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THE CENTRAL BOND $^{13}C = {}^{13}C$ ISOTOPE EFFECT FOR SUPERCONDUCTIVITY IN THE HIGH-T_C β^*-$(ET)_2I_3$ PHASE AND ITS IMPLICATIONS REGARDING THE SUPERCONDUCTING PAIRING MECHANISM IN TTF–BASED ORGANIC SUPERCONDUCTORS

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Abstract We report a new study, based on magnetization measurements, of the isotope effect for ^{13}C substitution in the electronically active central double-bonded carbon atoms (C=C) of the TTF moiety of ET [bis(ethylenedithio)tetrathiafulvalene] in β^*-$(ET)_2I_3$ [also denoted as β_H-$(ET)_2I_3$], which is the crystallographically ordered form of β-$(ET)_2I_3$ produced by application of pressure. A recent report by Merzhanov et al. [*C. R. Acad. Sci., Paris, 314*, 563 (1992)] has shown that this same ^{13}C substitution leads to a "giant" isotope effect ($\Delta T_c = -0.6$ K) in resistive determinations of T_c (~ 8 K) for β^*-$(ET)_2I_3$, which lends experimental support to a theory by Yamaji [*Solid State Commun., 61*, 413. (1987)] for salts of TTF-analogue donor molecules that includes optical phonons of symmetric intramolecular vibrations as a source of mediation for superconducting pairing of charge-carriers. In contrast to this result, our study shows the *absence* of an isotope effect within a precision of ± 0.1 K (~1 %), indicating that the central atom C=C stretching motion (~ 1500 cm^{-1}) of ET cannot be a dominant mechanism for phonon exchange. Our results are consistent with those of a very recent study of the same isotope effect for κ-$(ET)_2Cu[N(CN)_2]Br$ and κ-$(ET)_2Cu(NCS)_2$ [*Inorg. Chem., 32*, 3356 (1992)].

INTRODUCTION

An interesting aspect of all presently-known organic superconductors derived from radical-cation electron-donor molecules, such as bis(ethylenedithio)tetrathiafulvalene (abbreviated as BEDT-TTF or simply ET), is that the organic donor species *in all cases* are derivatives of the sulfur-based tetrathiafulvalene (TTF) molecule or the equivalent selenium-based tetrasalenafulvalenene (TSF) molecule.[1] This raises questions concerning the role and importance of the *TTF moiety* in achieving the superconducting state and to questions relating to the design of substantially different donor molecules for use in new materials having much higher superconducting transition temperatures (T_c).

An innovative theory proposed by Yamaji[2,3] suggests that the TTF moiety plays a crucial role in the superconductivity of organic charge-transfer salts derived from TTF-analogue donor molecules because bond-stretching *intra*molecular vibrations (optical phonons), in addition to the *inter*molecular acoustic phonons of conventional Bardeen-Cooper-Schrieffer (BCS) theory,[4] may be a significant source of phonon exchange for the superconducting pairing of charge-carriers. This theory is based on the fact that the valence-level holes constituting the conduction band in the charge-transfer salts of the TTF-analogue molecules strongly couple to the totally symmetric vibrational modes of the molecule (a_g modes for a D_{2h} point group), especially those modes composed of the C–S ($\nu_6 \sim 500$ cm^{-1}) and C=C stretching ($\nu_3 \sim 1500$ cm^{-1}) motions involving the *central* carbon atoms and their neighboring sulfur atoms in the TTF moiety.[5-7] In the model proposed by Yamaji, the pairing of charge-carriers mediated by these a_g modes is viewed as one in which the potential-energy lowering at a molecular site induced by the passing of one hole favors the attraction of a second hole coming to the same site.[2,3]

