

Broken-Symmetry Band Structure of Ditetramethyltetraselenafulvalene- X [(TMTSF) $_2X$]

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The author derives a set of two-dimensional band structures arising from spin- and/or lattice-induced commensurate symmetry breaking of the high-temperature, ambient-pressure phase of ditetramethyltetraselenafulvalene- X . These band structures are proposed as the framework for many of the low-temperature transport properties of these compounds and are shown to be consistent with experiment in those cases where the broken symmetry conditions have been well established.

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Besides superconductivity, the 2:1 Bechgaard salts of tetramethyltetraselenafulvalene (TMTSF) exhibit an extraordinarily rich variety of other condensed matter phenomena.¹ Their high-temperature metallic state is characterized by an open quasiplanar Fermi surface,²⁻⁴ yet certain low-temperature experiments⁵⁻⁷ indicate that the physics of (TMTSF) $_2X$ in this latter region is dominated by two-dimensional interactions. However, it seems unlikely that the inter-TMTSF-stack coupling is sufficiently volume sensitive to cause the Fermi surface to close at moderate pressures or low temperatures.⁴ In this Letter, I suggest that the intrinsic interstack interaction plays a different role under pressure and/or low temperature because of symmetry changes imposed by antiferromagnetic (AF) or anion ordering (AO) on the high-temperature band structure. This picture is qualitatively different from other current proposals,⁸ being purely single particle in nature. Broadly speaking, two distinct, but possibly connected, symmetry-breaking mechanisms can arise. One is through creation of a magnetic superlattice of standing spin-density waves (SDWs) or simple AF ordering,⁹ and the other by ordering of noncentrosymmetric anions.¹⁰ For the former, direct experimental details of the magnetic superlattice are currently unavailable. For the latter, x-ray data indicate a doubling of the unit cell in one, several, or all directions, as the temperature is lowered.^{10,11} These types of ordering, the antiferromagnetic and anion, if commensurate, produce a potential often doubly periodic in the direct lattice. We thus consider here the two-dimensional reciprocal space symmetries $Q = (\frac{1}{2}, 0)$, $(\frac{1}{2}, \frac{1}{2})$, and $(0, \frac{1}{2})$.¹²

The general picture is schematically summarized in Fig. 1, which shows an idealized cation arrangement in $Q = (\frac{1}{2}, \frac{1}{2})$ symmetry for (TMTSF) $_2X$. In each oval I have lumped a single dimer and its net spin. Essentially, I have ap-

proximated the upper branch of the folded-cosine high-temperature band structure with a single cosine function giving the benefit of algebraic simplification without loss of physical content. The different site energies are denoted by ϵ, ϵ' , arising from AF and/or anion ordering, and $t_{\parallel}, t'_{\parallel}, t_{\perp}, t'_{\perp}$, are the interdimer transfer integrals associated with displacive distortions. For AF ordering, ϵ, ϵ' represent the different site exchange potentials seen by a carrier of given spin.¹³ Exactly the same model holds for anion ordering except, of course, that ϵ, ϵ' now represent the different cation-site electrostatic potentials arising from the ordered anion lattice. In the absence of cation distortion, whose omission does not affect qualitatively the discussion to follow, Fig. 1 can be described by a simple fourth-order secular equation in the three parameters $\Delta = (\epsilon - \epsilon')/2$, t_{\parallel} and t_{\perp} . Figure 2 summarizes the solutions for each of the three symmetries on taking $t_{\parallel}/t_{\perp} = 10$ and $\Delta = 2t_{\perp}$.¹⁴ The energy axis indicates the de-

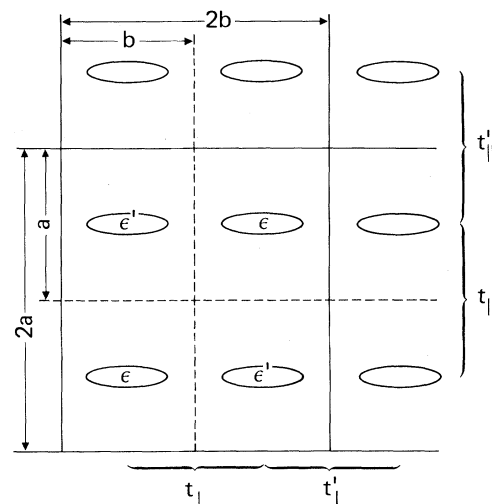


FIG. 1. Idealized schematic of the 2×2 ordered lattice of (TMTSF) $_2X$.

