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A SPIN-CHARGE SEPARATION HYPOTHESIS BASED ON THE STRUCTURE OF THE SALTS $(TMTSF)_2 \times (X=PF_6^-, AsF_6^-)$

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A detailed study of the three-dimensional structure of $(TMTSF)_2AsF_6$ isomorphous to the PF_6 and ClO_4 salts) has led to the conclusion that these salts are pseudo two-dimensional, that there are strong interactions between certain selenium atoms in specific ways (clustering) and that there is a periodic lattice of anions. These anion sheets could stabilize partial separation of positive charges and unpaired electrons (spins). This separation can be used to formulate an hypothesis to explain the apparent absence of CDW's in these salts.

INTRODUCTION

When Bechgaard first reported on the series of salts $(TMTSF)_2X$ $(X = AsF_6, PF_6, SbF_6, BF_4, NO_3)$[1], a surprising feature was the very low temperature associated with the metal to insulator transition (T_{MI}) of at least two of the salts (PF_6^- and AsF_6^-). Shortly thereafter, Pedersen concluded that the metal to insulator

transition may have some magnetic character.[2] It was not until Walsh discovered the restoration of metallic behavior below T_{MI} of the PF_6^- and AsF_6^- salts that it was proposed that weak pinning of spin density waves (SDW) and not the classic pinning of charge density waves (CDW), i.e., Peierls distortion was responsible for the metal to insulator transition[3] in these members of the Bechgaard phase.

The obvious question then arises: Why do these salts have their metal to insulator transition driven by SDW's and not CDW's? This paper describes the proposition of an answer which is based on observations made on a three dimensional model of the structure of $(TMTSF)_2\ AsF_6$[4].

STRUCTURE

The structures of the PF_6[5] and AsF_6[4], as well as ClO_4[6], ReO_4[6], TaF_6[7], SbF_6 and FSO_3[8] salts are all isomorphous, triclinic, and belong to the space group $P\bar{1}$. Of these, the ClO_4^- and FSO_3^- have the smallest unit cell volume and the SbF_6^- salt has the largest. In Table I are unit cell parameters of these salts and other important comparative data. Figure 1 is an ORTEP drawing of a view of two unit cells down the *a* axis. Table II contains comparative intramolecular bond distances for TMTSF in the AsF_6 salt[4] and in the neutral state.[9] Table III contains intra and interstack selenium-selenium contacts.

DISCUSSION

Figure 2 is a schematic illustration of unique selenium-selenium interactions in the Bechgaard phase. This figure, in conjunction with Table III, shows quite dramatically a chain of selenium atoms (*involving two stacks*) reminiscent of selenium metal.[10] Another feature of the structure depicted in Figure 2 by dotted lines is selenium clustering. These clusters are "bonded" *via* the shortest *interstack* selenium distance (Se2—Se2′) of, for example, 3.905Å in the case of the AsF_6^- salt. These clusters reflect the fact that each one of the four selenium atoms in the TMTSF stacks has a

different "connectivity" as shown in Table IV.

Table IV

Selenium in TMTSF (cf Fig. 2)	Number of *Interstack* Homoatomic Nearest Neighbors
Se 4	3
Se 2	2
Se 1	1
Se 3	0

The Se 3's have an "interstack" methyl and an AsF_6 as nearest neighbor (cf Figure 1).

All selenium-selenium distances, with the exception of Se2-Se4′ are shorter than the van der Waals radus of selenium as given by Pauling[11] (4.0Å) or longer than the Bondi[12] (3.8Å) value.

(A) Comparisons with Other Highly Conductive Triclinic Salts.

The organic metals TMTSF TCNQ and HMTSF TNAP[13] and those of the Bechgaard phase have two aspects in common: (a) they are all triclinic and, (b) they all have relatively short interstack Se-Se contacts (TMTSF·TCNQ, 3.98, 4.04Å; HMTSF·TNAP, 3.77Å; $(TMTSF)_2PF_6$, 3.879, 3.959, 3.934Å). They differ in that the first two have uniform stacks of donors and acceptors where the donors are stacked in roughly "double bond-over-ring" fashion.[13] On the other hand, in the Bechgaard salts the donors repeat with a displacement alternating in the long molecular axis direction while forming stacks along *a*; similar to $(TMTTF)_2X$ ($X = BF_4, ClO_4, Br$)[14] but without alternation[15] in "interdimer" distance.

