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# Band-structure parameters of a series of tetramethyltetraselenafulvalene [(TMTSF)$_2X$] compounds

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Using semiempirical molecular-orbital calculations, we have obtained the principal transfer integrals which parametrize the band structure of tetramethyltetraselenafulvalene salts [(TMTSF)$_2X$] [$X=ClO_4$, $ReO_4$, $FSO_3$, $PF_6$ (300 and 4 K), and $AsF_6$]. Contrary to what has generally been believed, we find the most important interaction determining interchain bandwidth dispersion to be between third-nearest-neighbor TMTSF cations with respect to Se-Se contact distances. Moreover, we find this interaction to yield a transverse bandwidth of order 47–52 meV for all values of the anion $X$ we considered. This bandwidth is large enough to sustain quasi-two-dimensional coherent transport behavior well above the metal-insulator transition and possibly at room temperature as well, but of not sufficient magnitude to create a closed Fermi surface within the first Brillouin zone. In addition, we determine the strain components for the major transfer integrals. From these we conclude that the experimental temperature and pressure behavior of the conductivity cannot arise solely from a simple effective-mass dependence on the (TMTSF)$_2X$ transfer integrals.

Tetramethyltetraselenafulvalene (TMTSF) forms a number of simple 2:1 salts with a variety of monovalent inorganic anions. Several interesting physical properties of (TMTSF)$_2X$ with $X=PF_6$, $AsF_6$, $ClO_4$, $ReO_4$, and $FSO_3$ have been discovered within the past two years. Among these are high-room-temperature electrical conductivity ($\sim 10^3$ $\Omega^{-1}\text{cm}^{-1}$), superconductivity at low temperatures under moderate pressures ($\sim 6$ kbar), spin-density-wave transitions, antiferromagnetism, anion ordering, and anomalous magnetoscillatory effects.[1] Few other material systems exhibit such a rich variety of phenomena. In particular, the occurrence of superconductivity in these possibly quasi-one-dimensional (quasi-1D) organic compounds has engendered considerable theoretical interest.[2–4] A common feature of their crystal structures is the presence of closely stacked partially oxidized planar cation molecules along which normal-state conductivity proceeds.[5] In this regard, they have much in common with the other organic conductors of the tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) variety. However, in the latter system, charge-density-wave instabilities invariably occur which destroy the high-temperature metallic state. These instabilities eventually condense into a Peierls insulating state with a three-dimensional (3D) ordering temperature between 40–200 K. The question naturally arises as to why most of the (TMTSF)$_2X$ compounds are immune to these lattice instabilities, at least to low enough temperatures and sufficient pressures to permit superconductivity to occur.

Efforts are being made to answer this question. One approach uses the "$g$-ology" framework to impose conditions on the $k=0$ and $2k_F$ scattering amplitudes to favor the appearance of the appropriate divergence for singlet or triplet superconductivity.[4,6] This is essentially a one-dimensional picture in which the presence of nearby cation stacks plays a perturbative role. Allied with one-dimensional concepts is the idea that superconductivity may be present far above the 3D transition temperature of approximately 1 K.[2] Here support derives from the reported observation of pairing phenomena via tunnel spectroscopy in the (20–40)-K range in (TMTSF)$_2PF_6$ and (TMTSF)$_2ClO_4$.[7] These results would imply a mean-field superconducting transition temperature in the range 10–20 K. On the other hand, it was noted almost immediately upon the discovery of these materials that the selenium-selenium interchain contacts were considerably shorter than in most other selenium charge-transfer salts.[1] Thus, it is alternatively possible that the (TMTSF)$_2X$ compounds are electronically two dimensional (2D) in the sense that static Fermi-

 

surface instabilities are suppressed, at least near their ordering temperatures and pressures. If such were the case, then the advent of superconductivity could be perceived as a normal and perhaps usual event, since, in fact, most metals superconduct at sufficiently low temperatures in a variety of pressure environments. The experimental support for this viewpoint comes from the observation of Shubnikov–de Haas oscillations[8] in $(TMTSF)_2PF_6$, which, in a conventional interpretation, can only arise given a closed Fermi-surface topology, and the occurrence of a transverse plasma edge in the optical reflectance of the same compound.[9] Additional support derives from arguments based on the pressure dependence of interchain coupling.[10]

