Pressure-induced structural phase transition in the Bechgaard-Fabre salts

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Abstract
The crystal structures of the quasi-one-dimensional organic salts (TMTTF)\textsubscript{2}PF\textsubscript{6} and (TMTSF)\textsubscript{2}PF\textsubscript{6} were studied by pressure-dependent x-ray diffraction up to 10 GPa at room temperature. The unit-cell parameters exhibit a clear anomaly due to a structural phase transition at 8.5 and 5.5 GPa for (TMTTF)\textsubscript{2}PF\textsubscript{6} and (TMTSF)\textsubscript{2}PF\textsubscript{6}, respectively.

Key words:

1. Introduction
The Fabre salts (TMTTF)\textsubscript{2}X and the Bechgaard salts (TMTSF)\textsubscript{2}X represent prime examples of quasi-one-dimensional electronic systems demonstrating a large variety of phenomena such as superconductivity, charge order, Mott-Hubbard insulating state, spin-density-waves etc. which have been extensively studied over the last three decades\textsuperscript{[1,2,3,4]}. The structure of these salts consist of molecular stacks formed by tetramethyltetraithiafulvalene (TMTTF) or tetramethyltetraselenafulvalene (TMTSF) cations separated by the monovalent \textit{X}\textsuperscript{-} anions. At room temperature the (TMTTF)\textsubscript{2}X salts are typically Mott-Hubbard insulators due to the strong correlation of electrons and a weak interchain coupling\textsuperscript{[5]}. On the other hand, the (TMTSF)\textsubscript{2}X salts are good quasi-one-dimensional metals although their properties are still strongly affected by correlation effects\textsuperscript{[3,6]}.
In the Bechgaard-Fabre salts the interstack separation and therefore the interchain hopping integral can be nicely tuned either by changing the size of the \( X^- \) anions or the type of the cation (chemical pressure effect), or by applying external pressure. It has been demonstrated that the effect of chemical and external hydrostatic pressure are virtually equivalent; i.e. numerous physical quantities of \((\text{TMTSF})_2X\) resemble those of \((\text{TMTTF})_2X\) under pressure. This provides the possibility to construct a generic temperature-pressure phase diagram \([7, 8]\) of the Bechgaard-Fabre salts. Continuous tuning of external pressure and temperature is the best way to explore the phase boundaries in this diagram. Jaccard et al. \([9]\) employed a diamond anvil cell (DAC) to generate extreme pressures that made it possible, for instance, to tune \((\text{TMTTF})_2\text{PF}_6\) throughout the phase diagram starting from the insulating spin-Peierls up to the superconducting state. A DAC has also been used in infrared spectroscopy experiments that demonstrated pressure-induced insulator-to-metal transition in the TMTTF family \([10, 11]\). For a correct quantitative analysis of data obtained in the above mentioned experiments, knowledge of the crystal structure is crucial. However, the compressibility and structure at high pressures of the Bechgaard-Fabre salts has not been measured up to the present day. To the best of our knowledge, the highest pressure at which the structure has been determined is 1.6 GPa for the example of \((\text{TMTSF})_2\text{PF}_6\) - the first organic superconductor \([12, 13]\). On the other hand, high-pressure dc transport of \((\text{TMTTF})_2\text{PF}_6\) has been investigated at pressures up to 8 GPa \([9]\), much higher than any structural study of the Bechgaard-Fabre salts reported up to now.

In this paper, we present results of single-crystal x-ray diffraction performed on two typical salts \((\text{TMTTF})_2\text{PF}_6\) and \((\text{TMTSF})_2\text{PF}_6\) for pressures up to 10 GPa. We determine the pressure dependence of the unit cell constants and volume compressibility of the crystals. Moreover, we found pressure-induced structural phase transitions which take place at high pressures in both studied salts.

2. Experiment

Single crystals of \((\text{TMTTF})_2\text{PF}_6\) and \((\text{TMTSF})_2\text{PF}_6\) were grown by a standard electrochemical procedure \([14]\). The room-temperature x-ray diffraction experiments were carried out at beamline ID09A of the European Synchrotron Radiation Facility in Grenoble. The wavelength used for the experiments was 0.413 Å. X-ray diffraction patterns were collected on an im-
Figure 1: (Color online) Normalized unit cell parameters of (TMTTF)$_2$PF$_6$ and (TMTSF)$_2$PF$_6$ as a function of pressure obtained at room temperature. Full lines are guides to the eye. The dotted blue lines correspond to the fit of the pressure-dependent unit-cell volume using the Birch equation.

