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ESR studies of two new organic superconductors: β'' -(BEDT-TTF)₂SF₅CH₂CF₂SO₃ and κ_L' -(BEDT-TTF)₂Cu(CF₃)₄(DBCE)

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Abstract

The normal-state ESR properties of two new organic superconductors, β'' -(BEDT-TTF)₂SF₅CH₂CF₂SO₃ and κ_L' -(BEDT-TTF)₂Cu(CF₃)₄(DBCE) are reported. Both compounds showed metallic properties below 140 K. The former gave ESR line widths and *g*-values of 23 to 34 G and 2.004 to 2.012, respectively. The latter gave line widths and *g*-values of 45 to 58 G and 2.006 to 2.012, respectively. The orientation-dependent line widths and *g*-values of the κ_L' -phase were found to be similar to that of the κ -(ET)₄Hg₃Br₈ but not to the κ_L -phases in general.

Keywords: Organic superconductors, ESR, line width, *g*-value, microwave conductivity

1. Introduction

The β -phase and κ -phase structures are the most common packing motifs among the BEDT-TTF based organic superconductors, where BEDT-TTF is bis(ethylenedithio)-tetrathiafulvalene, or ET. The β -phase salts consist of ET molecules stacked face-to-face to form a honeycomb-like donor layer while the κ -phase salts show ET dimers surrounded by four orthogonal ET dimers. To date, there are four β -(ET)₂X (*X* = I₃, IBr₂, AuI₂, and β^* -I₃) superconductors [1] and nearly 30 κ -(ET)₂X superconductors [*X* = Cu(NCS)₂, Cu[N(CN)₂]Br, M(CF₃)₄(Solv), etc.] [2]. We recently reported a new β'' -(ET)₂SF₅CH₂CF₂SO₃ superconductor with a *T_c* at 5.2 K [3]. The β'' -phase differs from the β -phase in two aspects, i.e., the 60° angle between the ET stacking axis and the molecular plane, and the almost coplanar configuration of the nearest neighboring ET molecules. In these Proceedings, we also report a new monoclinic κ_L' -(ET)₂Cu(CF₃)₄(DBCE) superconductor with a *T_c*

near 4 K (DBCE is 1,2-dibromo-1-chloroethane) [4]. In this article, we present the ESR properties of these two novel superconductors.

2. β'' -(ET)₂SF₅CH₂CF₂SO₃

The synthesis and crystal structure of the β'' -(ET)₂SF₅CH₂CF₂SO₃ sample has been described in the literature [3]. All ESR studies were carried out on an IBM ER200 X-band spectrometer with a TE₁₀₂ rectangular cavity. The low temperature measurements were accomplished with use of an Oxford 900 flow through cryostat. The *g*-values were calibrated against a strong pitch standard (2.0028).

Rotation around the *b* axis of a rectangular crystal of β'' -(ET)₂SF₅CH₂CF₂SO₃ gave ESR peak-to-peak line widths and *g*-values of 23 to 34 G and 2.004 to 2.012, respectively. Rotation of the same crystal around the *c** axis revealed Dysonian line shapes with corresponding line widths and *g*-values of 24 to 27 G and 2.004 to 2.008. These *g*-values: 2.012, 2.008, and 2.004, arose from the direction along the long molecular axis (central C=C bond direction), short molecular axis, and normal to the molecular plane, respectively. The *g*-values resulted from rotation around *c** axis are plotted in Figure 1. From the Dysonian line shape analysis, microwave conductivities were calculated and also plotted in Figure 1. The maximum and

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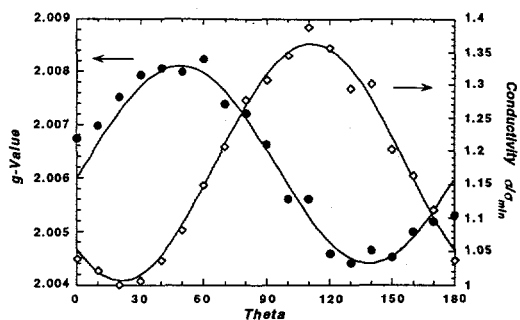


Fig. 1. Rotation around the c^* axis of a β'' -(ET) $_2$ SF $_5$ CH $_2$ -CF $_2$ SO $_3$ crystal showing the g -values and microwave conductivities in the ab plane.

minimum conductivities correspond to the b axis and the ET molecule stacking axis (a axis), respectively.