It is not our intent in this paper to choose unequivocally amongst the above alternative theories. Rather, we wish to point out that the nature and size of the electronic interchain interaction is central to all these ideas and to try to identify, through simple band-structure calculations on compounds whose complete crystal structures have been measured, its magnitude and dependence on cation interpositional variations. However, our results will definitely favor a picture containing more two dimensionality than may have been previously assumed. Our paper will concentrate solely on the cation stacks and neglect anion effects of any kind. We recognize that this is a serious oversimplification when noncentrosymmetric anions such as $ClO_4^-$ and $ReO_4^-$ are involved and disorder-order effects dominate the low-temperature transport behavior.[11]

We used the Mulliken-Wolfsberg-Helmholtz[12] (MWH) formalism as the basis of our calculations.[13] In particular we calculated the dimer splitting of the highest occupied molecular orbital (HOMO) for the cation monomer for each pertinent nearest-neighbor pair. It has been shown that the dimer splitting is formally identical in the tight-binding approximation to twice the transfer integral. In their work on TTF-TCNQ, Herman, Salahub, and Messmer[14] used this approach to calculate its band structure. These transfer integrals then become the sole parameters in a simple tight-binding band structure for $(TMTSF)_2X$.[15] Our method neglects the $k$ dependence of the transfer integrals; however, our more complete calculations, as well as those of Whangbo *et al.*[16] show that this assumption is rather good and certainly suffices for the arguments to be made herein. Because one suspects that the major portion of the intermolecular interaction will occur between the central seleniums and carbons, we replaced the methyl groups by hydrogen in order to reduce the amount of computation required. Thus we are in reality dealing with tetraselenafulvalene (TSF) instead of TMTSF. The effect of this approximation is probably to underestimate all intermolecular overlaps slightly. One point that always arises in semiempirical calculations such as these concerns possible contributions to the valence states from chalcogenide virtual $d$ orbitals. The problem is essentially one of assigning appropriate ionization potentials to unoccupied orbitals. Our position is that to attempt the inclusion of $d$ states in a calculation on this level of low sophistication would be at best arbitrary and at worst erroneous. The evidence is that $d$ orbitals participate significantly only when the chalcogenide is bonded to highly electronegative ligands in contrast to Se in the TMTSF molecule.[17] The issue must really await the results of self-consistent-field calculations on both neutral and positively charged TMTSF. We only remark that compounds in which chalcogenide virtual $d$ orbitals contribute to bonding in a major way are distinguished by their relative scarcity. On the other hand, we do wish to point out what is in fact the major weakness in non-self-consistent calculations such as these which utilize analytic basis sets. All existing MWH band-structure calculations of the charge-transfer salts, including those reported here, employ single-$\zeta$ Slater-type orbitals (STO) for reasons of obvious computational efficiency. We have found the use of multi-STO basis sets, which in principle are more accurate at the large overlap distances involved in these compounds, to yield much higher values of intermolecular overlap. Therefore, the absolute values of the transfer integrals reported here are to be considered approximate and as lower limits to the true magnitudes. However, their relative anisotropies, upon which much of the interesting physics depends, are less affected by the choice and size of the basis set.[15]

We now discuss the general features of the $(TMTSF)_2X$ crystal structure in regard to the cation electronic interaction. One can identify five principal nearest neighbors in the $(TMTSF)_2X$ structure. Two are in the stacking, or $a$ direction, and three are in the interstack, or $b$ direction. We expect these five nearest-neighbor directions to provide the strongest electronic interactions, and are those for which we will calculate the five transfer integrals which will parametrize our band structure. For the $c$ direction the cations are separated by the anion planes and minimal electronic interaction between them is to be expected. The situation is summarized in Figs. 1–3 which define the above in-