The DAC rotation angle varied from $-30^\circ$ to $+30^\circ$ for (TMTTF)$_2$PF$_6$ and from $-20^\circ$ to $+20^\circ$ for (TMTSF)$_2$PF$_6$ with $2^\circ$ step. Liquid helium served as pressure transmitting medium in the DAC. The diffraction patterns have been analyzed using the XDS package. The pressure in the DAC was determined in situ by the ruby luminescence method.

3. Results and Discussion

The single-crystal x-ray diffraction analysis confirms the space-group symmetry $P\overline{1}$ of both studied compounds in the low-pressure phase reported previously. The pressure dependence of the normalized cell parameters of (TMTTF)$_2$PF$_6$ and (TMTSF)$_2$PF$_6$ compounds is shown in Fig. 1. The compression of both compounds is anisotropic: The intrastack molecular separation defined by the unit cell parameter $a$ suffers an approximately two times larger variation under pressure compared to the $b$ and $c$-axes lattice parameters, which are related to the interstack separation. The maximal softness in the stacking direction is in accord with the anisotropy of the thermal expansion coefficient that is largest along the $a$ axis.

The change of the unit cell volume can be well fitted with the Birch...
equation of state [19]:

$$P(V) = \frac{3}{2} B_0 (x^7 - x^5) \left[ 1 + \frac{3}{4} (B'_0 - 4)(x^2 - 1) \right]$$

(1)

with $x = (V_0/V)^{1/3}$, where $V_0$ is the unit cell volume at ambient pressure; $B_0$ denotes the bulk modulus and $B'_0$ its pressure derivative. The parameters of the fit together with the absolute values of the unit-cell dimensions are given in Tab. 1. The values reported for (TMTSF)$_2$PF$_6$ are in reasonable agreement with previous structural studies under moderate pressure [12, 13].

Table 1: The unit cell parameters of (TMTTF)$_2$PF$_6$ and (TMTSF)$_2$PF$_6$ at ambient pressure, and the bulk modulus $B_0$ and its pressure derivative $B'_0$ obtained from the fit according to Eq. (1).

|                  | (TMTTF)$_2$PF$_6$ | (TMTSF)$_2$PF$_6$ |
|------------------|-------------------|-------------------|
| $a$ (Å)          | 7.156             | 7.281             |
| $b$ (Å)          | 7.572             | 7.681             |
| $c$ (Å)          | 13.211            | 13.486            |
| $\alpha$         | 82.427            | 83.08             |
| $\beta$          | 84.661            | 86.322            |
| $\gamma$         | 72.321            | 70.829            |
| $V_0$ (Å$^3$)    | 675.02            | 706.95            |
| $B_0$ (GPa)      | 7.27 ± 0.64       | 12.71 ± 0.97      |
| $B'_0$           | 9.98 ± 1.15       | 4.23 ± 0.75       |

Upon increasing the pressure further, the unit-cell parameters experience an abrupt jump indicating a pressure-induced structural phase transition. The transition occurs at 5.5 GPa in (TMTSF)$_2$PF$_6$ and at 8.5 GPa in (TMTTF)$_2$PF$_6$. The most salient changes across the transition are the doubling of the unit cell along the $b$ axis and the increase of the angle $\gamma$ to 90° (see Fig. 2), which basically modifies the crystal symmetry from triclinic to orthorhombic. This seems to be a stable configuration that does not change with pressure any more.

The phase transition also affects the unit cell length along the $c$ axis, however, the $a$ axis unit cell length remains unaffected. This is illustrated in Fig. 2 for both studied compounds. The abrupt increase of the $c$ axis dimension at the transition pressure is of approximately 5% and it is clearly noticeable. The variation of the $a$ parameter seems to be smooth across the whole studied pressure range without signs of any sharp anomaly.
Figure 2: Unit cell parameters of (TMTTF)$_2$PF$_6$ [(a) and (c)] and (TMTSF)$_2$PF$_6$ [(b) and (d)] as a function of pressure up to 10 GPa. Both the interstack separation $b$ [left axes of (a) and (b)] and the $\gamma$ angle [right axes of (a) and (b)] exhibit abrupt jumps that indicate structural phase transitions. The unit cell length along the longest interstack separation $c$ axis [right axes (c) and (d)] shows an anomaly around the phase transition in both salts. At the same time the $a$ axis parameter does not reveal any noticeable discontinuity [left axes of (c) and (d)].