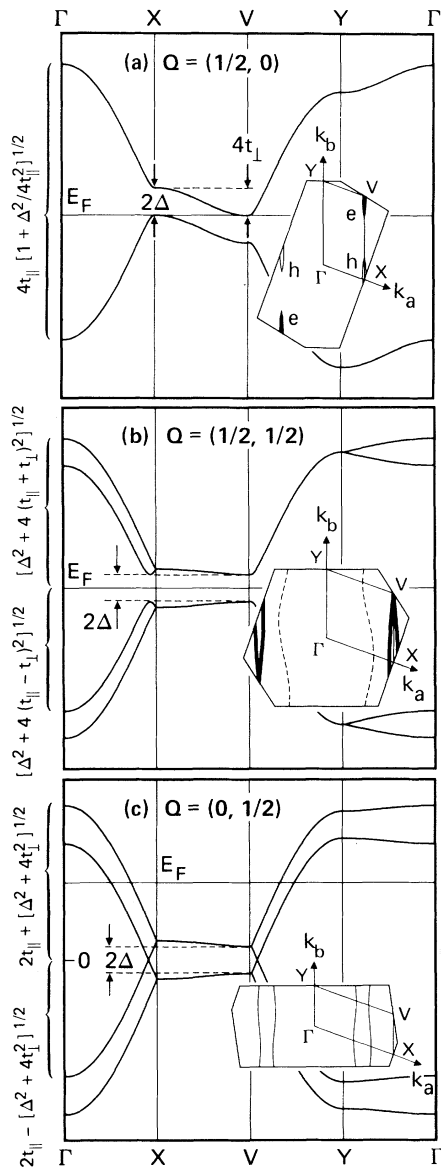


FIG. 2. Model band structures for the three most highly commensurate two-dimensional broken symmetries (a) $Q = (\frac{1}{2}, 0)$; (b) $Q = (\frac{1}{2}, \frac{1}{2})$; (c) $Q = (0, \frac{1}{2})$.

pendence of the major band features on the parameters Δ , t_{\parallel} , and t_{\perp} . The crystal momentum axes are not to scale; however, the Brillouin-zone insets are. The figures are representative of the entire $(\text{TMTSF})_2X$ family. Figure 2(a) recalls the high-temperature metallic phase if we imagine E_F bisecting the upper band and Δ as the cation dimerization gap. We now discuss each symmetry in detail.

$Q = (\frac{1}{2}, 0)$: Depending on the relative values of the Madelung and/or AF exchange parameter Δ and the b -axis bandwidth $4t_{\perp}$, we obtain either a

semimetal ($2\Delta < 4t_{\perp}$) or an indirect-gap semiconductor ($2\Delta > 4t_{\perp}$). Figure 2(a) explicitly contains the bands for $2\Delta = 4t_{\perp}$, i.e., those of a zero-band-gap semiconductor. Its Brillouin-zone inset, on the other hand, shows a semimetallic case ($\Delta/2t_{\perp} = \frac{2}{3}$) and the associated hole-electron pockets. This picture provides a possible explanation of the behavior of $(\text{TMTSF})_2\text{NO}_3$ between 40 and 12 K. Parkin *et al.*,¹⁵ have observed a conductivity anomaly at 40 K which seems associated with a $Q = (\frac{1}{2}, 0, 0)$ AO transition¹⁰ at the same temperature. Below 40 K the conductivity remains metallic until a metal-insulator (MI) transition occurs at 12 K which is probably due to further anion ordering that is quenched at high pressure. The transition at 40 K is relatively unaffected by pressure and superconductivity does not occur, at least up to pressures of 24 kbar.¹⁵ The hole-electron pockets formed at X and V, respectively, create an unfavorable Fermi topology for SDW instabilities and give rise to a lower density of states consistent with the absence of superconductivity and the 50% drop in thermopower observed by Bechgaard *et al.*¹⁶

$Q = (\frac{1}{2}, \frac{1}{2})$: Here the Brillouin zone has the same shape as the high-temperature phase but with one-fourth the area. The high-temperature Fermi contour, indicated by dashed lines in Fig. 2(b), shows a strong $2k_F$ nesting tendency in the $[1, 1]$ direction and provides a natural mechanism for SDW formation in centrosymmetric-anion $(\text{TMTSF})_2X$ compounds. Note that the condensation of this SDW into an AF state will invariably produce an insulator with direct gap 2Δ , however weak the exchange interaction. This is the only symmetry of the three considered here that yields an insulator for every finite value of 2Δ .¹⁷ I therefore propose Fig. 2(b) as the band structure for AF-ordered $(\text{TMTSF})_2X$ ($X = \text{PF}_6, \text{AsF}_6, \text{SbF}_6, \text{TaF}_6$) and anion-ordered $(\text{TMTSF})_2X$ ($X = \text{ReO}_4, \text{NO}_3$) below their respective MI transition temperatures. For the AF compounds, the assignment is at present speculative, while for ReO_4 the symmetry is known to be $Q = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.¹⁰ We would not expect this gap to be removable by pressure. We would predict for $(\text{TMTSF})_2\text{ReO}_4$, e.g., that if the temperature were lowered below its MI transition at ambient pressure, the subsequent application of high pressure would not restore the metallic state without some further change in symmetry. The direct band gap is created by the removal of a virtual crossing near X by the AF or AO interaction. Thus, for $2\Delta \ll 4t_{\parallel}$, we expect $m^* \ll 1$ with an attendant high mobility. In the Fig. 2(b)