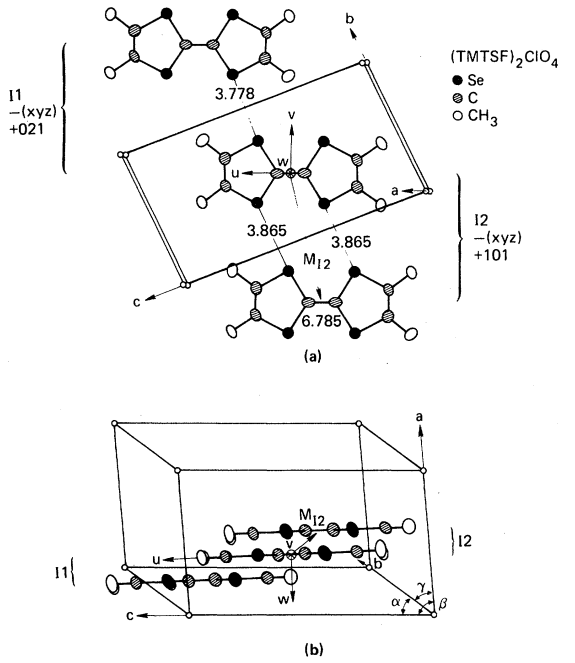


FIG. 1. TMTSF $I1$ and $I2$ nearest-neighbor interchain positions in $(TMTSF)_2ClO_4$ as viewed from the point at infinity. The $ClO_4^-$ anions are centered on the eight corners of the indicated unit cell. Also shown are the $I1$, and $I2$ symmetry operations. The Se-Se distances are in Å. A Cartesian coordinate system, suitable for describing relative molecular motions, is shown defined on the plane and long axis of the central molecule. $M_{I2}$ is the vector between molecular centers in the $I2$ direction: (a) View perpendicular to the central molecular plane; (b) view perpendicular to the long axis of the central molecule.

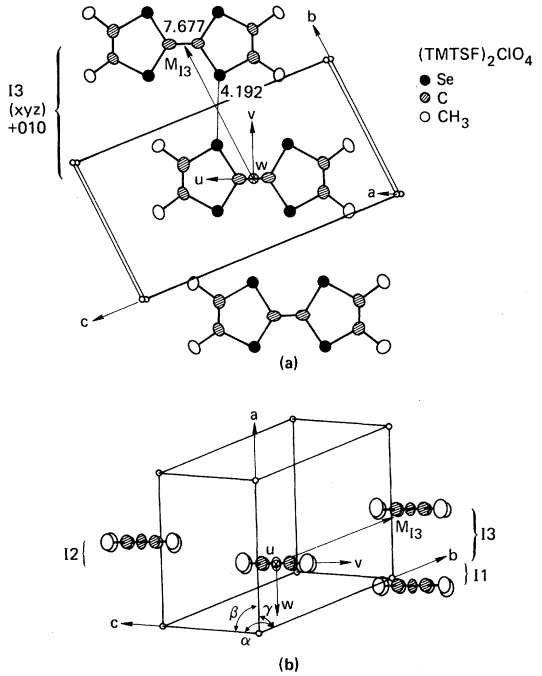


FIG. 2. TMTSF $I3$ interstack interaction viewed from infinity. Se-Se distances are in Å. The $\{uvw\}$ coordinate system of Fig. 1 is repeated: (a) View perpendicular to the central molecular plane; (b) view down the long axis of the central molecule showing all three major interchain interactions.

teractions explicitly for $(TMTSF)_2ClO_4$. All $(TMTSF)_2X$ structures considered here are triclinic with space group $P\bar{1}$. For the interstack directions shown in Figs. 1 and 2, we designate $I1$ as the interaction between the closest neighbor, $I2$ as that in the negative-$b$ direction and slightly more removed, and $I3$, generated by a pure $b$-axis translation, as that for the third nearest neighbor. Each interselenium distance is approximately equal to a van der Waals radius of 3.8 Å, slightly smaller for $I1$, slightly larger for $I2$, and about 10% larger for $I3$. Note that the closest, $I1$, has essentially one Se-Se contact with the central cation while $I2$ has two. Figure 3 shows the $(TMTSF)_2X$ stack to be slightly dimerized with two cations per unit cell. This small amount of dimerization may seem surprising in a conducting charge-transfer salt due to the concomitant gap it will introduce in the electronic structure; however, because of the 2:1 stoichiometry, this gap is not at the Fermi energy. In analogy to the interchain case, we refer to the two possible intermolecular interactions as $S1$ and $S2$, ordered with respect to increasing separation.