We suggest a tentative model illustrated in Fig. 3 to explain the pressure-induced structural distortion. By looking along the $c$ axis, the figure basically shows the projection of the crystal structure onto the $ab$ plane for pressures above and below the transition $P_c$. The fluorine and hydrogen atoms are not shown for simplicity. The initial compression of the crystal lattice pushes the molecular stacks of cations closer to each other. This effect is in particular strong along the $b$ axis, since the interstack separation is already small at ambient pressure compared to the separation in $c^*$ direction. Above the critical pressure $P_c$ the interstack interaction becomes strong enough to drive the structural instability. It leads to a small tilting of the cation molecules in the stacks such that two neighboring unit cells become inequivalent. As a result the unit cell doubles and the new unit cell translational vector $b$ is defined as shown in Fig. 3. However, we have to stress that although the unit cell parameters depicted in Fig. 3 corresponds to our experimental data taken for the (TMTSF)$_2$PF$_6$ sample, the atomic positions could not be
unambiguously extracted from the x-ray diffraction data and, therefore, the depicted structural distortion is only schematic.

The unit cell parameters of the new structure are directly related to the unit cell parameters in the low pressure phase:

\[
b^* = \sqrt{a^2 + 4b^2 - 4ab\cos\gamma}
\]

\[
\gamma^* = 180 - \arcsin\left(\frac{2b\sin\gamma}{b^*}\right)
\]

\[
V^* = 2V
\]

Thus, in order to verify the real discontinuity, i.e., the one which is not related to the new definition of the unit cell, we have to compare the unit cell parameters defined as in Eq. 3 at pressures below and above \(P_c\). Fig. 4
shows such a comparison of \( b^* \), \( \gamma^* \) and \( V^* \) for both studied salts. One can observe the clear discontinuities in \( b^* \) and \( \gamma^* \) indicating that the structural phase transition is of first order. The anomaly in the unit cell volume \( V^* \) is almost invisible due to the increase in \( c \) axis parameter (see Fig. 2) which compensates decrease in \( b^* \).

The reason for the unit cell doubling and formation of the quasi-orthorhombic structure could be the enhancement of the interaction between the cation molecules in the stacks and the anions, which becomes particularly strong for \( \gamma^* = 90^\circ \), i.e., when the planar cation molecules and the anions arranged within the same crystallographic plane.

Remarkably, the pressure offset between the structural transitions in \((TMTTF)_2PF_6\) compared to \((TMTSF)_2PF_6\) is about 3 GPa, i.e., almost exactly the same as the offset between electronic phases of both compounds in the generic phase diagram of the Bechgaard-Fabre salts.\[^7\] However, it seems unlikely that the structural distortion is related to some kind of electronic instability, since in this case the spectrum of electronic excitations would change. This is, however, not observed in infrared spectra of \((TMTSF)_2PF_6\) above the structural transition, i.e., for \( P > 5.5 \) GPa. The reflectivity along the \( a \) and \( b' \) direction shows a metallic character with a rather small anisotropy. No indication of an energy gap and other sudden changes was observed \[^{11}\].

4. Summary

We performed room temperature x-ray diffraction study under pressure of the quasi-one-dimensional salts \((TMTTF)_2PF_6\) and \((TMTSF)_2PF_6\). The pressure dependence of the unit cell constants has been obtained for pressures up to 10 GPa. A structural phase transition from triclinic to nearly orthorhombic phase is observed at 5.5 and 8.5 GPa in \((TMTSF)_2PF_6\) and \((TMTTF)_2PF_6\), respectively. The transition is accompanied by a doubling of the unit cell in direction of the \( b \) axis. Several unit cell parameters (\( b^* \), \( \gamma^* \) and \( c \)) show a considerable discontinuity across the transition pressure indicating the phase transition of the first order. The tentative model of the structural distortion related to the modulation of the cation tilting in the stacks is proposed.
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Figure 4: (Color online) The parameters for the doubled quasi-orthorhombic unit cell of \((\text{TMTTF})_2\text{PF}_6\) and \((\text{TMTSF})_2\text{PF}_6\) as a function of pressure up to 10 GPa. Open symbols correspond to the parameters in the high-pressure phase directly obtained from the x-ray diffraction analysis. The full symbols are the parameters calculated using Eq. [3] in the low-pressure phase.