# Neutron-diffraction evidence for structural phase transitions in the organic conductors bis-tetramethyltetraselenafulvalenium salts [$(TMTSF)_2X$, $X = ClO_4^-$ and $BF_4^-$]

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Single-crystal neutron-diffraction experiments using the time-of-flight Laue technique establish that organic conductors, bis-tetramethyltetraselenafulvalenium salts [$(TMTSF)_2X$, $X = ClO_4^-$ and $BF_4^-$], undergo crystallographic phase transitions at low temperatures. This is the first neutron-diffraction evidence for structural phase transitions in any TMTSF salts. The phase transition in the $ClO_4^-$ salt leads to the creation of two crystallographically independent TMTSF columns with the possibility of different electron-transport properties for each column which can lead to independent low-temperature phase transitions.

The charge-transfer salts of tetramethyltetraselenafulvalene [$(TMTSF)_2X$, where $X$ is a monovalent anion] exhibit metallic conductivity at room temperature. Under pressures of about 5–10 kbar, the majority of these salts become superconducting at low temperatures ($T_c \simeq 1$ K).[1] Notable exceptions are the "slow-cooled" anion-ordered state of the $ClO_4^-$ salt, which is the only known ambient pressure Se-based organic superconductor,[2] and the $BF_4^-$ and $NO_3^-$ salts, which, although they remain metallic under pressure at very low temperature, do not become superconducting.[1] In fast-cooled $(TMTSF)_2ClO_4$, a magnetic state appears with no evidence of anion ordering.[3] At ambient pressure, except for the $ClO_4^-$ salt, these compounds undergo metal-insulator ($M$-$I$) transitions at low temperature. Recent experiments indicate that for anions which have tetrahedral geometry (i.e., $ReO_4^-$, $FSO_3^-$, and $BF_4^-$), the $M$-$I$ transitions appear to coincide with long-range ordering of the anions which are required to be disordered at room temperature due to the presence of a crystallographic inversion center.[4] Although the $M$-$I$ transition is not observed for the $ClO_4^-$ salt, a structural phase transition does occur at about 24 K at ambient pressure, as suggested from superlattice reflections observed in x-ray diffuse scattering experiments.[5] However, superlattice reflections were not observed in a preliminary neutron-diffraction study performed at 7 K.[6] Interestingly, the $ClO_4^-$ salt is the only Se-based ambient pressure superconductor and the only TMTSF salt to undergo an ($a, 2b, c$)-type structural transition (see Table I). It is apparent that the nature of the low-temperature

crystallographic phase transitions in these organic metals, e.g., ($a, 2b, c$) in $(TMTSF)_2ClO_4$ and ($2a, 2b, 2c$) in $(TMTSF)_2ReO_4$, is closely related to their low-temperature electrical conductivity characteristics. In this Rapid Communication we report the first neutron-diffraction evidence for the structural phase transitions in the $ClO_4^-$ and $BF_4^-$ salts of TMTSF.

All diffraction data were obtained by the time-of-flight Laue technique using the single-crystal diffractometer (SCD) at the Argonne National Laboratory Intense Pulse Neutron Source (IPNS).[7] The instrument consists of an unique $^6Li$-glass scintillation detector with an active area of $30 \times 30$ cm$^2$ and a spatial resolution of 3.5 mm. The IPNS is pulsed at a repetition rate of 30 Hz and the wavelengths of the scattered neutrons are obtained from their measured times of flight using the de Broglie equation $\lambda = (h/m)(t/l)$, where $h$ is Planck's constant, $m$ the neutron mass, and $t$ the time of flight for a distance $l$. This technique permits us the unique opportunity to sample a large volume of the reciprocal lattice simultaneously, which is especially helpful when searching for structural transitions at reduced temperature. A systematic search of the data for unknown superlattice reflections can be performed after the data collection has been completed.

Large single crystals of $(TMTSF)_2ClO_4$ and $(TMTSF)_2BF_4$ were grown by electrocrystallization.[1,8] The dimensions of the crystals used in the present study are $0.5 \times 0.5 \times 3.4$ mm$^3$ (3.4 mg) and $0.4 \times 0.4 \times 3.3$ mm$^3$ (2.1 mg) for the $ClO_4^-$ and $BF_4^-$ salts, respectively. Using a lo-

TABLE I. Summary of the different types of crystallographic phase transitions in the $(TMTSF)_2X$ salts.

