the superconducting state with vanishing resistivity. (c) The single crystal is mounted on a cone in the He-bath cryostat ($T \geq 2$ K) in order to measure reflectivity in out-of-plane orientation ($E \parallel c$); here the surface was 0.3×1 mm^2. (d) The electrical resistivity was probed *in situ* by four gold wires glued to the specimen by carbon paste. Electrical isolation was achieved by a sapphire plate, the surface of which was rough and misaligned in order to avoid any parasitic signal. After all, only back-reflection off the sample was measured.

B. Charge order and superconductivity

The question now arises, whether charge disproportionation is still present in the superconducting phase; in other words, is there a region where charge-order and superconductivity coexist? While the normal and superconducting states of β''-SC and β''-d_8SC have been exhaustively studied[15,19,20,24,28–30], the interplay of charge order and superconductivity is still unexplored and the border region remains *terra incognita*. In analogy to superconductivity in the vicinity of a magnetically ordered phase, where a certain range of coexistence was identified[5,7], one could imagine that also charge disproportionation and superconductivity appear simultaneously in a specific region of the phase diagram. Possible scenarios include a competition with metal-insulator phase segregation like in Mott systems, or superconductivity emerging from a charge-ordered metal.

To tackle this fundamental issue, the charge-sensitive ν_{27} mode was measured down to lowest temperatures $T < 5$ K. As shown in Fig. 4(a), in the single crys-

tal probed here superconductivity is established at $T_c = 5.5$ K as identified by a sharp drop of the spin susceptibility, indicating high sample quality; at this temperature also the dc resistivity has completely vanished. *In-situ* dc-transport measurements [Fig. 4(c,d) shows experimental realization] monitored the actual temperature of the crystal and provided clear evidence for the onset of superconductivity[31]. Fig. 4(b) illustrates the time dependence of the sample resistance during the experiment; after ramping, the temperature was equilibrated for several minutes in order to perform the optical measurement (2×2 min acquisition time), which is corroborated by the resistivity plateaus corresponding to the stabilized temperature. Each green symbol denotes the starting point of an optical experiment. The last spectra in this series were certainly recorded in the superconducting state as the four-point resistivity has completely vanished. Yet, a considerable volume fraction is still in the metallic state when the temperature is only 1 K below T_c.

The raw data of the optical reflectivity of β''-SC are plotted in Fig. 5 in the spectral range around the ν_{27} mode. For the first time, the charge-sensitive vibrations are monitored while entering the superconducting state. The overall splitting $\Delta\nu_{27}$ due to the differently charged molecules on the A and B sites is not affected by the phase transition; i.e. 2δ remains constant at all measured temperatures and no additional features appear. Though, both peaks become more intense as the sample turns superconducting, as highlighted by the inset of Fig. 5(a).

For a more quantitative analysis, the vibrational features are fitted by one Fano function each; the corresponding fit parameters are presented in Fig. 5(b-e) as a function of temperature. While the resonance frequency and width of the modes are constant within the error bars in the entire temperature range $T < 10$ K, the intensity is enhanced by about 15 % when the sample becomes superconducting. The oscillator strength saturates at a certain level rather than continuing to increase upon cooling. The Fano parameter q is a measure of the coupling to the electronic background; the significant modification may reflect the interaction between charge fluctuations and Cooper pairs. We interpret the enhanced intensity of the infrared-active vibration mode as a result of modified screening in the superconducting state. An in-depth analysis and theoretical description is a desideratum subject to future efforts.