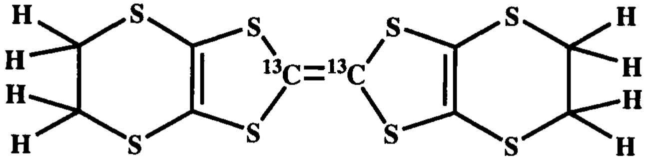
Taking into account the attractive interactions mediated by these intermolecular a_g modes, in addition to mediation by acoustic phonons and the effects of Coulomb repulsions, Yamaji has shown[2] that one can circumvent the inadequacies of weak-coupling BCS theory in parameterizing the large change in T_c in β-(ET)$_2$I$_3$ from $T_c \approx 1.5$ K at ambient pressure to $T_c \approx 8.0$ K at mild applied pressures. This theory gains additional support from the theoretical study by Tanaka et al.[8] that explains how deuteration of the terminal hydrogen atoms in the TTF-analogue donor molecules of salts such as κ-(ET)$_2$Cu(NCS)$_2$ can lead to an *inverse* isotope effect via distortions in the C=C stretching motions. This theory has now received direct experimental affirmation in the very recent studies of Merzhanov et al.,[9] who report that ^{13}C substitution in the central double-bonded carbon atoms (C=C) of the TTF moiety of ET leads to a "giant" isotope effect ($\Delta T_c = -0.6$ K) in resistive determinations of T_c for β^*-(ET)$_2$I$_3$ [often denoted as β_H-(ET)$_2$I$_3$], which has a resistive T_c of ~ 8 K in the non-isotopically substituted salt and is the crystallographically ordered form of β-(ET)$_2$I$_3$ achieved by application of pressure.[10]

In this article, we report a new study, based on magnetization instead of resistive measurements, of the isotope effect for ^{13}C substitution in the central C=C atoms of ET in β^*-(ET)$_2$I$_3$. This work complements our recent earlier study[11,12] of the same ^{13}C isotopic substitution in the two ambient-pressure κ-phase superconducting salts, κ-(ET)$_2$Cu[N(CN)$_2$]Br[13] and κ-(ET)$_2$Cu(NCS)$_2$.[14] The β^*-(ET)$_2$I$_3$ salt, as well as other members of the β-phase class, and the κ-phase salts differ in the nature of their anion arrays and the packing motifs of the organic donor molecules, the former consisting of discrete anions and stacks of ET molecules and the latter consisting of anion chains and an orthogonal arrangement of discrete dimers of the ET donor molecules.[1a,c] Otherwise, both phase-types are similarly layered, quasi two-dimensional synthetic metals consisting of a layer of organic donor molecules separated by a layer of anions.

In the context of Yamaji's model of superconducting pairing,[2] one does not particularly expect any difference in the pairing mechanism for the β^*- and κ-phase salts arising from differences in the anion linkages or packing motifs of the ET donor molecules. The ^{13}C isotope effect for the central C=C double bond in β^*-$(ET)_2I_3$ reported by Merzhanov et al.,[9] which yields a decrease in T_c from 8.0 ± 0.1 K (resistive transition midpoint) for the normal isotopic salt to $T_c = 7.4 \pm 0.1$ K for the ^{13}C-substituted salt ($\Delta T_c = -0.6$ K), represents an abnormally large effect. This shift in T_c clearly indicates that the central C=C stretching motion is a ***dominant exchange mechanism*** for superconducting pairing in this salt, because the conventional BCS isotope effect for acoustic phonons, assuming that only the vibrations of the ET molecule as a whole are involved, predicts a shift of $\Delta T_c = T_c(^{12}C)[(386/384)^{-1/2} - 1] = -0.02$ K (0.25%), where $T_c(^{12}C)$ represents the T_c of the salt with natural isotopic abundance. On the other hand, our previous study[11,12] of the κ-phase salts showed *no evidence*, within a precision of ± 0.1 K, of an isotope effect involving the central C=C stretching motion. As we have previously remarked,[11] this difference in results indicates either a surprising difference in the superconducting pairing mechanisms between the β^*- and κ-phase salts or some change, induced by the ^{13}C substitution, in the modulated structure[15] of ambient-pressure β-$(ET)_2I_3$ that alters the isotope effect for β^*-$(ET)_2I_3$; otherwise, this discrepancy represents difficulties in obtaining a reproducible T_c for β^*-$(ET)_2I_3$.[16]

SYNTHESIS AND CHARACTERIZATION OF THE β AND β* SALTS

The ^{13}C substitution in the central C=C atoms of ET is illustrated in the following diagram:



ET in natural isotopic abundance and ET with $^{13}C=^{13}C$ in the central double-bonded carbon atoms were synthesized in *identically parallel* experiments from natural CS_2 and

$^{13}CS_2$ with the use of the synthetic route described by Larsen and Lenoir[17] and by Rae[18] (also see ref. 12 for an illustration of the synthetic scheme). This route is *site-specific* for the central $^{13}C{=}^{13}C$ isotopic labeling. The $^{13}CS_2$ reagent used in this synthesis was obtained from Cambridge Isotope Laboratory, Woburn, MA, and was labeled as having a 99 % enrichment. The ET products used here in the preparation of β^*-$(ET)_2I_3$ were used also in our earlier preparation of the κ-phase salts.[11,12]