The most interesting aspect of the comparisons in Table I is that while AsF_6^- is larger than PF_6^- and FSO_3^- is of the same size as ClO_4^-, the *a* dimension of the former salts' unit cell is *shorter*

than the same parameter of the latter salts. The difference in size of the AsF_6^- and PF_6^- anions is reflected correctly in the *c* dimension and the volume of the respective unit cells there is no obvious explanation for the expansion of the *c* dimension in the FSO_3^- when compared to the ClO_4^- salt. Examination of the closest interstack selenium distances[5] (Table III) and interplanar distances reveals that, from a structure point of view, the AsF_6^- salt is slightly more "one-dimensional" than the PF_6^- salt and the FSO_3 salt is slightly more "one dimensional" than the ClO_4^- salt.

Examination of Figure 2 and intermolecular distances (Tables III and I), it is clear that the observered high conductivity cannot arise from carbon-carbon π orbital overlap since the distances are much too large to produce a bandwidth of ~1eV. Therefore, this bandwidth must be derived entirely from homoatomic selenium overlap.[16] The same tables reveal that the difference between interstack and intrastack selenium distances is practically zero for the PF_6^- salt and almost negligible for the AsF_6^- salt, indicating that *these compounds are pseudo two-dimensional* consisting of sheets of donors and sheets of anions. Thus all theories based on premises of one dimensionality[17] developed to explain the properties of these salts may not be applicable.

Based on the foregoing structural analysis, an hypothesis can be constructed which can explain why spin density waves (antiferromagnetic ordering) and not charge density waves exist in at least three of these solids (PF_6^-, AsF_6^-, and ClO_4^-).

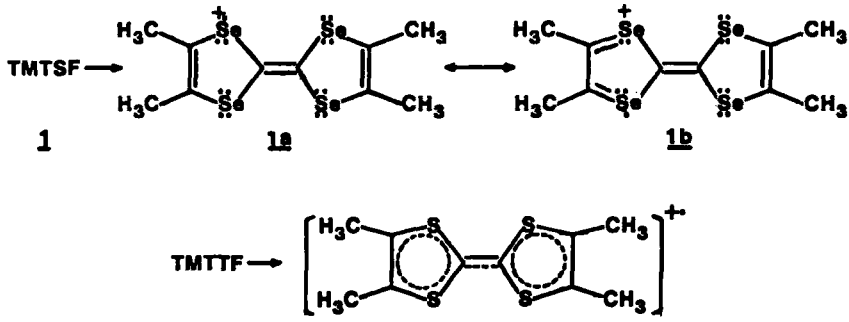
(B) The Spin-Charge Separation and Charge-Localization Hypothesis.

This SCSCL hypothesis is based on two premises. (a) Separation of spin and charge in a radical ion and (b) partial localization of charge due to electrostatic ion-pairing in the solid state.

(a) Separation of Spin and Charge (SSC).

It is usually assumed that both the charge (positive or negative) and the spin (unpaired electron) of a radical ion such as $TMTSF^{+\cdot}$ are always delocalized and indistinguishable. There are, however, situations when this may not apply.[18a,c] Since selenium is a

relatively high atomic number element, organic radical ions containing this element will exhibit a substantial decrease in conjugation due to mismatch in C-Se orbital size.[18d,16] As a result of this poor overlap, there will be a more inhomogeneous charge and spin distribution in TMTSF[16] than in TMTTF as depicted below.