IV. DISCUSSION

These experimental results unambiguously demonstrate that the charge disproportionation persists unaltered in the superconducting state. No additional peaks appear around the frequency of BEDT-TTF$^{+0.5}$, implying that pairing takes place in presence of a sizeable charge-density modulation. *Vice versa*, the condensation of the conduction electrons to Cooper pairs does not af-
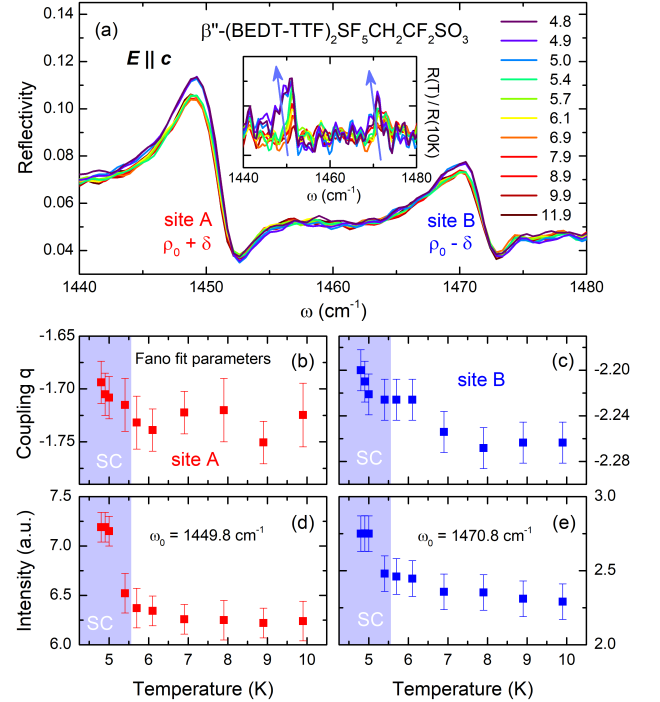

FIG. 5. (a) Splitting of the charge sensitive $\nu_{27}(B_{1u})$ mode in β''-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ recorded at $T < 12$ K. While the resonance frequencies of the two peaks do not change, the intensity is enhanced below $T_c = 5.5$ K, as illustrated by the reflectivity ratio (inset). The two peaks A and B corresponding to site charges $\rho_0 + \delta$ and $\rho_0 - \delta$, respectively, were fitted by one Fano function each. There are significant modifications of the coupling parameter q (b,c) and the intensity (d,e) when entering the superconducting state.

fect the charge on the different A and B sites. In other words, by locally probing the electronic density our spectroscopic investigations provide compelling evidence for a coexistence of charge order and superconductivity.

The stability of pairing with respect to charge disproportionation in quarter-filled systems is distinct from Mott insulators, where a phase segregation between metal/superconductor and (antiferromagnetic) insulator occurs below the critical endpoint of the first-order transition[5,7]. In the latter case a clear competition of the two ground states is oberved; on the other hand, the imbalance between site charges in β''-SC tends to cooperate with the correlated metallic state and enable superconductivity.

To that end, it remains highly desirable to elucidate what happens upon approaching and, eventually, crossing the metal-insulator transition in the material under investigation. The phase diagram in Fig. 1(b), based upon 2δ determined in this work and Ref. 14, substantiates that the closely related compounds β''-I and β''-MI are subject to even stronger Coulomb interactions. While under ambient conditions they are on the insulating side, external pressure can reduce the effective correlations V/W. Our ongoing optical and dc trans-

port investigations under pressure target at this unresolved issue, and the role of structural effects and anion polarity for charge disproportionation in β''-(BEDT-TTF)$_2$SF$_5$$RSO_3$. Following the line of photoexcited nonequilibrium superconductivity[32] we further suggest to selectively excite the molecular vibrations, which may provide a route to stimulate charge fluctuations and thus enhance superconductivity.