The transfer-integral results and attendant anisotropies are summarized in Table I. As mentioned earlier, the magnitudes of the transfer integrals are taken to be half the appropriate dimer splittings. The signs, however, depend on the relative phases of the eigenvectors on each member of the pair. We determined these by superposing the monomer states in the various geometries, and also by inspection of the actual dimer eigenvectors for the HOMO level involved. It turns out that the $S1$, $S2$, and $I3$ interactions are all antibonding, while $I1$ and $I2$ are bonding. The low-temperature $(TMTSF)_2PF_6$ structure used here was obtained from the work of King and La Placa[5] on changes of unit-cell parameters with temperature. The intracellular atomic positions were calculated by fixing the intramolecular atomic distances and imposing maximum packing conditions. We see from Table I that $t_{I2} > t_{I1}$ (except for $X = AsF_6$) despite the closer

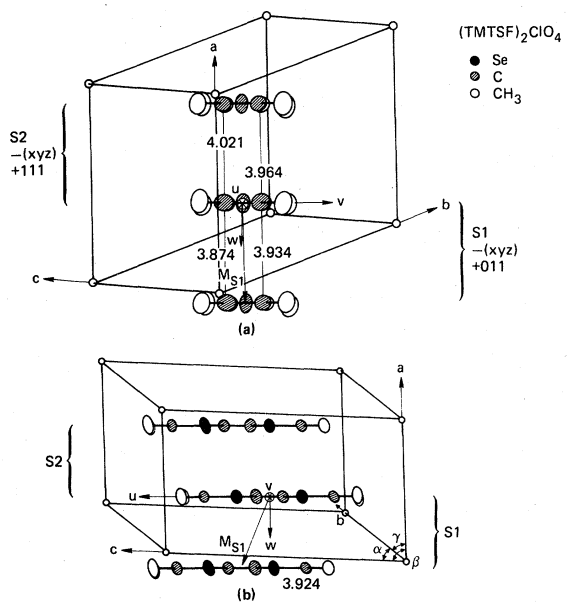


FIG. 3. TMTSF nearest-neighbor intrastack positions in $(TMTSF)_2ClO_4$ as viewed from the point at infinity. The interactions $S1$ and $S2$ are shown along with their symmetry operations. The Se-Se distances are in Å. The $\{uvw\}$ coordinate system described in Fig. 1 is shown with $M_{S1}$ connecting molecular centers in the $S1$ direction: (a) View along the long axis of the central molecule; (b) view perpendicular to the long axis of the central molecule.

Se-Se contact for the latter. The contact distance is roughly 2% closer for the $I1$ direction in $(TMTSF)_2ClO_4$, yet $t_{I2}\sim 2-6t_{I1}$. The reason, of course, is that there is much more overlap along $I2$ and $I1$. Not only are there two Se pairs in close opposing contact (3.865 Å), but one of each pair diagonal from each other are reasonably close as well.

What is really remarkable is that the $I3$ interaction is as strong or stronger than $I2$, yet in terms of Se-Se contacts, it is the third nearest neighbor. Moreover, it hardly varies over the six compounds considered, while $t_{I2}$ decreases by a factor of 18 from $X=ReO_4$ to $AsF_6$. Figure 2(b) shows that the overlap producing $t_{I3}$ is $\sigma$-like and antibonding between adjacent $\pi$ lobes of the dimer HOMO states. This picture is confirmed by charge-density contours computed for the $I3$ dimer.[18] It is interesting to note that if we go to the fourth-nearest-neighbor interaction, generated by a $-a,+b$ translation of the unit cell, we obtain a transfer integral of about 1 meV, only slightly less than $t_{I1}$, the first nearest neighbor.

Turning now to the stack transfer integrals $t_{S1}$ and $t_{S2}$, we find good agreement with the scattered-wave calculations on TSF dimers by Herman.[19] He finds $t_S\approx 150$ MeV for the slipped stacking configuration of TSF in TSF-TCNQ, a geometry very close to that in $(TMTSF)_2X$. The cation stacking distance in TSF-TCNQ is 3.49 Å,[19] while in $(TMTSF)_2X$ compounds in the $S1$ direction it is around 3.63 Å,[5] roughly 4% larger. Given that the scattered-wave calculations evolve from a completely different theoretical foundation than ours and used a large extended basis set that included $d$ partial waves, we find the agreement with our results quite remarkable.