| Anion ($X$) | Transition temperature (K) | Superlattice unit cell | Superlattice space group | Reference |
|---|---|---|---|---|
| $NO_3^-$ | 41 | $2a, b, c$ | $P\bar{1}$ | 13 |
| $ReO_4^-$ | 177 | $2a, 2b, 2c$ | $F\bar{1}$[a] | 12 |
| $FSO_3^-$ | 87.5 | $2a, 2b, 2c$ | $F\bar{1}$ | 14 |
| $ClO_4^-$ | 24 | $a, 2b, c$ | $P\bar{1}$ | 5, this work |
| $BF_4^-$ | 38 | $2a, 2b, 2c$ | $F\bar{1}$ | This work |

[a]The space group $F\bar{1}$ is chosen to facilitate direct comparison of the different phase transitions.
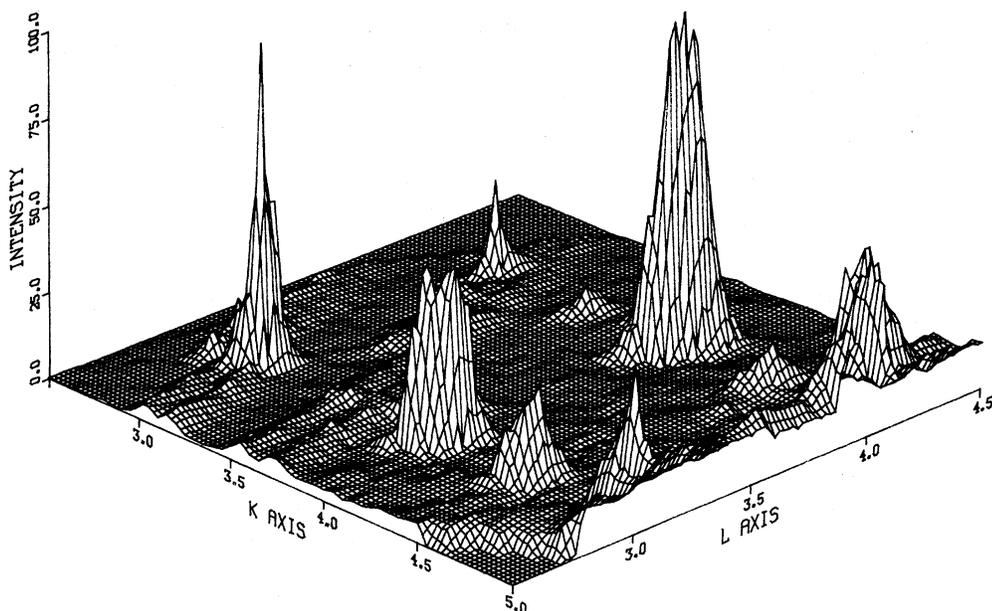
FIG. 1. Plot of the intensity distribution on the $(1,k,l)$ plane of $(TMTSF)_2ClO_4$ at 15 K. The superlattice reflections $(1,\frac{9}{2},3)$, $(1,\frac{9}{2},4)$, and $(1,\frac{7}{2},4)$ are clearly observed.

cally modified Displex® (Air Products and Chemicals, Inc., Model CS-202) closed-cycle helium refrigerator mounted on the SCD, these samples were cooled quickly (4 K/min) to about 60 K and then slowly (0.3 K/min) through the phase-transition temperatures of 24 and 39 K, respectively, for the $ClO_4^-$ and $BF_4^-$ salts. Data were obtained in histogram form for $(TMTSF)_2ClO_4$ at sample temperatures of 15, 20, 24, and 40 K and for $(TMTSF)_2BF_4$ at 20, 37, 40, 43, and 60 K. A noteworthy feature of the time-of-flight experiment is that only one crystal orientation was needed at all temperatures for each of the samples, which emphasizes the simplicity of this method.

Positions of Bragg reflections were obtained by automatic peak searches of the 15- and 20-K histogram data from the $ClO_4^-$ and $BF_4^-$ salts, respectively. In each case, an orientation matrix was calculated using an autoindexing routine with selected Bragg peaks. It was determined at this stage that the histogram data from both crystals contained Bragg reflections arising from twin components comprising about 40% of the $(TMTSF)_2ClO_4$ crystal and about 10% of the $(TMTSF)_2BF_4$ crystal. A second orientation matrix was then obtained in each case. All the observed Bragg peaks were then properly indexed using one of the two orientation matrices associated with each sample. For clarity, all subsequent discussion refers to indexing based on the unit cell for the high-temperature phase in each case.

