Band-structure anisotropy and superconducting fluctuations in ditetramethyltetraselenafulvalenium salts $(TMTSF)_2X$

H. J. Schulz
Institut Laue-Langevin, Boîte Postale 156X, F-38042 Grenoble, France

D. Jérome and K. Bechgaard*
Laboratoire de Physique des Solides, Université Paris-Sud, F-91405 Orsay, France

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This Comment shows that the anisotropy of the band structure of the $(TMTSF)_2X$ conducting salts derived from experimental data $t_a:t_b:t_c \approx 300:30:1$ is not inconsistent with large superconducting precursor effects around 10 or 15 K. This is a temperature domain which is about 10 times higher than the maximum temperature for the onset of long-range ordered three-dimensional superconductivity ($T_c \approx 1.2$ K). Furthermore, there is a large number of experimental results which are not consistent with single-particle transport properties at low temperature. Likewise the interpretation of the pseudogap and the magnetoresistance in terms of spin-density waves has to our knowledge no experimental support. The existence of superconducting fluctuations seems, at least presently, to be the only consistent interpretation.

The quasi-one-dimensional organic salts of the type $(TMTSF)_2X$ (TMTSF = tetramethyltetraselenafulvalene, $X = PF_6$, AsF_6, TaF_6, ClO_4, ReO_4, ...) exhibit a wide variety of interesting low-temperature properties: unusually high dc conductivity[1] sensitive to magnetic field, superconductivity,[2-5] spin-density waves (SDW),[6-8] SDW superconductivity competition,[9-11] and order-disorder transitions of the inorganic anions.[12,13] An overview of the properties of the $(TMTSF)_2X$ compounds can be found in recent conference proceedings[14] and in review articles.[15] A particularly debated point has been the possibility of important effects of superconducting fluctuations above the critical temperature $T_c \approx 1.2$ K, as proposed by the present authors on the basis of conductivity[2,16] and tunneling[17] measurements. In a recent Communication[18] Kwak reanalyzed the plasma-edge data of Jacobsen *et al.*[19] and concluded that the resulting band-structure anisotropy is far too small to allow large fluctuation, i.e., the superconducting transition should be essentially mean-field-like. In the present Comment we point out that the results of Kwak are not inconsistent with strong fluctuations. Furthermore, we comment on several erroneous or misleading statements of Ref. 18, showing that the "flaws" in the fluctuation picture, mentioned by Kwak, are actually nonexisting. Finally, we show that there is a number of experimental results which are hard to reconcile with single-electron transport, whereas superconducting fluctuations provide at least a qualitative explanation.

Following Kwak,[18] we approximate the triclinic structure of the $(TMTSF)_2X$ salts[20] by an orthorhombic one. Further, we assume a tight-binding band structure

$$\epsilon(\vec{k}) = -2\sum_{j=a,b,c} t_j \cos(jk_j) - E_F \ , \tag{1}$$

where a is the direction of the molecular stacks, t_a, t_b, and t_c are transfer integrals, and E_F is the Fermi energy. We neglect the weak dimerization of the stacks,[20] which modifies the single-electron energies near $k_a = \pi/2a$, but not near the Fermi level $k_F \approx 3\pi/4a$. We thus have[20] $a = 3.6$ Å, $b = 7.7$ Å, and $c = 13.5$ Å. The analysis of Ref. 18 then yields $t_a = 0.35$ eV and $t_a/t_b = 10$. The value of t_a is very large compared to other organic conductors,[15] and is also larger than calculated values[21] by more than a factor 2. The problem may lie in the Drude fit of the optical data[19] especially in the determination of the background dielectric constant. A reasonable compromise seems to be $t_a = 0.25$ eV. Using the relation[22] for the conductivity anisotropy,

$$\sigma_a/\sigma_b = (at_a/bt_b)^2 \ , \tag{2}$$

one finds $\sigma_a/\sigma_b \approx 25$, in agreement with results of Greene *et al.*[23] However, other groups[1,16,24] have reported $\sigma_a/\sigma_b = (2-4)\times 10^2$, requiring, from Eq. (2), $t_a/t_b \gtrsim 30$. Because there are inherent uncertainties both of the Drude fit and of Eq. (2), we assume $t_a/t_b \approx 10-20$. The anisotropy in the b-c plane is much less problematic: both from conductivity[24] and critical-field anisotropies[23] one obtains[15] $t_b/t_c = 30$. As noted in Ref. 18, the above results imply a Fermi surface open in the transverse (b,c) directions.