Laser desorption Fourier transform mass spectroscopy[11,12] of the ^{13}C-labeled ET showed molecular ions of mass 386 ($^{13}C{=}^{13}C$), 385 ($^{13}C{=}^{12}C$), and 384 ($^{12}C{=}^{12}C$) in the ratio 95:5:0, corresponding to a 97-98 % enrichment of the starting $^{13}CS_2$ material and 95 % enrichment of the ET product. Raman and Fourier-transform infrared spectroscopy measurements of the ET products exhibited the expected isotopic shifts in vibrational frequencies.[11,12] The Raman spectra are illustrated in Figure 1. The vibrational modes relating to the C=C stretching motions of the central and outer-ring double-bonded carbon atoms of the TTF moiety are associated in about equal percentages with the bands at 1550 cm^{-1} and 1493 cm^{-1} for the $^{12}C{=}^{12}C$ material,[7] and these bands shift to frequencies of 1521 cm^{-1} and 1465 cm^{-1}, respectively, for the $^{13}C{=}^{13}C$ material, in excellent agreement with the isotopic product rule of vibrational spectroscopy.

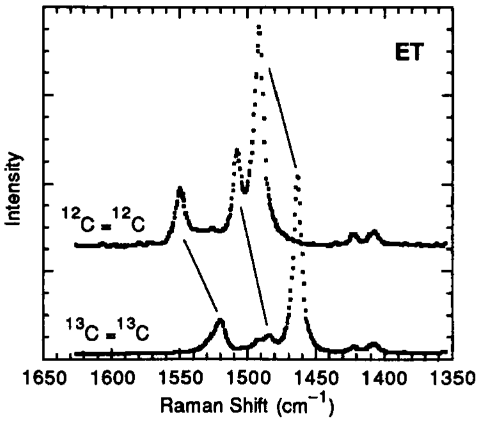


FIGURE 1 Raman spectra (λ_{exc} = 1064 nm) of $^{13}C{=}^{13}C$ labeled and unlabeled ET at room temperature in 180 deg backscattering geometry; resolution = 4 cm^{-1}. Spectra obtained with the use of a Bio-Rad, Digilab Division, FT Raman Spectrometer.

Crystals of the unlabeled and ^{13}C-labeled ambient-pressure β-$(ET)_2I_3$ salt, of mass 0.1-0.5 mg, were grown by electrocrystallization techniques following previously described methods.[19,20] Dry tetrahydrofuran (THF) was used as solvent. All crystals used in the determination of the superconducting transition curves were investigated with the use of ESR spectroscopy and gave typical β-type peak-to-peak linewidths of 20–24 G at room temperature. Two crystals were subjected to ESR line-shape analyses,[21] and these studies showed no evidence of contamination by an α-phase component.

No significant differences in the crystallographic lattice constants were found between the unlabeled and ^{13}C-labeled crystals of β-$(ET)_2I_3$. The unit cell and the modulation vector of a ^{13}C-labeled β-$(ET)_2I_3$ crystal were determined at 123 K with the use of a Syntex $P2_1$ four-circle diffractometer equipped with a nitrogen gas flow cooling device. The satellite structure produced by this crystal is illustrated in Figure 2. 32 fundamental reflections with $20° < 2\theta < 31°$ and 39 first-order satellite reflections with $7° < 2\theta < 17°$ were carefully centered. The cell of the average structure [$a = 6.558(3)$ Å, $b = 9.006(3)$ Å, $c = 15.161(4)$ Å, $\alpha = 95.12(2)°$, $\beta = 95.93(3)°$, $\gamma = 110.24(3)°$, $V = 828.0(5)$ Å^3] and the modulation vector [0.077(3) a^*, 0.274(10) b^*, 0.204(13) c^*] agreed within the precision of the measurement with the earlier work on β-$(ET)_2I_3$ containing carbon atoms in natural isotopic abundance.[15,22,23] Thus, the unique incommensurate modulation found in the ambient-pressure, "low-T_c" phase of β-$(ET)_2I_3$ is still present in the ^{13}C-labeled crystals, and the size and direction of the modulation vector is the same as in the material with natural isotopic abundance.