How do each of these transfer integrals affect the various topological band-structure features? Since $t_{I3}$ results from a pure unit-cell translation, it will appear in the diagonal terms of the crystal Hamiltonian, while $t_{S1}$, $t_{S2}$, $t_{I1}$, and $t_{I2}$ connect inequivalent cation sites and therefore emerge as off-diagonal elements. The stack terms $t_{S1}$ and $t_{S2}$ set the major portion of the folded conduction bandwidth at $k=0$, whereas their difference, in linear combination with $t_{I1}$ and $t_{I2}$, determine the zone-boundary splittings and band gaps. The latter two transfer integrals, especially $t_{I2}$, affect the interchain bandwidth dispersion at the top and bottom of the conduction band. However, the principal interaction dominating the interchain coupling is $t_{I3}$. In fact, near $k=k_F\approx\pi/2a$, mostly $t_{I3}$ contributes

TABLE I. Transfer integrals and anisotropies for $(TMTSF)_2X$ compounds of known crystal structure. All transfer integrals are in meV ($10^{-3}$ eV) and $A_{21}=|t_{S2}/t_{I1}|$, etc. Refer to Figs. 1, 2, and 3 for notation convention. The Table is ordered with respect to decreasing $t_{I2}$. TMTSF-TCNQ values are shown for comparison.

| $X$ | $t_{S1}$ | $t_{S2}$ | $t_{I1}$ | $t_{I2}$ | $t_{I3}$ | $A_{11}$ | $A_{12}$ | $A_{13}$ | $A_{21}$ | $A_{22}$ | $A_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $ReO_4$ | 146 | 117 | −1.3 | −7.3 | 11.5 | 116 | 20 | 13 | 93 | 16 | 10 |
| $ClO_4$ | 146 | 117 | −1.3 | −7.1 | 12.4 | 116 | 21 | 12 | 94 | 17 | 9 |
| $FSO_3$ | 143 | 118 | −1.2 | −7.0 | 12.6 | 117 | 21 | 11 | 96 | 17 | 9 |
| $PF_6$ (4 K) | 170 | 118 | −2.1 | −4.3 | 13.1 | 79 | 40 | 13 | 55 | 28 | 9 |
| $PF_6$ (300 K) | 147 | 114 | −0.3 | −2.0 | 12.0 | 482 | 72 | 13 | 374 | 56 | 10 |
| $AsF_6$ | 149 | 118 | −0.9 | −0.4 | 11.5 | 171 | 395 | 13 | 136 | 313 | 10 |
| TCNQ | 162 | | −1.0 | 13.2 | | 162 | 12 | | | | |

with only minor additions from $t_{I1}$ or $t_{I2}$ for many of the compounds in the $(TMTSF)_2X$ family. The inescapable conclusion is that in spite of the major variations in $t_{I2}$ between the several compounds, the Fermi-surface topology, which is open, and therefore the degree of two dimensionality, is dominated by $t_{I3}$ which Table I shows us to be independent of the anion $X$ for all practical purposes. We do not rule out, however, that small differences in Fermi-surface shapes may affect nesting properties and spin- and/or charge-density-wave formation. This point is undergoing further exploration. Wudl[20] has discussed the effects of interstack Se-Se interactions with regard to spin-charge separation and pseudo-two-dimensionality. Whereas he states that the interstack seleniums are bonded along the $I1$ direction, our results indicate that $I3$ is much stronger and is the source of the significant interchain interaction near the Fermi level.[18] Thus the geometrical details of the interchain HOMO overlaps override consideration of the Se-Se contact distance alone. We certainly agree, however, that the idea of interchain selenium clusters[20] is central to any quasi-2D model of $(TMTSF)_2X$.