A measure for the importance of fluctuation effects can be obtained from the first fluctuation correction to the mean-field transition temperature T_c^0, as calculated from Ginzburg-Landau theory. For mean-field theory to be valid, this correction should be small. For an open Fermi surface a Ginzburg-Landau–type free-energy functional has been derived previously[16,25] as

$$F = \sum_{mn}\int dx\left\{\alpha|\psi_{mn}|^2 + \beta|\psi_{mn}|^4 + \gamma\left|\frac{\partial\psi_{mn}}{\partial x}\right|^2 - 2\lambda_b \mathrm{Re}(\psi^*_{mn}\psi_{m+1,n}) - 2\lambda_c \mathrm{Re}(\psi^*_{mn}\psi_{m,n+1})\right\} \ , \tag{3}$$

where (m,n) number the chains in the b and c directions, and $\psi_{mn}(x)$ is the superconducting order parameter on chain (m,n). The coefficients in F are

$$\alpha = \alpha' \ln(T/T_c^0) \approx \alpha'(T/T_c^0 - 1) \ , \tag{4a}$$

$$\alpha' = 8\pi^2 T^2/7\zeta(3) m v_F^2 \chi[(2\pi\tau T)^{-1})] \ , \tag{4b}$$

$$\beta = \alpha'(2mv_F)\chi[(2\pi\tau T)^{-1}] \ , \tag{4c}$$

$$\gamma = 1/2m \ , \tag{4d}$$

$$\lambda_j = t_j^2/mv_F^2, \quad j = b,c \ . \tag{4e}$$

Here v_F is the Fermi velocity, $m = k_F/v_F$ is the Fermi-surface effective mass, the electron lifetime parameter τ is related to the mean free path l by $l = v_F\tau$, $\zeta(x)$ is the Riemann's ζ function, $\chi(x)$ is the Gorkov function[26]

$$\chi(x) = \frac{8}{7\zeta(3)x}\left\{\frac{\pi^2}{8} + \frac{1}{2x}\left[\psi\left(\frac{1}{2}\right) - \psi\left(\frac{1+x}{2}\right)\right]\right\} , \quad (5)$$

and $\psi(x)$ is the diagamma function. From Ref. 25, to lowest order in the fluctuations, the critical temperature is

$$T_c = T_c^0(1 - T_c^0/J) \quad (6a)$$

with[27]

$$J = \left(\frac{t_b t_c}{2}\right)^{1/2} \chi[(2\pi\tau T)^{-1}]\left[\left(\frac{t_b}{t_c}\right)^{1/2} \operatorname{arcsinh}\frac{t_c}{t_b} + \left(\frac{t_c}{t_b}\right)^{1/2} \operatorname{arcsinh}\frac{t_b}{t_c}\right]^{-1} = \frac{t_b}{7.2}\chi\left(\frac{0.884\zeta_0}{l}\right) . \quad (6b)$$

In the second part in Eq. (6b) we have used $t_b/t_c = 30$ and have introduced the BCS coherence length $\xi_0 = 0.18 v_F/T_c^0$. In the "clean limit" $l >> \xi_0$ one has $\chi = 1$. Following our above discussion, for $t_b = 25$ meV and $t_b = 12$ meV (the first value has also been obtained theoretically[21]) one derives $J = 40$ K and $J = 20$ K, respectively. These values are certainly consistent with a mean-field behavior around $T_c^0 = 1$ K, as proposed by Kwak.[18] On the other hand, the picture of strong fluctuations[15,16] implies $T_c^0 = 10$–15 K, so that, from Eq. (6a), fluctuation effects can no more be considered as small. Further, the assumption of the "clean limit" is far from obvious. For example, the Drude fit to the low-temperature plasma edge[19] implies $l \approx 10a$, leading to $J = 3$–6 K. Together with $T_c^0 = 10$ K this value of J implies large fluctuation effects. This shows that the band-structure parameters derived by Kwak[18] are actually consistent both with either a mean-field-like transition at $T_c^0 = 1$ K or with $T_c^0 = 10$–15 K and large fluctuation effects. Theory cannot decide for or against one of the possibilities from the band-structure data alone. In any case, even being optimistic, the above theory cannot be expected to be accurate to within less than a factor 2. This is especially true in quasi-one-dimensional systems with their competition between superconducting and density or spin-wave instabilities.