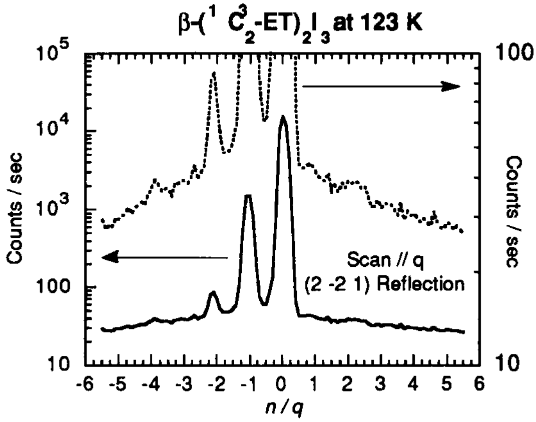


FIGURE 2 Step scan through the (2 –2 1) reflection of ^{13}C-labeled β-$(ET)_2I_3$ at 124 K in the direction of the modulation vector [0.077(3) a^*, 0.274(10) b^*, 0.204(13) c^*]. Satellites with order –1, –2, and –4 are clearly visible.

SUPERCONDUCTING TRANSITION STUDIES

Superconducting transition curves of β^*-$(ET)_2I_3$ were determined with the use of a commercial SQUID magnetometer. Crystals of the high-T_c β^*-$(ET)_2I_3$ phase were produced from the ambient-pressure β-$(ET)_2I_3$ crystals with the use of the five-step recipe previously described.[24,25] This process involves the following steps: (1) applying 0.7 kbar pressure of Ar to the crystal at ambient temperature; (2) quenching the crystal to 77 K by immersing it in liquid nitrogen; (3) warming the crystal to ~ 110 K; (4) releasing the Ar pressure; and (5) flushing the crystal with He gas to remove the Ar. This recipe results in a complete transformation of the crystal into the high-T_c β^*-$(ET)_2I_3$ phase, which is stable below about 125 K. Two crystals with natural abundance $^{12}C = {}^{12}C$ and two with $^{13}C = {}^{13}C$ were transformed using this procedure. The transformed samples were transferred under liquid nitrogen to the SQUID magnetometer without warming above ~ 80 K.

In the first experiment, a $^{13}C = {}^{13}C$ crystal and a $^{12}C = {}^{12}C$ crystal were studied *simultaneously*. For this study, both the normal and isotopically substituted crystals were transformed to β^*-$(ET)_2I_3$ together by use of the above recipe, both were placed together in the magnetometer container, and the combined superconducting transition curve was determined. This transition curve exhibited a *single* superconducting transition curve with onset of the diamagnetic signal occurring at 7.4 ± 0.1 K. Generally, inductively measured values of T_c are smaller than resistively measured values by ~ 1 K, and they are better representations of the bulk property. Following this experiment, each of the same two crystal specimens were transformed separately, and the magnetization curves of each were determined separately, yielding onset transition temperatures of 7.3 ± 0.1 K for the $^{13}C = {}^{13}C$ crystal and 7.0 ± 0.1 K for the $^{12}C = {}^{12}C$ crystal. In a third experiment, two nearly identically shaped crystals, one of mass 0.31 mg with $^{13}C = {}^{13}C$ substitution and the other of mass 0.37 mg with natural abundance $^{12}C = {}^{12}C$, were transformed to β^*-$(ET)_2I_3$ separately, and their superconducting transitions curves were determined in separate measurements. The results of these measurements are illustrated in Figure 3.

Figure 3 shows a plot of the Meissner signals (cooling in an applied magnetic field of 0.5 mT [5 G]) as a function of temperature for the separate $^{13}C = {}^{13}C$ and $^{12}C = {}^{12}C$ crystals. The isotopically labeled crystal has an onset T_c of 7.25 ± 0.10 K and the $^{12}C = {}^{12}C$ crystal exhibits an onset T_c of 7.20 ± 0.10 K. In the linear region of the superconducting transition at lower temperatures, the $^{13}C={}^{13}C$ crystal appears to exhibit an isotopic shift of about – 0.1 K. However, we have observed that crystal specimens of the same isotopic composition exhibit variations of 0.2 K, and our precision is of the order of ± 0.1 K. We therefore conclude that there is no significant isotope effect, within a precision of about ± 0.1 K, relating to a dominant exchange mechanism involving phonons of the central C = C bond-stretching motion of the TTF moiety of the ET molecule. As evidence that our transformation recipe results in an essentially complete transformation of the ambient-pressure crystal to the high-T_c β^*-$(ET)_2I_3$ phase, the Meissner fractions at 5 K exhibited by the data of Figure 3 are 2.1 for the $^{13}C = ^{13}C$ crystal and 1.2 for the $^{12}C = ^{12}C$ crystal, both calculated without correction for demagnetization. These uncorrected Meissner fractions would not be realized for crystals with incomplete transformations.