To investigate in more detail the effects of intermolecular distance changes, we computed the strain dependence of $t_{S1}$, $t_{I2}$, and $t_{I3}$ with respect to variations up to $\pm 10\%$ of each component in the $\{uvw\}$ coordinate system of Figs. 1–3. The results for $(TMTSF)_2PF_6$ are summarized in Table II. The overall behavior is more or less as expected. The important point is that no unusually large changes will occur in interchain coupling with applied pressure. Using the compressibility data of Morosin *et al.*,[21] one estimates the maximum change in any given interchain coordinate to be about 1% at pressures of 12 kbar where the metallic state is well-established and superconductivity occurs at low temperatures. Applying this number to the data in Table II results in an estimated increase of at most 2 meV in $t_{I3}$ and well under 1 meV in $t_{I2}$. In conjunction with this, we note that variations in $M_{I3}$ among our six compounds amount to about 1%, or the equivalent of 12 kbar of pressure. Certainly changes in structural positions between compounds or with pressure are unlikely to result in Fermi-surface closure as long as the original crystal space group is preserved. The Shubnikov–de Haas oscillations observed by Kwak *et al.*[8] would have to derive from some mechanism, such as that proposed by Horowitz, Gutfreund, and Weger,[4] which breaks the ground-state crystal symmetry. Moreover, we do not have evidence from our calculations for any correlation of physical properties with the length of $c$ axis as proposed by Parkin *et al.*[22] for the superconducting critical pressure. If such a correlation exists, it is related to factors other than those considered here, e.g., anion-cation interactions.

TABLE II. Absolute values of the strain dependence of the $S1$, $I2$, and $I3$ nearest-neighbor transfer integrals for $(TMTSF)_2PF_6$ with respect to the intermolecular coordinate system defined in Figs. 1–3. Units are meV ($10^{-3}$ eV) per unit strain. Shown are differential strain coefficients computed at total strains of $-10\%$, $-5\%$, $+5\%$, and $+10\%$.

| | −0.10 | −0.05 | 0.05 | 0.10 |
|---|---|---|---|---|
| $\lvert u\Delta t_{I2}/\Delta u\rvert$ | 1.89 | 1.76 | 1.55 | 1.44 |
| $\lvert v\Delta t_{I2}/\Delta v\rvert$ | 58.7 | 18.6 | 10.7 | 11.2 |
| $\lvert w\Delta t_{I2}/\Delta w\rvert$ | 41.9 | 41.1 | 39.4 | 2.2 |
| $\lvert u\Delta t_{S1}/\Delta u\rvert$ | 284 | 272 | 247 | 233 |
| $\lvert v\Delta t_{S1}/\Delta v\rvert$ | 1.37 | 1.43 | 1.55 | 1.62 |
| $\lvert w\Delta t_{S1}/\Delta w\rvert$ | 1264 | 1107 | 844 | 737 |
| $\lvert u\Delta t_{I3}/\Delta u\rvert$ | 0.58 | 0.41 | 3.00 | 4.49 |
| $\lvert v\Delta t_{I3}/\Delta v\rvert$ | 330 | 233 | 123 | 92 |
| $\lvert w\Delta t_{I3}/\Delta w\rvert$ | 8.68 | 11.3 | 15.2 | 16.5 |

Direct experimental determinations of the intra- and interchain bandwidths are hard to produce. Jacobsen, Tanner, and Bechgaard[9] have performed normal-incidence polarized reflectance measurements on $(TMTSF)_2PF_6$ and $(TMTSF)_2ClO_4$. They estimate the intrachain bandwidth $W(a)\approx 1.2$ eV and interchain $W(b)\approx 13$ meV from plasma energies obtained by Drude fits to the polarized reflectance data for $(TMTSF)_2PF_6$. Exactly how one converts plasma energies into bandwidths is model dependent and Jacobsen *et al.*[9] give no details of their method. For example, our experience with $(SN)_x$ indicated that the effective-mass approximation is often invalid for partially filled tight-binding bands and that the plasma energy really depends on a dyad product of first partial derivatives of the dispersion near the Fermi energy.[23] Using values from Table I we obtain for the total folded conduction bandwidth at $k=0$, $W(a)=2(t_{S1}+t_{S2}+t_{I1}+t_{I2})=0.52$ eV. This is in reasonable agreement with the slipped-overlap cation bandwidth deduced from the Drude edge of TSF-TCNQ (Ref. 24) (and with the scattered-wave calculation referred to earlier), whose plasma energy is 1.4 eV, almost identical to that found by Jacobsen *et al.*[9] for $(TMTSF)_2PF_6$. Given the similarity in cation stacking configurations between $(TMTSF)_2X$ and TSF-TCNQ, we do not understand the origin of the large bandwidth obtained by these workers. Moreover, for the $b$ direction we get $W(b)\approx 4t_{I3}$