The intensity distribution in the $(1kl)$ reciprocal-lattice plane for $(TMTSF)_2ClO_4$ at 15 K is presented in Fig. 1. Superlattice reflections are observed with indices of $h,k + \frac{1}{2},l$. Hence, an $(a,2b,c)$-type crystallographic transition consistent with the x-ray diffuse scattering results[5] is confirmed. A total of seven such reflections were located in the histogram and their normalized integrated intensities are plotted versus temperature in Fig. 2. The $I/\sigma(I)$ ratios at 15 K are in the range of 5 to 21 for the superlattice reflections and more than 50 for the fundamental reflections. The superlattice reflections disappear at 24 K, in agreement with the

known phase-transition temperature.[5,9]

The crystallographic phase transition in $(TMTSF)_2ClO_4$ is unique among the TMTSF salts (see Table I). The most common type of phase transition $(2a,2b,2c)$ always leads to
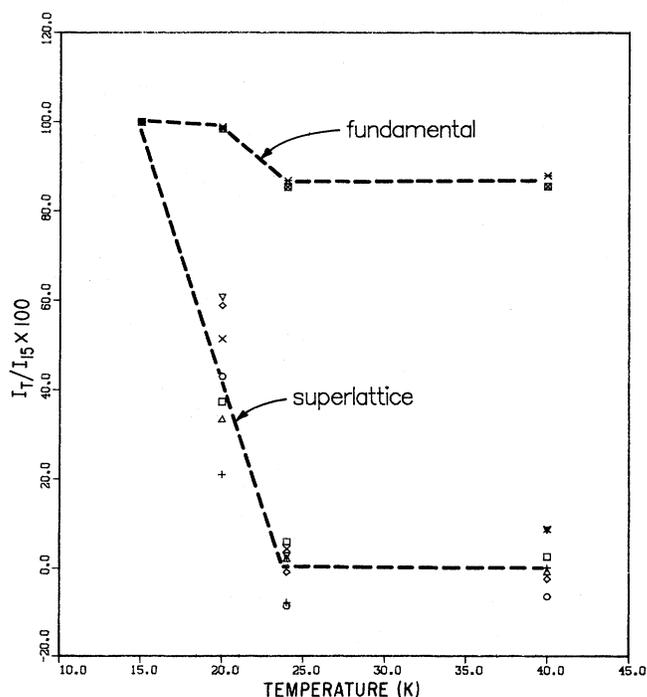


FIG. 2. Plot of the integrated intensities vs temperature of selected fundamental and superlattice Bragg reflections of $(TMTSF)_2ClO_4$. The different symbols denote independent reflections. For comparison, intensities of all fundamental and superlattice peaks are normalized to a nominal value of 100 at 15 K. Negative values result from the statistical variation of backrounds and peaks with zero intensities.
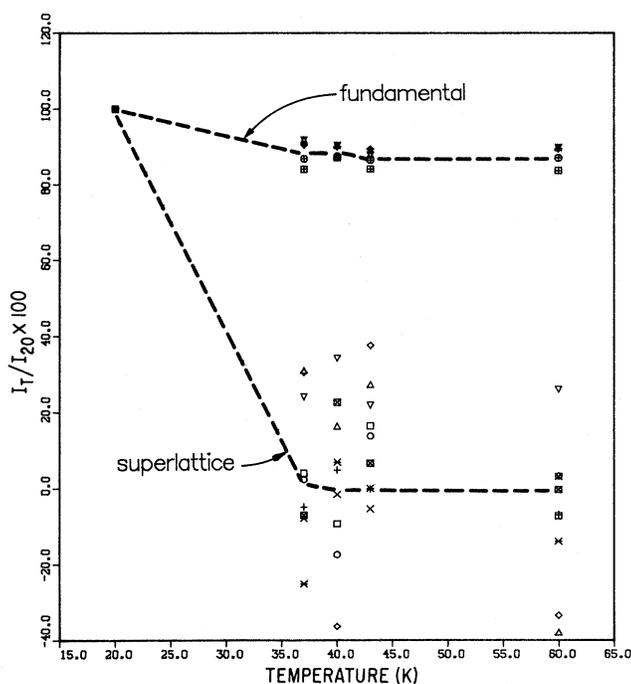
FIG. 3. Plot of the integrated intensities vs temperature of selected fundamental and superlattice Bragg reflections of $(TMTSF)_2BF_4$. Symbols and intensity normalization are as in Fig. 2.



