

Novel structure of the organic superconductor: κ - δ -(BEDT-TTF)₂Ag(CF₃)₄(TCE)

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Introduction

In 1994, the group of Argonne National Laboratory discovered new organic superconductors based on BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene, see Fig. 1(a)) using the anion of $M(\text{CF}_3)_4$ ($M = \text{Cu}, \text{Ag}, \text{Au}$) [1,2]. They found that there were low- and high- T_c phases. Although the low- T_c phase was the usual κ -type structure, the structure of the high- T_c phase was unknown. The lattice parameters of the high- T_c phase were presented in 1995, and suggested that the large unit cell contained four κ -type conducting layers [2]. It is important to clarify the crystal structure of the high- T_c phase of the $M(\text{CF}_3)_4$ superconductors with T_c of 10 K class. We report that the high- T_c phase of the $\text{Ag}(\text{CF}_3)_4$ salts has the unusual crystal structure, the dual layered structure (κ - and δ -types), among the organic superconductors. Recently, another research group has succeeded independently the crystal structure analysis for the high- T_c phase of (BEDT-TTF)₂Ag(CF₃)₄(TCE) [3]. However, their result differs from ours; the crystal system is triclinic and the value of the unit cell is about half of our result. Several results show that there are two kinds of high- T_c phases for the $\text{Ag}(\text{CF}_3)_4$ salts ($T_c = 9.4$ K and 11.1 K) [1]. This means that our solved structure is the third phase in the superconducting $\text{Ag}(\text{CF}_3)_4$ salts.

Results and Discussion

The structure was solved using the direct method (SIR2004) and was refined using the full-matrix least-squares procedure (SHELXL) [4,5]. Anisotropic thermal parameters were adopted for all non-hydrogen atoms.

Figure 1(b) shows the crystal structure of the high- T_c phase [6]. The chemical composition is (BEDT-TTF)₂Ag(CF₃)₄(TCE), and all atoms are ordered state. There are two kinds of donor arrangements, κ - and δ -types, and the unit cell contains four crystallographically independent donors, two independent anions, and two independent solvent molecules. Both two crystallographically independent polar solvent molecules, TCE, in the anion layer have the skew type rotational configuration and they are ordered as an antiferroelectric arrangement.

A method for determining experimentally the charges of the BEDT-TTF molecules has been developed using the intramolecular bond lengths [7]. The parameter

defined as $\delta = (b + c) - (a + d)$ is sensitive to the charge transfer degree of the BEDT-TTF molecule (Fig. 1(a)). The parameter δ decreases as the charge transfer degree increases. The charge transfer degrees estimated from the bond lengths of two crystallographically independent molecules in the δ -layer are 0.97(7) and 0.30(7), respectively; the δ -layer is a charge ordered state. Moreover, the charge transfer degrees in the κ -layer are 0.3(1) and 0.3(1), respectively. It seems that the present compound is an interlayer charge disproportionation.

In summary, we have solved the crystal structure of the high- T_c $\text{Ag}(\text{CF}_3)_4$ salt, and the present structure is the third phase in the superconducting $\text{Ag}(\text{CF}_3)_4$ salts.

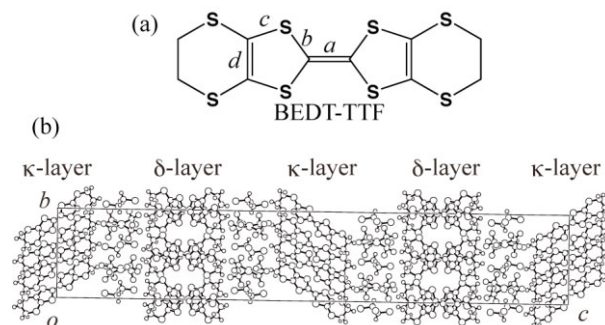


Figure 1: (a) BEDT-TTF molecule. (b) Crystal structure of the high- T_c phase of (BEDT-TTF)₂Ag(CF₃)₄(TCE) projected onto the bc -plane at 66 K.

References

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- [6] Crystal data of κ - δ -(BEDT-TTF)₂Ag(CF₃)₄(TCE) at 66 K: monoclinic, space group $P2_1/n$, $a = 8.4013(2)$ Å, $b = 13.1846(2)$ Å, $c = 75.3636(7)$ Å, $\beta = 90.1090(13)^\circ$, $V = 8347.8(2)$ Å³, $Z = 8$, $R_1 = 0.1062$ for 14340 [$F_o^2 > 2.0\sigma(F_o^2)$] observed reflections. The lattice parameters are qualitatively the same as those in Ref. 2.
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