$=47-52$ meV, roughly 4 times greater than Jacobsen *et al.*[9] Since $\omega_p^2 \sim W$ in the effective-mass approximation, a twofold error in either the estimate of the $b$-axis plasma energy or the model used for analysis could account for this discrepancy. As the authors themselves point out, it is an open question whether Drude analysis itself is valid for such small plasma energies and high carrier concentrations. Note that Table I would predict little variation of the transverse plasma energy with anion $X$, in agreement with all data taken so far.[9] It is important that the magnitude of the interchain bandwidth be determined accurately. Our values of $t_{I3}$ yield an effective interchain bandwidth temperature of 560 K implying that $(TMTSF)_2X$ by the measure used by Jacobsen *et al.*[9] remains quasi-2D well above room temperature. In fact, because of the limited single-$\zeta$ basis set choice and neglect of $d$ functions in the HOMO state, whose correction would serve only to increase $t_{I3}$, our value of effective temperature should be taken as a lower limit.

We should mention that given even this large amount of interstack coupling, some remnants of quasi-one-dimensionality might survive. Weger[25] has argued that if $E_F > \hbar/\pi_{||} > t_\perp$, where $\tau_{||}$ is the scattering time for conductivity parallel to the stack and $t_\perp$ is the interstack transfer integral, then we are in the regime of coherent 1D conduction along stacks with diffusive transport between them. Taking $\sigma_{||} \approx 10^3\ \Omega^{-1}\,\mathrm{cm}^{-1}$ as a typical room-temperature conductivity, $E_F \approx 250$ meV and $t_{||} \approx 130$ meV from Table I, we find $\hbar/\tau_{||} \approx 100$ meV $> t_\perp \approx 12$ meV. Thus, by Weger's standard, we have still preserved quasi-one-dimensionality at room temperature despite the large interchain interaction. If we now proceed to calculate $\sigma_{||}$ at which $\hbar/\tau_{||} \approx t_\perp$, we find a value of $\sim 10^4\ \Omega^{-1}\,\mathrm{cm}^{-1}$, which, according to the data of Bechgaard *et al.*[26] occurs in $(TMTSF)_2PF_6$ at 60 K and which would be, by these considerations, the 1D-2D crossover temperature. Interestingly, this is near the temperature at which Jacobsen *et al.*[9] observe a sharpening of the transverse Drude edge. We caution, however, against interpreting Drude scattering effects as identical to scattering processes affecting the dc conductivity.[27] In addition to the above ideas, but from a completely different theoretical viewpoint, Horowitz, Gutfreund, and Weger[28] have devised a criterion for the application of mean-field theory to quasi-1D systems containing significant interstack bandwidths. Stated simply, it gives the range of interstack coupling over which one can use mean-field theory in one dimension and yet avoid large fluctuation effects. Although derived explicitly for Peierls-Frohlich instabilities, it may hold for the spin-density-wave situation as well. The mean-field bounds on the stack-perpendicular transfer integral $t_\perp$ (our $t_{I3}$) are $4T_P \le t_\perp \le 3(T_P T_F)^{1/2}$ where the lower bound is the 1D mean-field transition temperature ($\sim 48$ K for $T_P = 12$ K), and the upper bound the temperature beyond which Fermi-surface curvature would inhibit nesting ($\sim 560$ K for $E_F = 0.25$ eV). Thus our value of $t_\perp \approx 140$ K falls well within the mean-field regime for spin-density waves with negligible 1D fluctuations. On the other hand, Schulz *et al.*[29] have developed a Landau-Ginzburg model for 3D and 1D superconducting fluctuations in $(TMTSF)_2X$. In their model, the parameter $B = 2\pi^2 t_\perp^2/\Theta$ is introduced as the temperature above $T_C$ at which crossover from 3D to 1D fluctuations takes place. Treating $B$ as a numerical fitting parameter in equations expressing the fluctuation-depressed resistivity in the region above $T_C$, they find $B = 0.75$ K. However, using our $t_\perp$ and their value of $\Theta = 200$ K, we obtain $B \approx 1900$ K. Reducing $t_\perp$ by a factor of 10 still gives $B \approx 19$ K. Clearly this rather large discrepancy needs to be clarified. Given our results, it seems difficult to substantiate a significant 1D fluctuation regime.