Assuming the strong fluctuation picture to be valid the above numbers imply a longitudinal Ginsburg-Landau coherence length $\xi_a(0) = 3\xi_0[\chi(0.884\xi_0/l)]^{1/2}/4$ of about $20a$. Further, as discussed in Ref. 16, *above* T_c^0 strong fluctuation effects can be approximately described replacing T_c^0 by an effective temperature $T_0 \approx T_c^0/3$. Using $t_a/t_b = 10$–20 we then find a crossover temperature, defined by $\xi_b(T_b^*) = b$, $T_b^* \approx T_c^0$. Above T_b^* the fluctuations are essentially one dimensional so that the analysis developed in Ref. 16 and showing good qualitative agreement between the fluctuation picture and the measured resistivity should be valid. *Below* T_c^0 strong fluctuation effects can no more be accounted for by the Hartree-Fock–type theory used in Ref. 25. For relatively wide (on an atomic scale) superconducting strips, having a small Ginzburg critical region around T_c^0, the low-temperature conductivity can be described in terms of the dynamics of the phase of the order parameter alone,[28] leading to much higher conductivity than obtained from Ginzburg-Landau theory. However, in the present case the Ginzburg critical region *around* T_c^0 is comparable[25] to T_c^0, and furthermore there are non-negligible interchain correlations below T_c^0.[29] Thus the theory of Ref. 28 is not applicable in the present case. A transport theory valid under these conditions is still lacking. These points imply that the theory we presented previously[16] is inapplicable below T_c^0. Therefore we do not think that the problems related to the parameter B and discussed by Kwak[18] can be taken as conclusive evidence against the fluctuation picture.[30]

In $J < T_c^0$ [Eq. (6a)], fluctuations reduce the actual transition temperature T_c so much below T_c^0 that Ginzburg-Landau theory can no more be used as a starting point. For this, a recent theory[31] considering only phase fluctuations, taking into account their quantum nature and treating interchain coupling in a mean-field approximation, has demonstrated that the relations between T_c ($<< T_c^0$), the condensation energy and the normal-state specific heat are BCS-like, the linearly temperature-dependent normal-state specific heat being due to phase fluctuations rather than to single electron excitations. Further, the critical region around T_c is quite narrow. These results allow an interpretation of the specific-heat results of Garoche *et al.*[32] in terms of the fluctuation picture contrary to the assertions of Kwak.[18]

Our above arguments do not allow to discriminate between the two pictures: (i) a mean-field-like transition at $T_c^0 \approx 1$ K, assuming the "clean limit" to hold (i.e., $l >> \xi_0 = 0.2 v_F/T_c^0 = 800a = 3000$ Å) and implying essential single-electron transport above T_c^0; or (ii) the picture of strong fluctuations, with $T_c^0 \approx 10$–15 K and $l < \xi_0 = 80a$. Let us now discuss some experimental results we find hard to understand within the mean-field–single-particle picture, whereas the fluctuation picture provides an (at least qualitative) explanation.

The main feature of the low-temperature electronic properties of conducting phases in this family of compounds is a depression of the density of states and the sensitivity of this depression to magnetic fields. This is directly demonstrated in three different experiments: (1) specific heat, (2) thermal conductivity, and (3) low-frequency spectroscopy.

At low temperature ($T < 3$ K) the electronic contribution to the specific heat of $(TMTSF)_2ClO_4$ has been measured as a function of a magnetic field applied along the c^* direction.[32] An increase of $N(E_F)$ ranging from 70 to 100% is observed in a field of 20 kOe. Similarly, the study of the thermal conductivity[33] of $(TMTSF)_2ClO_4$ and $(TMTSF)_2PF_6$ at ambient and 12 kbar, respectively, clearly shows a significant drop of κ below 50 K. This behavior is striking for two reasons. (i) In the same T domain σ_{dc} is strongly T dependent[4] and therefore one could expect heat to be carried by the electrons when σ_{dc} reaches $\approx 2\times 10^5$ $(\Omega\ \mathrm{cm})^{-1}$ at helium temperature according to the Wiedemann-Franz proportionality relation between κ_e and σ. (ii) The drop of κ diminishes significantly, especially below 25 K, by the application of a magnetic field[33] (the largest effect is achieved for H along the c direction). This sensitivity to a magnetic field

demonstrates that the drop of κ at low temperature can be attributed to a modification of the electronic structure and cannot be a simple phonon effect. In terms of the Wiedemann-Franz law, the field dependence of κ is in striking contrast with that of σ[24] because opposite field dependences are observed experimentally.