inset, I plot the constant energy contours for the electron-hole band extrema. These bands form a closed "trench" about the X - V direction. The effective masses m_{\parallel} and m_{\perp} are found to be reduced from their high-temperature metallic values by approximately $\Delta/2t_{\parallel}$ near X and $\Delta/2t_{\perp}$ at V , respectively. Chaikin *et al.*,¹⁸ have estimated $2\Delta \approx 4$ meV from the conductivity activation energy in the PF_6 compound below its 12-K MI transition [the gap shown in Fig. 2(b) is more representative of an AO gap such as seen in $(\text{TMTSF})_2\text{ReO}_4$ (Ref. 11)]. Taking the same t_{\parallel} , t_{\perp} used for $Q = (\frac{1}{2}, 0)$, we obtain $\frac{1}{300}$ and $\frac{1}{30}$ for the two reduction factors. The effective-mass components vary radically within the trench as a function of carrier position and population. The $Q = (\frac{1}{2}, \frac{1}{2})$ model is qualitatively consistent with the magnetoresistance measurements¹⁸ and nonlinear transport data^{19,20} of $(\text{TMTSF})_2\text{PF}_6$ below its MI transition.

$Q = (0, \frac{1}{2})$: In this symmetry, a finite 2Δ does not introduce any gaps near the high-temperature E_F ; in fact, the number of Fermi contours increases from two to four and the ground state remains metallic.²¹ X-ray studies show that slowly cooled $(\text{TMTSF})_2\text{ClO}_4$ displays a $Q = (0, \frac{1}{2}, 0)$ distortion at 22 K thought to be due to a ClO_4 AO effect²² and stays metallic in agreement with the model. Furthermore, the density of states stays high in the new symmetry, a supporting condition for superconductivity. Moreover, Fig. 2(c) shows that for $\Delta \approx 2t_{\perp}$, any nesting tendency between the four Fermi contours would require an incommensurate superlattice period. I believe this requirement stabilizes the $Q = (0, \frac{1}{2})$ symmetry against SDW formation thus permitting superconductivity to occur. Recently, it has been shown that slowly cooled $(\text{TMTSF})_2\text{ClO}_4$ exhibits a depressed spin-lattice relaxation rate²³ right down to the superconducting transition temperature in agreement with this feature of the model. Finally, I point out that the $Q = (0, \frac{1}{2})$ state is relevant to the newly discovered organic superconductor $(\text{BEDT-TTF})_4(\text{ReO}_4)_2$ [*bis*(ethylenedithio)tetrathiafulvalinium rhenate].²⁴ In this material, there are two cation stacks per unit cell and the ReO_4 anions alternate in rotational position perpendicular to the long axis of the cation thus producing a pseudo $(0, \frac{1}{2})$ symmetry.

Of the three models, $Q = (\frac{1}{2}, 0)$ is the most natural to support quantum oscillations. Yet there is currently no direct experimental evidence for this, or any, mode of symmetry breaking under pressure and/or magnetic field. It would be re-

quired that a magnetic field applied in the c^* direction somehow create $Q = (\frac{1}{2}, 0)$ ordering of the spin lattice. Clearly, structural measurements as a function of temperature, pressure, and magnetic field should be given high experimental priority.

In summary, we have derived three separate two-dimensional band structures produced by AF and/or AO induced commensurate symmetry breaking of the high temperature, open Fermi-surface phase of $(\text{TMTSF})_2X$. The $Q = (\frac{1}{2}, 0)$ model seems appropriate for the low-temperature transport properties of $(\text{TMTSF})_2\text{NO}_3$ and possibly the high-magnetic-field, low-temperature metallic regime of $(\text{TMTSF})_2\text{PF}_6$ and $(\text{TMTSF})_2\text{ClO}_4$. The only completely insulating phase is $Q = (\frac{1}{2}, \frac{1}{2})$ which provides an excellent framework for the semiconducting behavior of the AF-ordered centrosymmetric anion compounds. Finally, we find for $Q = (0, \frac{1}{2})$ a retention of the metallic state with a less commensurate Fermi contour structure which suppresses the SDW instability in agreement with recent data on $(\text{TMTSF})_2\text{ClO}_4$.

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¹Mol. Cryst. Liq. Cryst. **79**, No. 1 (1981).

²P. M. Grant, Bull. Am. Phys. Soc. **26**, 213 (1981).

³M. H. Whangbo, W. M. Walsh, R. C. Haddon, and F. Wudl, Solid State Commun. **43**, 637 (1982).

