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Polymorphism in κ-(BEDT-TTF)$_2$M(CF$_3$)$_4$(solvent) superconductors

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Abstract

A new crystallographic modification (κ_L') was found in the BEDT-TTF:M(CF$_3$)$_4^-$:solvent (M = Cu, Ag, Au) system. The structure of monoclinic κ_L'-(BEDT-TTF)$_2$Cu(CF$_3$)$_4$(1,2-dibromo-1-chloroethane = DBCE) is reported. It differs from the orthorhombic κ_L-phase by having all BEDT-TTF molecules tilted in the same direction with respect to the conducting plane normal, whereas in κ_L the tilt direction alternates between layers.

Keywords: Organic superconductors, X-ray diffraction

1. Introduction

We have recently reported superconductivity in the organic radical-cation salts (BEDT-TTF)$_2M$(CF$_3$)$_4$(solvent), where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene, M = Cu, Ag, or Au, and the co-crystallized solvent is a 1,1,2-trihaloethane with chlorine and bromine as the halogen substituents [1–3]. Many of these salts form two distinct superconducting phases with characteristic morphologies, i.e., plates and thin needles. In all the examples found to date, the plates have the lower superconducting transition temperatures (T_c), ranging from 2.1 to 5.8 K (diamagnetic onset), and the needles have T_c values between 7.2 and 11.1 K. While complete crystal structures were determined [4] for the plate phases with M = Cu and Ag, and with solvent = 1,1,2-trichloroethane, the plate phases of many of the other possible combinations were shown to be isostructural by their lattice constants. The BEDT-TTF molecule packing in these salts was found to be of the κ-type, such as that found in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X (X = Cl or Br) [5] and in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ [6], thus we have denoted the plate phase as κ_L (the subscript L because they are the group with the lower T_c). Based on preliminary X-ray diffraction experiments and on the maximum in the electrical resistivity around 90 K (a characteristic of many κ-phase superconductors), we assigned the label κ_H (H for "high"-T_c) to the needle phase [2].

2. Monoclinic κ_L'-(BEDT-TTF)$_2$Cu(CF$_3$)$_4$(DBCE)

In the course of our investigation of the correlation between the lattice parameters and T_c of the κ_L-phase salts, we encountered somewhat thicker plate-like crystals with slanted side faces (indicative of symmetry lower than orthorhombic) among the regular κ_L-crystals with M = Cu and 1,2-dibromo-1-chloroethane (DBCE) as the solvent. A full crystal structure determination was carried out at 118 K on a Siemens SMART® CCD-area detector based X-ray diffractometer. The structure was found to be monoclinic [space group $C2/c$), a = 39.050(2) Å b = 8.4730(4) Å, c = 12.9659(6) Å, β = 102.677(1)°, V = 4185.4(3) Å^3, Z = 4, $R(F_o)$ = 0.037], and a projection along the 8.5 Å axis is shown in Figure 1 along with the corresponding view in a standard κ_L-phase. Atomic coordinates are given in Table 1.

While both structures contain two conducting BEDT-TTF donor molecule layers per unit cell, their difference is evident in the tilt pattern of the BEDT-TTF long molecular axis with respect to the layer normal. In the monoclinic phase, both layers are tilted in the same direction, whereas in the orthorhombic phase [4] the tilt direction zig-zags. Within the layers, the two structures are essentially identical, and even the anion-solvent layers are very similar (including the crystallographic disorder of the CF$_3$-groups and the solvent

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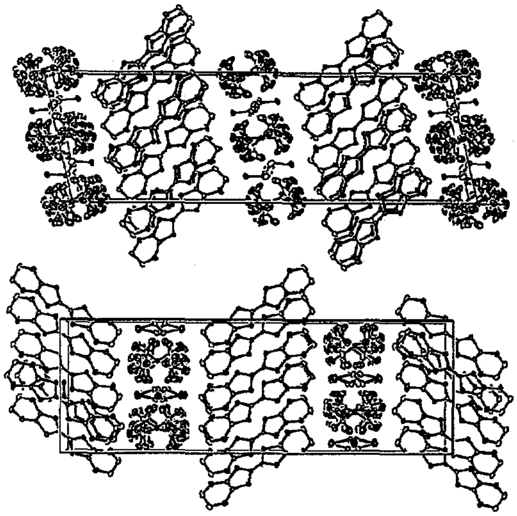

Fig. 1. Projection along the 8.5 Å axis of the crystal structures of κ_L'-(BEDT-TTF)$_2$Cu(CF$_3$)$_4$(DBCE) (top) and κ_L-(BEDT-TTF)$_2$Cu(CF$_3$)$_4$(TCE) (bottom).

molecules), allowing for slight difference due to the different symmetry requirements (mirror plane in the orthorhombic phase; inversion center on the anion and two-fold rotation axis through the disordered solvent molecule). Because of the close similarities, we denote the monoclinic structure type as κ_L'.