1 1a 1b

In the solid state, resonance structures (1*a* and *1b*)$^{+\cdot}$ become important contributors to the valence-bond wave function of $1^{+\cdot}$. In structure $1b^{+\cdot}$, the valence shell of selenium is expanded making use of *d* functions; thus, in $1b^{+\cdot}$, the unpaired spin would be in a selenium *spd* orbital.[16,19] Corroboration for the importance of resonance contributing structure $1b^{+\cdot}$ stems from comparisons of intramolecular bond distances in neutral TMTSF[9] and TMTSF in the $(TMTSF)_2AsF_6$ salt. Table II contains the bonds in question. Note that C7-C8 is *longer in the salt* than in the neutral molecule whereas *the reverse is true for* C1-C6 implying more central double bond character in the salt than in neutral TMTSF. Furthermore, in the salt, C8-C7 (*adjacent to Se3*) *is longer than* C2-C3.

(b) Charge Localization.

The structures of the Bechgaard phase are unique compared to other organic metals in that the anions form sheets in the *a-b*

plane giving rise to uniformly spaced regions of localized negative charge. These negative centers provide a driving force for the above described SSC. The positive charges then become "localized"[20] next to the anions as shown schematically in Figure 2; more specifically near the Se3's since the Se3 to F1 (from PF_6^-) distance is only 3.196Å. Interestingly (see Table IV), the Se3's have as their closest nearest neighbors the PF_6^- AsF_6^-, ClO_4^- and FSO_3^- counterions and, as mentioned above, *do not interact* with other interstack Se atoms.

As is shown below, this SCSCL hypothesis applies only to the explanation of the physical properties of salts of the solid state structure of $(TMTSF)_2X$ ($X = AsF_6^-, PF_6^-, ClO_4, FSO_3^-$) because the electrostatic field associated with the X^- Se^+3 interaction gives this family of solids a more polarized character than is possible in other organic metals.

(C) Implications of the SCSCL Hypothesis.

(a) Stiffening of the lattice, as a result of the ion pairing described above (see Fig. 2), interferes effectively with the electron phonon coupling responsible for charge density wave formation along the *a* direction or the *a-b* plane. (b) Since sulfur is of lower atomic number than selenium, SCSCL is not expected to be dominant in $(TMTTF)_2X$ salts and hence, these tend to dimerize just below room temperature[14] (probably due to CDW condensation). (c) The two-stack systems; for example, TMTSF·DMTCNQ[21] and HMTSF·TNAP[22] which are analogous (particularly the latter) in the interstack arrangement of TMTSF in $(TMTSF)_2X$, show metal to semiconductor transitions typical of CDW-driven low dimensional metals. The reason for this behavior, according to the SCSCL hypothesis, is that the charge of the $TMTSF^{+\cdot}$ counterions ($DMTCNQ^-$, $TNAP^-$, $TCNQ^-$) is *delocalized* along the anion stack and is thus too diffuse to stabilize SSC *via* ion-pairing. (d) The SCSCL hypothesis predicts that introduction of disorder in the anion[6] stack can wash out the condensation of SDW's because it would destroy their periodicity. In other words, the more the negative charge is located near Se3, the more the SSC will be stabilized. If there is a non-periodic variation in Coulomb field strength due to disorder in the negative charges

near the Se3's, there will be a corresponding variation in SSC and consequently spin density in the stack. Perfectly periodic SSC would lead to an insulating state because the $TMTSF^{+\cdot}$ molecules will behave more like typical organic *neutral* radicals ("$TMTSF^{\cdot}$") which have a strong driving force toward spin-pairing (antiferromagnetic ordering). An external electric field will influence the periodic $Se^{+}3{-}X^{-}$ interaction, resulting in a weakening of SCSCL with concomitant restoration of conductivity. Furthermore, SCSCL should be particularly sensitive to electric fields in the crystallographic *c* direction. Thus, with the metal-to-semiconductor transition eliminated *via* non-periodic SCSCL, the smooth transition from metal to superconductor becomes possible.[6]

With the introduction of an anion containing a dipole moment (e.g. FSO_3^-) a periodic potential will be crated and the Bechgaard phase would be expected to become insulating whenever the anion dipoles order in the lattice. This is in fact what is observed.[23]

CONCLUSION

A detailed study of the three-dimensional structure of $(TMTSF)_2AsF_6$ (isomorphous to the PF_6^-, ClO_4^- and FSO_3^- salts[8]) has led to the conclusion that these salts are pseudo two-dimensional, that there are strong interactions between certain selenium atoms in specific ways (clustering)[24] and that there is a periodic lattice of anions. These anion sheets could stabilize partial separation of positive charges and unpaired electrons. This separation can be used to formulate an hypothesis to explain the apparent absence of CDW's in these salts.