V. SUMMARY

From our comprehensive spectroscopic investigations on the series β''-(BEDT-TTF)$_2$SF$_5$$RSO_3$ we establish the experimental phase diagram of the bandwidth-tuned charge-order transition at $1/4$ filling. As these organic materials change from insulating to metallic, on the one hand, the charge disproportionation 2δ decreases in the sequence $R = $ CH$_2$ (β''-I), CHFCF$_2$ (β''-MI), CH$_2$CF$_2$ (β''-SC), CHF (β''-M); while on the other hand the width of charge-sensitive vibration modes increases suggesting enhanced charge fluctuations. We conclude a close relation between the charge imbalance and superconductivity in β''-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ – either directly by charge fluctuations mediating Cooper pairing[8],

or via the effective mass enhancement as a result of intensifying electronic correlations when approaching the insulator. In the deuterated analogue 2δ is larger and correspondingly T_c is enhanced, substantiating that superconductivity depends on charge order in these $1/4$-filled electron systems.

The charge-sensitive $\nu_{27}(\mathrm{B}_{1u})$ vibration was measured in the superconducting state below $T_c = 5.5$ K, as verified by *in-situ* transport experiments. We unambiguously observe charge order and superconductivity simultaneously, providing evidence that these two ground states do not compete with each other, but coexist – strikingly different from the Mott transition at $1/2$ filling where metallic and insulating states are phase-segregated.

1. M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. **70**, 1039 (1998).
2. A. Pustogow, M. Bories, A. Löhle, R. Rösslhuber, E. Zhukova, B. Gorshunov, S. Tomić, J. A. Schlueter, R. Hübner, T. Hiramatsu, Y. Yoshida, G. Saito, R. Kato, T.-H. Lee, V. Dobrosavljević, S. Fratini, and M. Dressel, Nat. Mater. **17**, 773 (2018).
3. M. Dressel and A. Pustogow, J. Phys. Condens. Matter **30**, 203001 (2018).
4. B. Keimer, S. A. Kivelson, M. R. Norman, S. Uchida, and J. Zaanen, Nature **518**, 179 (2015).
5. S. Lefebvre, P. Wzietek, S. Brown, C. Bourbonnais, D. Jérome, C. Mézière, M. Fourmigué, and P. Batail, Phys. Rev. Lett. **85**, 5420 (2000).
6. T. Vuletić, M. Héritier, D. Jérome, C. Pasquier, S. Tomić, K. Bechgaard, and P. Auban-Senzier, Eur. Phys. J. B **25**, 319 (2002).
7. P. Limelette, P. Wzietek, S. Florens, A. Georges, T. A. Costi, C. Pasquier, D. Jérome, C. Mézière, and P. Batail, Phys. Rev. Lett. **91**, 16401 (2003).
8. J. Merino and R. H. McKenzie, Phys. Rev. Lett. **87**, 237002 (2001).
9. J. Merino, A. Greco, N. Drichko, and M. Dressel, Phys. Rev. Lett. **96**, 216402 (2006).
10. S. Kaiser, M. Dressel, Y. Sun, A. Greco, J. A. Schlueter, G. L. Gard, and N. Drichko, Phys. Rev. Lett. **105**, 206402 (2010).
11. G. Koutroulakis, H. Kühne, H. H. Wang, J. A. Schlueter, J. Wosnitza, and S. E. Brown, (2016), arXiv:1601.06107.
12. M. Dressel, Naturwissenschaften **94**, 527 (2007).
13. S. Tomić and M. Dressel, Rep. Prog. Phys. **78**, 96501 (2015).
14. A. Pustogow, K. Treptow, A. Rohwer, Y. Saito, M. Sanz Alonso, A. Löhle, J. A. Schlueter, and M. Dressel, Phys. Rev. B **XX**, YYYYYY (2019).
15. J. Hagel, J. Wosnitza, C. Pfleiderer, J. A. Schlueter, J. Mohtasham, and G. L. Gard, Phys. Rev. B **68**, 104504 (2003).
16. M. Dressel and N. Drichko, Chem. Rev. **104**, 5689 (2004).
17. N. Drichko, S. Kaiser, Y. Sun, C. Clauss, M. Dressel, H. Mori, J. Schlueter, E. I. Zhyliaeva, S. A. Torunova, and R. N. Lyubovskaya, Physica B: Condens. Matter **404**, 490 (2009).
18. A. Girlando, M. Masino, S. Kaiser, Y. Sun, N. Drichko, M. Dressel, and H. Mori, Phys. Status Solidi B **249**, 953 (2012); A. Girlando, M. Masino, J. A. Schlueter, N. Drichko, S. Kaiser, and M. Dressel, Phys. Rev. B **89**, 174503 (2014).
19. U. Geiser, J. A. Schlueter, H. H. Wang, A. M. Kini, J. M. Williams, P. P. Sche, H. I. Zakowicz, M. L. VanZile, J. D. Dudek, P. G. Nixon, R. W. Winter, G. L. Gard, J. Ren, and M.-H. Whangbo, J. Am. Chem. Soc. **118**, 9996 (1996).
20. B. H. Ward, J. A. Schlueter, U. Geiser, H. H. Wang, E. Morales, J. P. Parakka, S. Y. Thomas, J. M. Williams, P. G. Nixon, R. W. Winter, G. L. Gard, H.-J. Koo, and M.-H. Whangbo, Chem. Mater. **12**, 343 (2000).
21. J. A. Schlueter, B. H. Ward, U. Geiser, H. H. Wang, A. M. Kini, J. Parakka, E. Morales, H.-J. Koo, M.-H. Whangbo, R. W. Winter, J. Mohtasham, and G. L. Gard, J. Mater. Chem. **11**, 2008 (2001).
22. T. Yamamoto, M. Uruichi, K. Yamamoto, K. Yakushi, A. Kawamoto, and H. Taniguchi, J. Phys. Chem. B **109**, 15226 (2005).
23. A. Girlando, J. Phys. Chem. C **115**, 19371 (2011).