Low temperature ESR measurements were carried out with the b axis vertical and the static field parallel to the c^* axis. The line width vs. temperature plot (not shown) revealed a slope change near 150 K. Between 295 and 140 K, the spin susceptibilities (χ) decreased by 35%, which was indicative of semiconductive behavior. Below 140 K, χ was nearly constant and indicated metallic behavior, in agreement with electrical resistivity measurements. Superconductivity was observed below \sim 6 K with use of low field ESR measurements.

3. Monoclinic κ_L' -(ET) $_2$ Cu(CF $_3$) $_4$ (DBCE)

The synthesis and crystal structure of the κ_L' -(ET) $_2$ Cu(CF $_3$) $_4$ (DBCE) salt are published in these Proceedings[4]. A plate-like crystal with slanted side faces was mounted vertically in the cavity. Room temperature orientation study was performed with 0° indicating the static field parallel to the crystal plane and 90° perpendicular to the crystal plane. The g -values (circles), peak-to-peak line widths (triangles), and the least square fit curves are plotted in Figure 2.

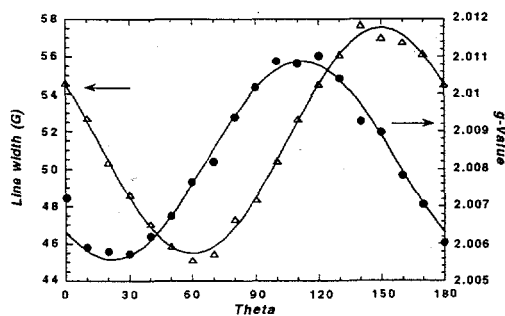


Fig. 2. Angular dependent ESR line widths and g -values of κ_L' -(ET) $_2$ Cu(CF $_3$) $_4$ (DBCE) salt.

The line widths and g -values ranged from 45 to 58 G and from 2.006 to 2.012, respectively. The most interesting feature was that the trend in the line width and g -value was totally different from the other κ -phase salts such as κ_L -(ET) $_2$ Cu(CF $_3$) $_4$ (TCE) [5] or κ -(ET) $_2$ Cu[N(CN) $_2$]Br, where the maximum g -value always corresponded to the minimum line width. However, there was a precedent for this behavior in κ -(ET) $_4$ Hg $_3$ Br $_8$ salt which had a similar structure as that of the κ_L' -phase [6]. Clearly, the g -value and line width correlation is caused by the tilt pattern in the donor molecule layer. The donor molecules in the κ_L -phase showed a zig-zag tilt pattern but a constant tilt angle from layer to layer in the κ_L' -phase [4].

The low temperature ESR measurements of the κ_L' -(ET) $_2$ Cu(CF $_3$) $_4$ (DBCE) salt showed a constant spin susceptibility from 140 to 10 K suggesting metallic behavior. The line width revealed a monotonic decrease with decreasing temperature and the trend was also consistent with metallic behavior.

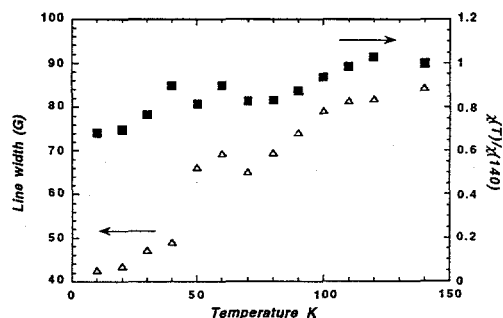


Fig. 3. Line widths (triangles) and spin susceptibilities (squares) of κ_L' -(ET) $_2$ Cu(CF $_3$) $_4$ (DBCE) salt as a function of temperature.

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