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$(TMTSF)_2BrO_4^8$ was mentioned in the lecture on passing but not in this written version.

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15. In $(TMTSF)_2AsF_6$, the differences between three consecutive least-squares planes are 3.648Å and 3.626Å; i.e., an "alternation" of .022Å. But the selenium atoms themselves are at roughly ±.014 from these planes and we, therefore, believe that it is practically meaningless to attach any significance to .02Å alternation in the planes.[8]

16. Whereas in $TTF^{+\cdot}$ the highest spin density is on the central carbon atoms, in $TSeF^{+\cdot}$ the highest spin density is on the seleniums cf F. B. Bramwell, R. C. Haddon, F. Wudl, M. L. Kaplan, and J. H. Marshall, J. Amer. Chem. Soc. **1978,** *100,* 4612 and reference 17 therein. However, the fact that a very short distance between two atoms is observed, does not necessarily imply orbital overlap because the directionality of the orbitals involved must also be considered. Thus, if the Se atoms in TMTSF were sp^2 hybridized, the overlap in the crystallographic *a* direction (stacking direction) will be larger than in the crystallographic *b* direction even though the two distances are equal in $(TMTSF)_2PF_6$. In the absence of detailed electron density measurements, one cannot know the hybridization of selenium in $(TMTSF)_2PF_6$. Experiments with highly refined x-ray crystallography data are currently in progress to find an answer to this fundamental question.

17. See, for example, E. M. Conwell, Chemica Scripta *17,* 19 (1981) among a number of theory papers in this volume of Chemica Scripta.

18a. P. H. Citrin, J. Amer. Chem. Soc. **1973,** *95,* 6472 has found that *i* (analogous in symmetry to $TMTSF^{+\cdot}$) has two distinguishable rutheniums via x-ray photoelectron spectroscopy.

i

18b. For a further discussion of the ongoing debate on compound *i* see P. H. Citrin and A. P. Ginsberg, J. Amer. Chem. Soc. **1981,** in press.

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19. There exists a continuing controversy over the effect of *d* orbitals on the chemistry of organosulfur compounds and less of a dispute in the case of organoselenium compounds. Selenium is more apt to expand its valence shell as corroborated by the increased stability of its tetravalent compounds ("Organic Selenium Compounds," D. Klayman and W. H. H. Gunther, Wiley-Interscience, N. Y., 1973).