Various spectroscopic techniques have provided an estimate of the energy width of the depression of the density of states around the Fermi energy. Schottky tunneling[17,34] performed on $(TMTSF)_2PF_6$ under 11 kbar or on $(TMTSF)_2ClO_4$ at ambient pressure point to an approximate width $2\Delta \approx 3$–4 meV of the pseudogap. Likewise, the far-infrared reflectance of $(TMTSF)_2ClO_4$ (Ref. 35) studied down to 2 K reveals an optical absorption threshold (sensitive to magnetic field) around 3.8 meV. Below 30 K a drastic increase of the dc conductivity is observed upon cooling instead of the drop which can be inferred from the decrease of $N(E_F)$ at low temperature in a single-particle model. The frequency dependence of the conductivity provides a low, nearly frequency- and magnetic-field-independent value of the conductivity above 30 cm^{-1} or so [$\sigma(\omega > 30\ cm^{-1}) \approx 2000\ (\Omega\ cm)^{-1}$] contrasted with the large dc conductivity $\gtrsim 10^5\ (\Omega\ cm)^{-1}$. The gap is observed at 3.8 meV and thus a giant conductivity (strongly field dependent) peak of width ≈ 1–$2\ cm^{-1}$ is expected at zero frequency when comparing dc and far-infrared reflectance data.[36] In summary, the above-mentioned experimental data strongly suggest the existence below 30 K or so of a significant pseudogap in the single-particle density of state around the Fermi level. The occurrence of a deltalike zero-frequency, collective mode of the electrical conductivity is also indicated. In $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$ at ambient pressure the ground state is clearly a SDW state.[6–8,37] Therefore, we may consider magnetic fluctuations towards the SDW ordering as the origin of both the conducting collective mode and the single-particle energy spectrum. We infer that such an interpretation of the precursor effects is very unlikely for the following reasons.

(i) Commensurability of the SDW instability would be expected to prevent (possible) fluctuating SDW's from contributing to the dc conduction,[38] especially at very low temperature when $kT < \omega_{pin}$ (where ω_{pin} is the pinning energy of the commensurate SDW).

(ii) There are no signs of magnetism in the low-temperature conducting phases provided either from NMR data[11,39–41] or from low-field ESR experiments.[42] Both experminental techniques are known to be very sensitive to the onset of magnetism.[6,7]

Kwak[18] argues that tunneling data can be interpreted by a *static* SDW ordering. Likewise the large magnetoresistance could be due to small pockets induced by SDW's. However, the above points (i) and (ii) rule out such an explanation. Furthermore, whenever a SDW state is stabilized in the $(TMTSF)_2X$ series, i.e., in $(TMTSF)_2PF_6$ or AsF_6 at low pressure or in the R state of $(TMTSF)_2ClO_4$ under high field it is further stabilized by the application of a magnetic field.[11,43] In contrast the anomalies in the tunneling data, heat conductivity and specific heat are *suppressed* by the application of a magnetic field. Finally we should mention that small pockets of Fermi surface in $(TMTSF)_2PF_6$ under pressure[44] or $(TMTSF)_2ClO_4$ (Ref. 45) (R state) exist only under high magnetic field, after a field-induced phase transition.[11,32,46]

In conclusion we have shown that the existing results on the band-structure anisotropy $t_a:t_b:t_c \approx 300:30:1$ of $(TMTSF)_2X$ salts are not inconsistent with large fluctuation effects around $T_c^0 \approx 10$–15 K. Furthermore, there is a large number of experimental results that are inconsistent with single-particle transport properties. Likewise the interpretation of the origin of the pseudogap and the magnetoresistance in terms of spin-density waves has, to our knowledge, no experimental support. The existence of superconducting fluctuations seems, at least presently, to be the only consistent explanation.

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*Permanent address: H. C. Ørsted Institut, DK-2100 Copenhagen Ø, Denmark.

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