FIG. 4. Packing diagrams on the $bc$ planes (a) of the observed superstructure of $(TMTSF)_2ReO_4$ and (b) of the proposed superstructure of $(TMTSF)_2ClO_4$. The two sheets of TMTSF molecules are above and below the plane of the anions in each figure. Short $O \cdots Se$ contacts ( $< 3.4$ Å) are indicated by broken lines.

an insulating state at ambient pressure.[10] However, under high pressure (5–10 kbar), these charge-transfer salts remain metallic to about 1 K and often become superconducting.[1] The $(a, 2b, c)$ transition in the $ClO_4^-$ derivative is the only transition which does not lead to an insulating state at ambient pressure and with slow cooling it is the only ambient pressure TMTSF superconductor at about 1 K.[2,11]

For the $BF_4^-$ salt, superlattice reflections with indices of $h + \frac{1}{2}, k + \frac{1}{2}, l + \frac{1}{2}$ (each of the indices is a half-integer) were observed below the 40-K transition which established a superlattice unit cell of $(2a, 2b, 2c)$. The integrated intensities of nine superlattice reflections are plotted versus temperature in Fig. 3. The $I/\sigma(I)$ ratios are about 4 to 14 for the superlattice reflections and more than 50 for the fundamental reflections at 20 K. To the best of our knowledge, this is the first direct observation of a low-temperature superlattice for $(TMTSF)_2BF_4$. As shown in Fig. 2, the intensities of the superlattice reflections become zero at about 37 K.

The only known crystal structure of the low-temperature phase (below the $M$-$I$ transition) of a TMTSF salt is for $(TMTSF)_2ReO_4$, which undergoes a $(2a, 2b, 2c)$ transition at 177 K.[4,12,13] Since the observed phase transition for the $BF_4^-$ salt is also the $(2a, 2b, 2c)$ type, the $BF_4^-$ anions are probably arranged in the crystal in the same way as the $ReO_4^-$ anions. As illustrated in Fig. 4, the orientation of the $ReO_4^-$ (and probably $BF_4^-$) ions in the low-temperature phase is such that adjacent anions in each of the three crystal axis directions are inversion related.

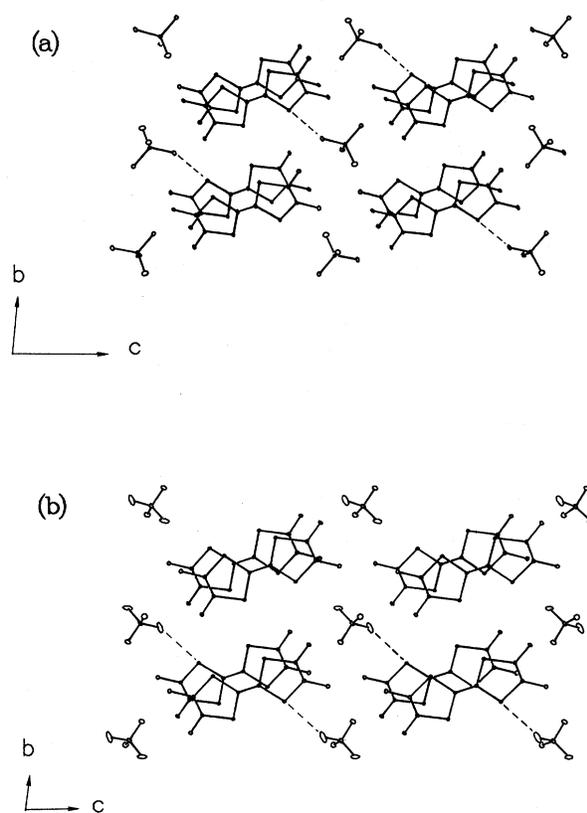On the other hand, the $(a, 2b, c)$ transition of the $ClO_4^-$

salt can result in a significant difference in the crystal packing of the anions. Although the $ClO_4^-$ ions in adjacent columns along the $b$ axis are inversion related, along unit cell $a$ (TMTSF stacking or column direction) and $c$ axes, they are in identical orientations, being related by the unit cell translations. Thus, in the low-temperature phase of $(TMTSF)_2ReO_4$, short $O \cdots Se$ contacts ( $< 3.4$ Å) occur to alternating TMTSF cations in every TMTSF column (see Fig. 4).[12] In $(TMTSF)_2ClO_4$, every TMTSF cation in alternating columns along the unit cell $b$-axis direction is involved in these $O \cdots Se$ interactions.[5] Hence, an $(a, 2b, c)$-type phase transition results in creation of two crystallographically distinct types of TMTSF columns each of which may contribute differently to the overall electron transport properties of the crystal.

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