[24] J. Schlueter, A. Kini, B. Ward, U. Geiser, H. Wang, J. Mohtasham, R. Winter, and G. Gard, Physica C: Superconductivity **351**, 261 (2001).

[25] BCS theory predicts T_c to scales with the Debye frequency, i.e. the square root of the inverse mass; implying that the critical temperature should be lowered when the hydrogen atoms in the BEDT-TTF cations are substituted by the heavier deuterium. The increase of T_c indicates that other effects are more important, such as the coupling of the terminating ethylene groups to the anion sheets.

[26] J. E. Eldridge, C. C. Homes, J. M. Williams, A. M. Kini, and H. H. Wang, Spectrochim. Acta A **51**, 947 (1995).

[27] E. Demiralp and W. A. Goddard, J. Phys. Chem. A **102**, 2466 (1998).

[28] M. Glied, S. Yasin, S. Kaiser, N. Drichko, M. Dressel, J. Wosnitza, J. Schlueter, and G. Gard, Synth. Met. **159**, 1043 (2009).

[29] S. Kaiser, S. Yasin, N. Drichko, M. Dressel, T. Rõõm, D. Hüvonen, U. Nagel, G. L. Gard, and J. A. Schlueter, Phys. Status Solidi B **249**, 985 (2012).

[30] G. Koutroulakis, H. Kühne, J. A. Schlueter, J. Wosnitza, and S. E. Brown, Phys. Rev. Lett. **116**, 67003 (2016).

[31] While the temperature sensor nominally showed temperatures down to 2.9 K, test measurements reveal that the actual temperature at the sample surface was 2 K higher as a result of the infrared radiation insufficiently compensated by thermal coupling. The temperature values have been corrected for this offset.

[32] S. Kaiser, C. R. Hunt, D. Nicoletti, W. Hu, I. Gierz, H. Y. Liu, M. Le Tacon, T. Loew, D. Haug, B. Keimer, and A. Cavalleri, Phys. Rev. B **89**, 184516 (2014); M. Mitrano, A. Cantaluppi, D. Nicoletti, S. Kaiser, A. Perucchi, S. Lupi, P. Di Pietro, D. Pontiroli, M. Riccò, S. R. Clark, D. Jaksch, and A. Cavalleri, Nature **530**, 461 (2016).