Preliminary magnetic susceptibility measurements on small crystals (the largest crystals obtained to date are 0.07 mg, which is at the sensitivity limit of the ac susceptometer) of the κ_L'-phase indicate the diamagnetic shielding signal typical of a superconductor with an onset T_c of ca. 4 K, compared to the value of 5.5 K obtained for the orthorhombic κ_L-phase of the same composition [3].

3. Conclusions

A new superconducting phase has been found in the BEDT-TTF:Cu(CF$_3$)$_4^-$:solvent system. We are currently examining whether the κ_L'-phase occurs in solvents other than DBCE and are studying its physical properties.

Table 1

Atomic coordinates. Atoms denoted with * were refined with 50% occupancy. The refined Br:Cl ratios were 69.7(3):30.3(3) and 62.4(5):37.6(5) for sites 1 and 2, respectively.

Atom	x	y	z
S1	0.20055(2)	0.47662(9)	0.34866(6)
S2	0.22911(2)	0.73136(9)	0.23773(6)
S3	0.26635(2)	0.48318(10)	0.53696(6)
S4	0.30021(2)	0.72848(9)	0.43280(6)
S5	0.13615(2)	0.42888(10)	0.18465(6)
S6	0.16939(2)	0.74329(10)	0.05535(6)
S7	0.32721(2)	0.41878(10)	0.70744(7)
S8	0.36910(2)	0.70639(11)	0.58129(8)
C1	0.23477(8)	0.6085(4)	0.3477(2)
C2	0.26376(8)	0.6088(4)	0.4287(2)
C3	0.17519(8)	0.5341(4)	0.2259(2)
C4	0.18816(8)	0.6525(4)	0.1758(2)
C5	0.31003(8)	0.5285(4)	0.5941(2)
C6	0.32571(8)	0.6404(4)	0.5461(2)
C7	0.11206(8)	0.5624(4)	0.0855(3)
C8	0.13270(9)	0.6137(4)	0.0048(3)
C9	0.36856(9)	0.5158(5)	0.7559(3)
C10	0.38856(9)	0.5519(4)	0.6712(3)
Cu	0.0000	0.0000	0.5000
C11	0.04011(11)	0.1364(7)	0.4990(4)
F1A*	0.03266(15)	0.3078(6)	0.5157(4)
F2A*	0.0559(2)	0.1488(8)	0.4206(5)
F3A*	0.06774(12)	0.1277(6)	0.5886(4)
F1B*	0.0364(2)	0.1864(9)	0.4006(6)
F2B*	0.0469(2)	0.2308(12)	0.5666(8)
F3B*	0.07051(14)	0.0326(9)	0.4986(5)
C12	−0.03133(12)	0.1629(6)	0.4249(5)
F4A*	−0.0565(2)	0.112(2)	0.3377(10)
F5A*	−0.06351(13)	0.1648(6)	0.4750(4)
F6A*	−0.0200(2)	0.3076(6)	0.4618(4)
F4B*	0.0128(2)	−0.2541(8)	0.6550(4)
F5B*	0.0438(2)	−0.2751(10)	0.5357(5)
F6B*	0.0428(3)	−0.1491(10)	0.6649(7)
Br1	−0.06009(3)	0.44691(13)	0.69952(10)
Cl1	−0.0573(2)	0.4195(9)	0.7105(7)
Br/Cl2	0.0000	0.15328(10)	0.7500
C21*	−0.0104(2)	0.3792(11)	0.7153(7)
C22*	0.0102(3)	0.4679(11)	0.8019(7)

References

[1] J.A. Schlueter, U. Geiser, J.M. Williams, H.H. Wang, W.-K. Kwok, J.A. Fendrich, K.D. Carlson, C.A. Achenbach, J.D. Dudek, D. Naumann, T. Roy, J.E. Schirber and W.R. Bayless, *J. Chem. Soc., Chem. Commun.* (1994) 1599.

[2] J.A. Schlueter, K.D. Carlson, J.M. Williams, U. Geiser, H.H. Wang, U. Welp, W.-K. Kwok, J.A. Fendrich, J.D. Dudek, C.A. Achenbach, P.M. Keane, A.S. Komosa, D. Naumann, T. Roy, J.E. Schirber and W.R. Bayless, *Physica (Amsterdam) C230* (1994) 378.

[3] J.A. Schlueter, J.M. Williams, U. Geiser, J.D. Dudek, M.E. Kelly, S.A. Sirchio, K.D. Carlson, D. Naumann, T. Roy and C.F. Campana, *Adv. Mater. 7* (1995) 634.

[4] U. Geiser, J.A. Schlueter, J.M. Williams, D. Naumann and T. Roy, *Acta Crystallogr. B51* (1995) 789.

[5] A.M. Kini, U. Geiser, H.H. Wang, K.D. Carlson, J.M. Williams, W.K. Kwok, K.G. Vandervoort, J.E. Thompson, D.L. Stupka, D. Jung and M.-H. Whangbo, *Inorg. Chem. 29* (1990) 2555.

[6] H. Urayama, G. Saito, A. Kawamoto and J. Tanaka, *Chem. Lett.* (1987) 1753.