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Optical studies of the β''-$(ET)_2SF_5RSO_3$ ($R=CH_2CF_2$, $CHFCF_2$ and CHF) system: chemical tuning of the counterion

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Abstract

We compare the polarized optical spectra of the organic metal β''-$(ET)_2SF_5CHFSO_3$ and the β''-$(ET)_2SF_5CHFCF_2SO_3$ metal/insulator material with those of the first fully organic superconductor β''-$(ET)_2SF_5CH_2CF_2SO_3$. The small chemical modification of the counterion has a dramatic effect on the spectral and charge transport properties of these materials, and we discuss their electronic structure in terms of band structure, many-body effects, and disorder. Based on structural differences in the anion pocket of the three salts, we conclude that the unusual electronic excitations observed in the β''-$(ET)_2SF_5CHFCF_2SO_3$ metal/insulator material are caused by disorder-related localization.

Key words: Reflection spectroscopy, Organic conductors based on radical cation and/or anion salts

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1. Introduction

One of the recent most fruitful strategies of new ET (bis(ethylenedithio)-tetrathiafulvalene)-based materials development involves incorporating large discrete, chemically tunable anions into the complex [1], which allows the exploration of intermolecular interaction effects on the physical properties. In the β''-$(ET)_2SF_5RSO_3$ ($R=CH_2CF_2$, $CHFCF_2$ and CHF) system, small chemical modifications of the anion template result in stabilization of superconducting, semiconducting, or metallic ground states [2]. It is a comparison between β''-$(ET)_2SF_5CH_2CF_2SO_3$ (superconductor), β''-$(ET)_2SF_5CHFCF_2SO_3$ (metal/insulator material), and β''-$(ET)_2SF_5CHFSO_3$ (metal) that is of interest here.

The crystal structure of the β''-$(ET)_2SF_5RSO_3$ family consists of alternating layers of ET cations and $SF_5RSO_3^-$ anions. The ET molecules form stacks along the *a* directions, with close intermolecular contacts along *b*. The figure insets show the structure of the anion pocket in all three compounds. In the β''-$(ET)_2SF_5CH_2CF_2SO_3$ superconductor with $T_c \approx 5$ K (upper panel), the ethylene end groups of the ET cation form hydrogen bonds with the peripheral fluorines and oxygens of the anion, but not with the inner fluorines. The anion contains no chiral carbon, and the anion pocket is ordered [3]. In the β''-$(ET)_2SF_5CHFCF_2SO_3$ metal/insulator material (middle panel), the peripheral oxygen and fluorine atoms as well as the interior fluorine atoms of the anion compete for the intermolecular contacts with the ET donor molecules. The anion has a chiral carbon, and the anion pocket is disordered with the two possible configurations; the system undergoes metal→insulator transition near 180 K [4]. In the metallic β''-$(ET)_2SF_5CHFSO_3$ salt (lower panel), the anion contains a chiral carbon atom, and there are some intermolecular contacts between the interior fluorine and the ET molecule. The anion pocket, however, is well-ordered, similar to the superconductor. This material remains metallic to ≈ 6 K [2].

In order to provide further information on the electronic processes in the β''-$(ET)_2SF_5RSO_3$ system, we have investigated the polarized optical response of three materials in this family: superconductor ($R=CH_2CF_2$) metal/insulator ($R=CHFCF_2$) and metal ($R=CHF$).

