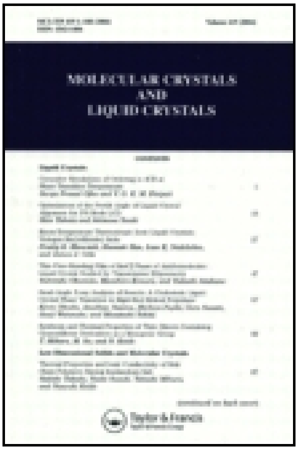

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Neutron Diffraction Study of $(TMTSF)_2BF_4$ after Slow and Rapid Cooling to 20 K

T. J. Emge [a], J. M. Williams [a], P. C. W. Leung [a], A. J. Schultz [a], M. A. Beno [a] & H. H. Wang [a]

[a] Chemistry and Materials Science and Technology Divisions, Argonne National Laboratory, and The Department of Chemistry, Brookhaven National Laboratory, Upton, New York, U.S.A., Argonne, Illinois, U.S.A.

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NEUTRON DIFFRACTION STUDY OF $(TMTSF)_2BF_4$ AFTER SLOW AND RAPID COOLING TO 20 K.

T. J. EMGE, J. M. WILLIAMS, P. C. W. LEUNG, A. J. SCHULTZ, M. A. BENO, AND H. H. WANG
Chemistry and Materials Science and Technology Divisions, Argonne National Laboratory, Argonne, Illinois, U.S.A. and The Department of Chemistry, Brookhaven National Laboratory, Upton, New York, U.S.A.

Abstract The structure of $(TMTSF)_2BF_4$ at 20 K has been determined from neutron diffraction data. It is completely ordered after both fast (6.0 deg. min $^{-1}$) and slow (0.1 deg min $^{-1}$) cooling through the metal-insulator (MI) transition at 40 K. Significant interactions in the 20 K dimerized phase include both short cation-cation (Se•••Se) and cation-anion (Se•••F and $-CH_3$•••F) contacts.

INTRODUCTION

Many $(TMTSF)_2X$ salts with tetrahedral anions undergo metal-insulator transitions (MI) that are often associated with crystallographic phase transitions at ambient pressure (including X = BF_4^-, ReO_4^-, FSO_3^-, $PO_2F_2^-$). Other than the ReO_4^- salt only the BF_4^- derivative is known to be ordered below the (MI) transition (this work). Above T_{MI} these organic metals have the common motif of interacting stacks of closely-connected TMTSF cations and disordered anions with at least one Se•••X interaction.[1] In a previous study of $(TMTSF)_2ReO_4$, (T_{MI} = 180 K), the F-centered 2ax2bx2c superstructure was examined at 120 K using x-ray diffraction data[2] and it contained a "dimerization" in the inter- and intra-stack distances (compared to the 298 K phase).[2] Diffuse x-ray scattering[3] studies of $(TMTSF)_2X$ with X = ReO_4^-, ClO_4^-, and NO_3^- suggest anion-ordering [AO] phase transitions. For $(TMTSF)_2ClO_4$, ordered or disordered ClO_4^- anions may be observed below 24 K depending on whether the cooling rate is slow or fast, respectively. It is not surprising that the anions are ordered in $(TMTSF)_2BF_4$ at 20 K even after fast cooling, since this anion is smaller than ClO_4^-. Using precise H-atom positions, we present definitive evidence of short $-CH_3 \cdots F$ contacts in $(TMTSF)_2BF_4$ at 20 K.

RESULTS

The space group and cell parameters of $(TMTSF)_2BF_4$ at 20 K[4] are similar to those of $(TMTSF)_2ReO_4$ in the low temperature phase.[2] Least-squares refinements converged at a high confidence level and positional parameters agreed within 2σ for both data sets. The superlattice diffraction peak profiles [h = odd reflections] had the same shape and width as sublattice (h = even) reflections. The perfectly octahedral geometry and small BF_4^- anion thermal motion (U_{ij} for the B and F atoms are within the range 0.005-0.009 $Å^2$) indicate complete ordering at 20 K for both slow- and fast-cooling. The most dramatic structural features, compared to the high-temperature phase, are found in the following changes in <u>inter-</u> and <u>intra</u>stack contact Se•••Se distances:

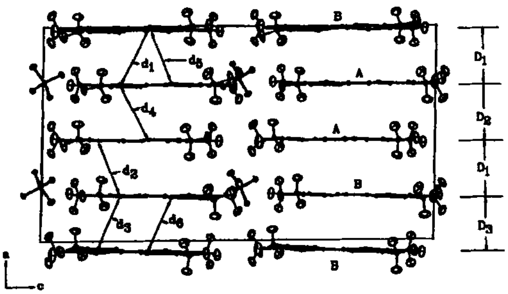

FIGURE 1

The <u>ac</u> projection of intrastack Se•••Se contacts (d_1 - d_6) and spacings between TMTSF cations A and B (D_1-D_3).