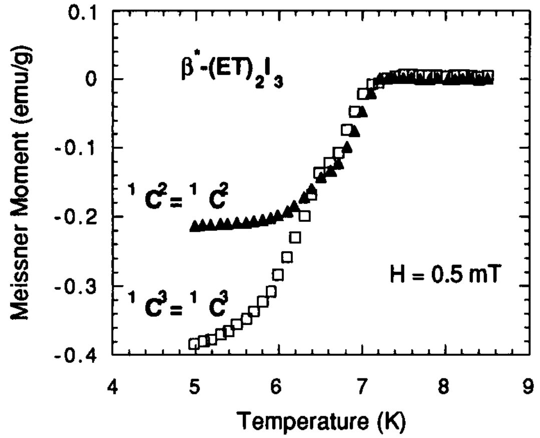


FIGURE 3 Superconducting transition curves determined from dc magnetization for field-cooled crystals of β^*-$(ET)_2I_3$ with ^{13}C=^{13}C in the central carbon atoms of ET and with natural isotopic abundance (^{12}C=^{12}C).

DISCUSSION

We are unable to provide a simple explanation for the difference between our result of no appreciable isotope effect and that of Merzhanov et al.[9] of a "giant" isotope effect for β^*-$(ET)_2I_3$ with the same ^{13}C substitution in the central C=C atoms of ET. The difference between our use of magnetization measurements in the present experiments as opposed to the use of resistive measurements in the experiments of Merzhanov et al.[9] cannot account for any appreciable difference in *relative* isotopic shifts, although these different techniques generally lead to different absolute values of T_c because magnetization measurements respond to a bulk property whereas resistivity measurements respond to the surface and filamentary properties of a crystal. Moreover, we observed no change in the modulated structure of ambient-pressure β-$(ET)_2I_3$ that would suggest a drastic disruption of the isotope effect due to the proximity of an electronic instability. The most likely source of the discrepancy is the problem of obtaining reproducible T_c's.[9,16,21] This problem arises from the unique features of the ET/I system itself that allows one to obtain phase-impure and stressed crystals of β-$(ET)_2I_3$ having a range of T_c's from 1.5 to 8 K depending on sample quality, chemical purity, applied temperatures, pressures, and a variety of mechanical stresses.[1,21,26,27] Our own observations herein of variations in T_c of the order of 0.2 K, for example, demonstrate the difficulties in obtaining consistent and precise superconducting transitions in β^*-$(ET)_2I_3$ crystals even under very carefully controlled conditions.

Our present results are entirely consistent with our previous finding[11,12] of zero isotope effect within a precision of ± 0.1 K for κ-$(ET)_2Cu[N(CN)_2]Br$ and κ-$(ET)_2Cu(NCS)_2$ with the same ^{13}C substitution in the central carbon atoms of the ET molecule. Therefore, we believe that the superconducting pairing mechanism, in fact, is the same for the β^*- and κ-phase salts, and whatever this mechanism may be, we have demonstrated that is *not dominated* by exchange of optical phonons of the central C=C stretching motion. In any case, as we have pointed out earlier,[11] the model of hole pairing mediated by *intra*molecular vibrations is not likely as a dominant mechanism in these organic superconductors because of their small charge-carrier densities—one hole per pair of ET donor molecules in a unit cell volume of ~ 850 Å^3 per chemical formula—amounting to a number density of ~ 10^{21} cm^{-3}. Our results suggest that the importance the the TTF moiety in organic superconductivity from a mechanistic standpoint will be known only after additional isotopic substitutions are performed and their isotope effects for T_c are studied. The absence of a significant isotope effect for the central C=C stretching motion does not necessarily rule out the possibility of pairing mediated by other bond-stretching motions nor pairing mediated in part by a spectrum of intramolecular vibrations.

ACKNOWLEDGEMENTS

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