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Third polymorph of the (BEDT-TTF)$_2$Ag(CF$_3$)$_4$(TCE) organic superconductor

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Introduction

In 1994, Argonne National Laboratory group discovered new organic superconductors based on BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene] using the anion of [M(CF$_3$)$_4$]$^-$ (M = Cu, Ag, 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]. We report that the high-T_c phase of the Ag(CF$_3$)$_4$ salts has the unusual crystal structure, the dual layered structure (κ- and α'-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)$_2$Ag(CF$_3$)$_4$(TCE) [3]. However, their result differs from ours; the crystal system is triclinic and the unit cell contains two donor layers, so-called κα'$_1$-phase. Several results show that there are two kinds of high-T_c phases for the Ag(CF$_3$)$_4$ salts (T_c = 9.4 K and 11.1 K) [1]. This means that our solved structure (κα'$_2$-phase) is the third polymorph in the superconducting Ag(CF$_3$)$_4$ salts. The magnetic torque measurements show that the superconducting critical temperatures are approximately 9.5 K and 11.0 K for the two-layered (κα'$_1$-phase) and four-layered (κα'$_2$-phase) phases, respectively.

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]. Figure 1(a) shows the crystal structure of the high-T_c phase [6]. The chemical composition is (BEDT-TTF)$_2$Ag(CF$_3$)$_4$(TCE), and all molecules are ordered. There are two kinds of donor arrangements, κ- and α'-types, and the unit cell contains four crystallographically independent donors, two independent anions, and two independent solvent molecules. The crystal structure is similar to that of the κα'$_1$-phase. The charge transfer degrees estimated from the bond lengths of two crystallographically independent molecules in the α'-layer are 0.97(9) and 0.18(10), respectively; the α'-layer is in a charge-ordered state [7]. This indicates that the κ-layer shows superconductivity. To determine the T_c values of the κα'$_1$- and κα'$_2$-phases, the magnetic torque has been measured after examining the lattice parameters using x-ray oscillation photographs. The magnetic torque clearly shows that the κα'$_1$-phase has a lower T_c than the κα'$_2$-phase.

In summary, we have found the third polymorph of the title compound with the charge ordered layers. The present structure is similar to the κα'$_1$-phase recently found in high-T_c Ag(CF$_3$)$_4$ salts. The onset superconducting transition temperatures determined from the magnetic torque are approximately 9.5 and 11.0 K for the κα'$_1$- and κα'$_2$-phases, respectively.

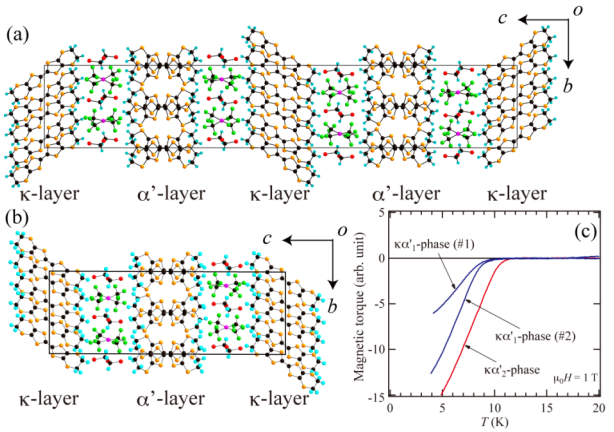

Figure 1: Crystal structure of the κα'$_2$-phase (a) and the κα'$_1$-phase from Ref.3 (b). (c) Temperature dependence of the magnetic torque.

References

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[6] Crystal data of κα'$_2$-(BEDT-TTF)$_2$Ag(CF$_3$)$_4$(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, β = 90.1090(13)°, V = 8347.8(2) Å^3, Z = 8, R = 0.1151 for all observed reflections (14775 reflections). The lattice parameters are qualitatively the same as those in Ref. 2.
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