Using a simple tight-binding expression[15] of the form

$$E(\vec{k}) = 2(t_b \cos \vec{k}\cdot\vec{b} + t_a \cos \tfrac{1}{2}\vec{k}\cdot\vec{a})$$

and Boltzman transport theory for a Fermi surface open in the $k_b$ direction, we predict $\sigma_a \sim t_a$, $\sigma_b \sim t_b^2/t_a$ where $t_a \approx \frac{1}{2}(t_{S1}+t_{S2})$, and $t_b \approx t_{I3}$. Note that the $b$-axis conductivity depends on both $t_a$ and $t_b$ and particularly on $t_b^2$. This fact makes suspect the analysis used by Jacobsen *et al.*[9] to derive the $b$-axis bandwidth from the transverse plasma energy. Note especially that the anisotropy in coherent normal-state conductivity, given by $\sigma_a/\sigma_b \sim (t_a a/t_b b)^2(\tau_a/\tau_b)$, where $\tau_a$ and $\tau_b$ are the stack and interchain scattering times, respectively, is identical to that predicted for diffusive interchain conductivity as well as the behavior derived for 3D superconducting fluctuations near $T_c$,[29] the superconducting transition temperature in $(TMTSF)_2X$. Therefore, it is *not possible* to differentiate between coherent, diffusive, or 3D fluctuation models of conductivity in $(TMTSF)_2X$ based on the power dependence of the anisotropy of transfer-integral ratios alone.

Greene *et al.*[30] and Jerome[2] have reported measurements of the dc conductivity magnitudes and anisotropies as a function of pressure and tempera-

ture. The former found $\sigma_a/\sigma_b \approx 25$ for $(TMTSF)_2ClO_4$ at room temperature and ambient pressure, while the latter obtained a figure nearer 800 for $(TMTSF)_2PF_6$ under the same conditions but with uncertain knowledge for the transverse crystallographic direction. On the other hand, Bechgaard *et al.*[26] and Jacobsen *et al.*[31] report $\sigma_a/\sigma_b \approx 200$ at room temperature. Using Table I values, we find $\sigma_a/\sigma_b \approx 30$ assuming $\tau_a = \tau_b$. Our calculations predict a small increase in anisotropy with pressure, opposite to, but in relative agreement with, the small amount actually observed,[30] resulting from the large magnitudes of the strain coefficients for $t_{S1}$ and $t_{S2}$ as compared to the interstack directions. On the other hand, Greene *et al.*[30] find a factor-of-3 increase in $\sigma_a$, and, by implication, $\sigma_b$, in the pressure range 1–8 kbar. Using the compressibility results of Morosin *et al.*[21] and our Table II figures, we would predict an increase of roughly 20% in $\sigma_a$ and a decrease of around 10% in $\sigma_b$ over this pressure range. It is hard to see, given the measured compressibility, how *any* reasonable calculation would predict a change in both $\sigma_a$ and $\sigma_b$ by a factor of 3 arising from effective-mass variations alone. In this regard the behavior of $(TMTSF)_2X$ is reminiscent of $(SN)_x$,[32] where the normal-state scattering process is mediated by mechanisms other than electron-phonon effects,[33] and it was the lattice-constant dependence of the scattering process which determined the pressure and temperature dependence of the conductivity.[34] Much the same statement can be made concerning all previously known organic metals. It remains to be seen whether a similar situation is the case for $(TMTSF)_2X$. Weger *et al.*[35] have proposed that the resistivity of organic metals at room temperature is dominated by two-libron processes. It may be that the pressure and temperature dependence of the libron scattering mechanism determines the observed conductivity behavior.

We conclude from our calculations that $(TMTSF)_2X$ is quasi-2D in terms of effective interchain bandwidth temperature at all temperatures up to room temperature and beyond. We have identified the third-nearest-neighbor interaction as that which dominates the interchain bandwidth and thus the electronic properties in that direction. It is our opinion that the approximations implicit in our calculational method (e.g., choice of MWH parameter, neglect of Se 4*d* virtual states, and use of single-$\zeta$ basis set and replacement of methyl groups by hydrogen) tend only to minimize overlaps rather than exaggerate them. These facts lead us to favor the view that the superconductivity in $(TMTSF)_2X$ arises from its quasi-2D nature. In this regard, we agree with conclusions reached by Greene *et al.*[10,30] Our results would suggest that the interstack interactions are too strong for the 1D fluctuation models of Jerome[2] and Schulz[3,29] to prevail.

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