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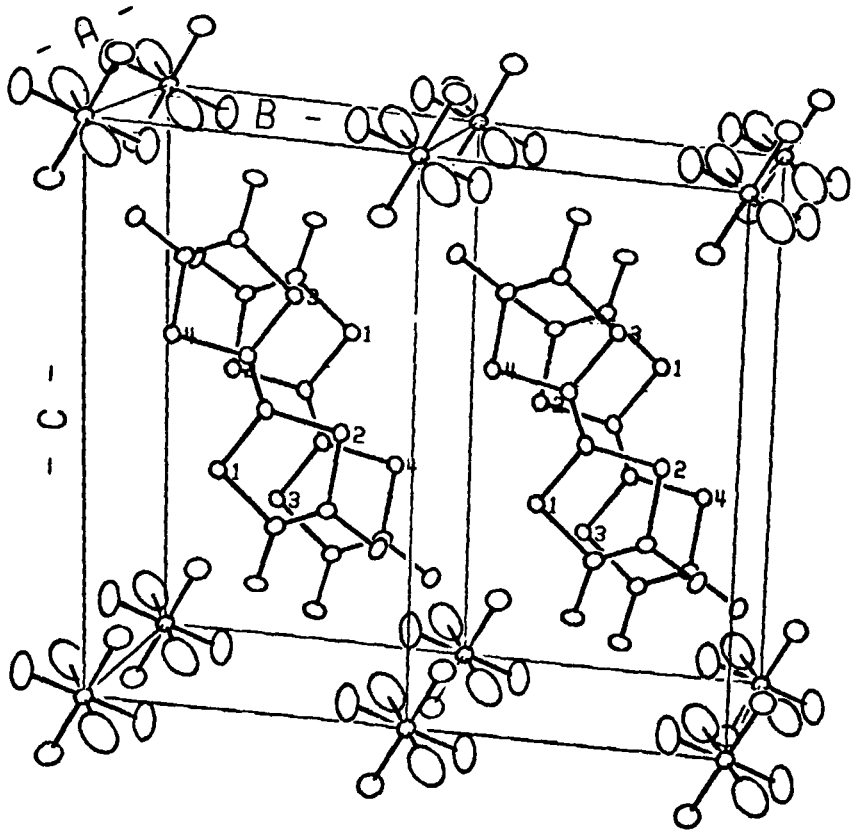

Figure 1. ORTEP drawing of two unit cells of $(TMTSF)_2AsF_6$ along b. The number of the selenium atoms corresponds to Table I. The α axis direction is into the plane of the paper.

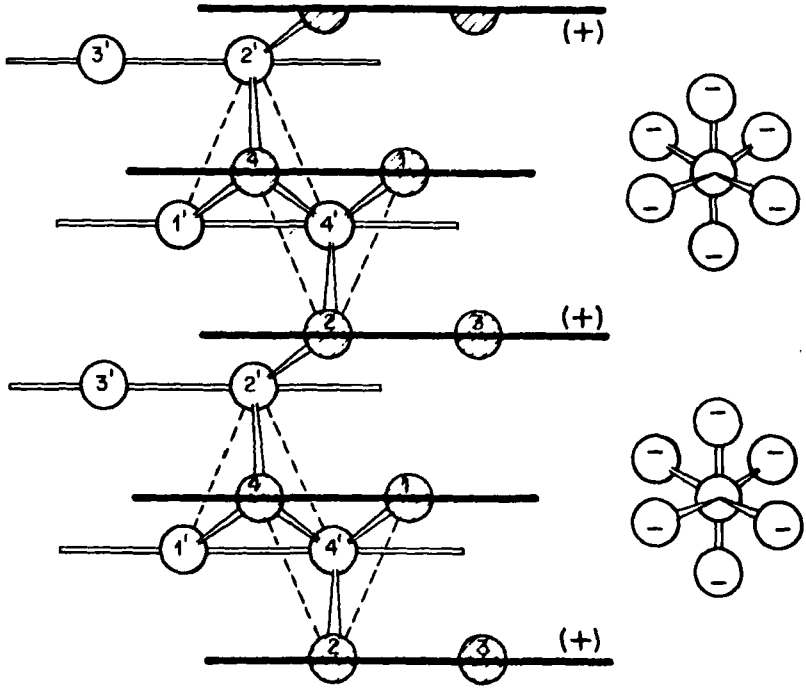

Figure 2. Schematic view of two stacks of $(TMTSF)_2AsF_6$. The heavy horizontal lines represent edge-on TMTSF molecules nearest the observer. The lighter horizontal lines represent TMTSF molecules behind the front stack. The numbering arrangement corresponds to a mirror image relative to the b-c plane (cf a direction) of the view shown in Fig. 1. The shaded circles are seleniums on the back of the front TMTSF's (only two seleniums per donor are shown in this figure). The open circles are front seleniums on the back stack. The primed numbers refer to the back stack. The anion octahedra on the left side were omitted for clarity. The negative charges imply that the whole anion bears a full negative charge which is distributed among six fluorine atoms. The plus signs imply some positive charge density in that region of the donors (near Se3). The α axis direction is from bottom to top, the c axis from right to left and the b axis into the page.