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$_3$)$_3$]$^+$ (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 $\kappa$-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 $\kappa$-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 ($\kappa$- and $\kappa'$-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 $\kappa\kappa'$-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 ($\kappa\kappa'$-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 $\kappa\kappa'$- and $\kappa\kappa''$-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, $\kappa$- and $\kappa'$-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 $\kappa\kappa'$-phase. The charge transfer degrees estimated from the bond lengths of two crystallographically independent molecules in the $\alpha$'-layer are 0.97(9) and 0.18(10), respectively; the $\alpha$'-layer is in a charge-ordered state [7]. This indicates that the $\kappa$-layer shows superconductivity. To determine the $T_c$ values of the $\kappa\kappa'$- and $\kappa\kappa''$-phases, the magnetic torque has been measured after examining the lattice parameters using x-ray oscillation photographs. The magnetic torque clearly shows that the $\kappa\kappa'$-phase has a lower $T_c$ than the $\kappa\kappa''$-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 $\kappa\kappa'$-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 $\kappa\kappa'$- and $\kappa\kappa''$-phases, respectively.

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

References

[6] Crystal data of $\kappa\kappa''$(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, $\beta = 90.1090(13)^\circ$, $V = 8347.8(2)$ 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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