TABLE 1. A) Intrastack interactions (See Fig. 1)*

Se•••Se	20 K	125 K	Se•••Se	20 K	125 K
d_1^a	3.938(2)/3.977(2) Å	3.981 Å	d_4^b	4.056(2)/4.039(2) Å	4.075 Å
d_2^a	3.852(2)/3.964(2)	3.934	d_5^a	3.822(3)/3.887(2)	3.872
d_3^b	3.770(2)/3.785(2)	3.813	d_6^b	3.856(2)/3.817(2)	3.879

B) Interstack Interactions (See Fig. 2)

Se•••Se	20 K	125 K	Se•••F	20 K	125 K
d_7^a	3.720(2)/3.713(2) Å	3.753 Å	d_{10}	3.182(2) Å	3.28 Å
d_8^a	3.837(2)/3.837(2)	3.879	d_{11}	3.864(2)	3.82
d_9^b	3.622(3)/3.572(3)	3.639			

C) Interplanar Spacings (See Fig. 1)

	20 K	125 K		20 K	125 K
D_1	3.51 Å	3.57 Å	D_3	3.56 Å	$=D_1$
D_2	3.50	3.55			

*The two values at 20 K are equivalent by symmetry in the high temperature phase only. All numbers refer to results derived after slow cooling, which do not differ significantly from those after fast cooling.

[a] Related by the transformation 1-x, 1/2-y, 1/2-z.
[b] Related by the transformation 1/2-x, 1-y, 1/2-z.

The TMTSF cations form tetrameric units along the (stacking) a-axis, and the cations are canted about their long in-plane molecular axis, creating shorter intra-stack distances at one edge of each molecule. This tilting augments the slight shifts of TMTSF cations, along their short in-plane molecular axis, toward the next stack. The third direction of interaction is along the long in-plane axis of the TMTSF cations, where the cation-anion contacts dominate. We stress the importance of

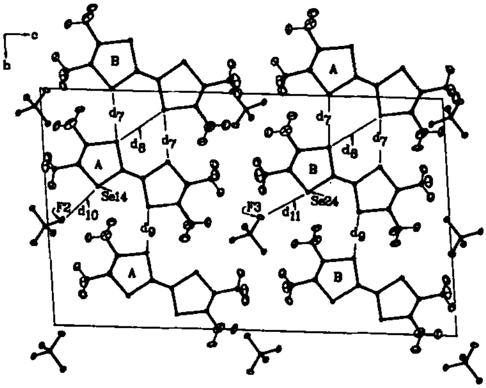

FIGURE 2
Projection of interstack Se•••Se contacts (d_7 - d_9) and inter-ion distances (d_{10} and d_{11}).

accurate H-atom positions, which are presented here as clear evidence of significant short H•••F contacts that describe the $-CH_3$•••F interactions:

TABLE 2 F•••H Distances (D < 2.5 Å) observed at 20 K and calculated at 125 K (See Fig. 3)

Interaction	20 K	125 K	Interaction	20 K	125 K
F2•••H25A	2.277(4) Å	2.41 Å	F4•••H19B	2.374(4) Å	2.64 Å
F2•••H24C	2.334(4)	2.54	F2•••H19A	2.380(4)	2.81
F1•••H15A	2.344(4)	2.71	F4•••H15A	2.475(4)	2.69
			F2•••H10C	2.476(5)	2.73

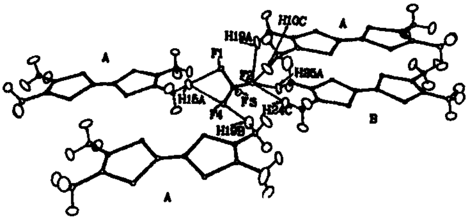

FIGURE 3
The cation-anion $-CH_3$•••F contacts less than 2.5 Å.

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