Structural properties of the organic superconductor $\kappa_{\text{H}}$(DMEDO-TSeF)$_2$[Au(CN)$_4$](THF)

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Introduction

Most organic superconductors have been obtained as clean single crystals; the donor molecules and anions are ordered states. Recently, two new organic superconductors with the same chemical composition, $\kappa_{\text{L}}$ and $\kappa_{\text{H}}$-(DMEDO-TSeF)$_2$[Au(CN)$_4$](THF), have been developed [1]. Although the solvent molecule THF of the high-$T_c$ (H) phase is ordered even at room temperature, THF of the low-$T_c$ (L) phase is disordered by the mirror symmetry. We have determined the structural phase transition in the L-phase; the orthorhombic system changes to two monoclinic domains below 209 K [2]. On the other hand, the H-phase has two crystallographically independent conducting layers, A and B. The quantum oscillation of this salt indicates that the interlayer charge disproportionation, where the difference charge is 0.05 degree, occurs despite of a bulk single crystal [3]. The present paper reports the low-temperature crystal structure of the H-phase.

Results and Discussion

The space group is $P2_1/1c$, and the lattice parameters at 34 K are $a = 38.583(1)$ Å, $b = 10.9621(3)$ Å, $c = 8.1480(4)$ Å, $\beta = 93.626(5)^\circ$, and $V = 3439.3(2)$ Å$^3$. The final $R$-value is $R1 = 0.069$.

![Figure 1: Labeling of the C-S (Se) and C=C averaged central bond lengths in (a) BEDT-TTF and (b) DMEDO-TSeF.](image)

A method for determining experimentally the charges of the BEDT-TTF molecules has been developed using the intramolecular bond lengths [4-6]. Oxidation of the BEDT-TTF molecule lengthens $a$ and $d$ (C=C bonds), and shortens $b$ and $c$ (C-S bonds) as shown in Fig. 1(a). The parameter defined as $\delta = (b + c)-(a + d)$ is sensitive to the charge transfer degree of the BEDT-TTF molecule. The parameter $\delta$ decreases as the charge transfer degree increases. We should use this method for the present compound on the assumption of the $D_{2h}$ symmetry for the tetraselenafulvalene unit of the DMEDO-TSeF molecule as shown in Fig. 1(b).

![Figure 1: Labeling of the C-S (Se) and C=C averaged central bond lengths in (a) BEDT-TTF and (b) DMEDO-TSeF.](image)

The bond lengths defined in Fig. 1(b) of the H-phase at 34 K are listed in Table I.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$d$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecule A</td>
<td>1.363(8)</td>
<td>1.888(3)</td>
<td>1.897(3)</td>
<td>1.345(6)</td>
</tr>
<tr>
<td>Molecule B</td>
<td>1.361(8)</td>
<td>1.888(3)</td>
<td>1.894(3)</td>
<td>1.350(6)</td>
</tr>
</tbody>
</table>

The parameter $\delta$ estimated from Table I is 1.08(1) for the A molecule, and is 1.07(1) for the B molecule, respectively. Therefore, we cannot distinguish the difference of the charge between of the A and the B molecules from the bond lengths. This result indicates that the bond lengths are not useful to clarify the interlayer charge disproportionation for the present compound. However, the resonant x-ray scattering method will be a powerful tool for this compound.

References


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