⁴P. M. Grant, Phys. Rev. B **26**, 6888 (1982).

⁵J. F. Kwak, J. E. Schirber, R. L. Greene, and E. M. Engler, Mol. Cryst. Liq. Cryst. **79**, 111 (1982).

⁶L. J. Azevedo, J. E. Schirber, and J. C. Scott, Phys. Rev. Lett. **49**, 826 (1982).

⁷R. L. Greene, P. Haen, S. Z. Huang, M. Y. Choi, and P. M. Chaikin, Mol. Cryst. Liq. Cryst. **79**, 183 (1982).

⁸V. J. Emery, R. Bruinsma, and S. Barisic, Phys. Rev. Lett. **48**, 1039 (1982); B. Horowitz, H. Gutfreund, and M. Weger, Mol. Cryst. Liq. Cryst. **79**, 225 (1982); J. F. Kwak, to be published.

⁹K. Mortensen, Y. Tomkiewicz, and K. Bechgaard, Phys. Rev. B **25**, 3319 (1982).

¹⁰J. P. Pouget, R. Moret, R. Comes, K. Bechgaard, J. M. Fabre, and L. Giral, Mol. Cryst. Liq. Cryst. **79**, 129 (1982).

¹¹S. S. P. Parkin, D. Jerome, and K. Bechgaard, Mol. Cryst. **79**, 213 (1982).

¹²That is, we consider here translational symmetry changes along only the $(\text{TMTSF})_2X$ direct-lattice a - and b -axis directions. Our preliminary calculations on the

strength of the c -axis interaction indicate a transfer integral less than 1 meV. See also Ref. 7.

¹³J. C. Slater, Phys. Rev. 82, 538 (1951).

¹⁴P. M. Grant (unpublished). These values result from an extended-basis-set calculation of the high-temperature (TMTSF)₂X band structure and an improved analysis of the optical data of C. S. Jacobsen, D. B. Tanner, and K. Bechgaard, Phys. Rev. Lett. 46, 1142 (1981). $\Delta = 4t_{\perp}$ was chosen for illustrative purposes.

¹⁵S. S. P. Parkin, F. Creuzet, D. Jerome, and K. Bechgaard, to be published.

¹⁶K. Bechgaard, C. S. Jacobsen, K. Mortensen, H. J. Pedersen, and N. Thorup, Solid State Commun. 33, 1119 (1980).

¹⁷Recently a report has appeared by K. Mortensen, C. S. Jacobsen, A. Lindegaard-Andersen, and K. Bechgaard (to be published) on a possible $Q = (\frac{1}{2}, \frac{1}{2})$ transition in (TMTSF)₂H₂F₃ in which the transport and magnetic data are interpreted in terms of incomplete gapping of the Fermi surface. However, the authors are unclear as to whether the $Q = (\frac{1}{2}, \frac{1}{2})$ state has actually been well established.

¹⁸P. M. Chaikin, P. Haen, E. M. Engler, and R. L. Greene, Phys. Rev. B 24, 7155 (1981).

¹⁹P. M. Chaikin, G. Gruner, E. M. Engler, and R. L. Greene, Phys. Rev. Lett. 45, 1874 (1980).

²⁰E. N. Conwell and N. C. Banik, Mol. Cryst. Liq. Cryst. 79, 95 (1982).

²¹The $Q = (0, \frac{1}{2}, \frac{1}{2})$ symmetry gives rise to an insulating state in (TMTTF)₂SCN: C. Coulon, A. Maaroufi, J. Amiell, E. Dupart, S. Flandrois, P. Delhaes, R. Moret, J. P. Pouget, and J. P. Morand, Phys. Rev. B 26, 6322 (1982). The c^* folding introduces double degeneracy into the four Fermi contours of Fig. 2(c), which are then split by the component of the Madelung potential arising from anion ordering along c . This potential is likely to be much larger than the c -axis transfer integral, thus creating a gap everywhere along E_F . The question of c -axis effects will be discussed in a subsequent, more comprehensive, publication.

²²J. P. Pouget, G. Shirane, K. Bechgaard, and J. M. Fabre, Phys. Rev. B (to be published).

²³T. Takahashi, D. Jerome, and K. Bechgaard, J. Phys. (Paris), Lett. 43, 573 (1982); Recently, it has been observed that rapidly cooled (TMTSF)₂ClO₄, which shows no $Q = (0, \frac{1}{2})$ symmetry, displays an SDW induced MI transition and no superconductivity: S. Tomic, D. Jerome, P. Monod, and K. Bechgaard, to be published.

²⁴S. S. P. Parkin, E. M. Engler, R. R. Schumaker, R. Lagier, V. Y. Lee, J. C. Scott, and R. L. Greene, Phys. Rev. Lett. 50, 270 (1983).