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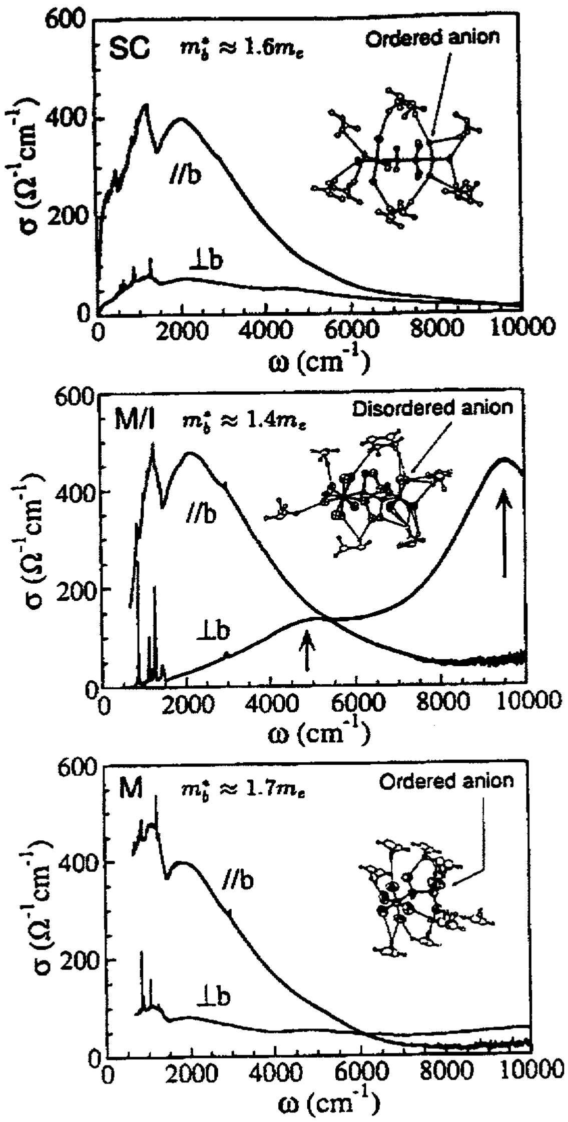
2. Results and Discussion



The figure shows the frequency dependent conductivity of β''-(ET)$_2$SF$_5$CH$_2$CF$_2$SO$_3$, β''-(ET)$_2$SF$_5$CHFCF$_2$ SO$_3$ and β''-(ET)$_2$SF$_5$CHFSO$_3$. All three samples show a strong electronic excitation in the $\|b$ direction at $\approx$ 2200 cm^{-1}. The $\|b$ effective masses were calculated from a partial sum rule of the conductivity, and found to be $m_b^* \approx 1.6m_e$, $m_b^* \approx 1.4m_e$, and $m_b^* \approx 1.7m_e$, for the superconductor, metal/insulator and metal, respectively. In the $\perp b$ response, the metal/insulator material differs dramatically from the other two compounds. It reveals a shoulder at 4800 cm^{-1} and a strong electronic band around 9500 cm^{-1} [5]. These features are not observed in the spectrum of the superconductor or the metal [6,7]. At the same time, the $\perp b$ spectra of the superconductor and metal are very similar. Differences in vibrational properties are discussed elsewhere [7].

The weakly conducting response in the $\|b$ direction is very similar in all three β''-(ET)$_2$SF$_5$RSO$_3$ materials and characteristic of other known β-phase conductors. In terms of an electronic band structure model, the excitation at $\approx$ 2200 cm^{-1} can be interpreted as an interband transition [7,8]. In the $\perp b$ direction, the low-energy residual conductivity of the metal and superconductor is replaced by a low and flat response in the metal/insulator material, with the broad excitation in the near infrared, suggestive of electron localization on donor sites. Therefore, the bands at 4800 and 9500 cm^{-1} can be characterized as charge transfer-type excitations in the dimerized ET chains. These excitations can be accounted for within a large U (on-site Coulomb repulsion) Hubbard approximation [9], but this does not necessarily mean that they are correlation-driven. If many-body effects were the cause of this localization, a much higher effective mass would be expected for the metal/insulator material compared to the superconductor and metal. Thus, we propose that the 4800 and 9500 cm^{-1} excitations observed in the $\perp b$ spectra of the β''-(ET)$_2$SF$_5$CHFCF$_2$SO$_3$ are the result of electron localization on ET dimers driven by disorder in the anion pocket. That the $\|b$ effective masses and overall structures for all three salts are so similar supports this argument. The investigations of β''-(ET)$_2$SF$_5$RSO$_3$ composite materials are underway, to estimate the length scale of this disorder.

3. Conclusion

We compare the polarized optical conductivity of three members of the β''-(ET)$_2$SF$_5$RSO$_3$ (R = CH$_2$CF$_2$, CHFCF$_2$, and CHF) system. The low-energy $\perp b$ excitations in the metal/insulator material (R = CHFCF$_2$), which are absent in the other two compounds, are caused by a disorder-driven charge localization on the ET stack.

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