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Isotope Effect in BEDT-TTF Based Organic Superconductors

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Abstract

The results of our comprehensive isotope effect studies, in which seven different isotopically labeled (involving ^{13}C, ^{34}S and ^{2}H labeling) BEDT-TTF derivatives and isotopically labeled anion $[Cu(^{15}N^{13}CS)_2]^-$ were utilized, are summarized. For the first time, convincing evidence for a genuine BCS-like mass isotope effect in an organic superconductor is revealed in our studies.

Keywords: Organic superconductors, BEDT-TTF or ET, isotope effect on T_c, magnetic measurements, BCS theory

1. Introduction

During the last 17 years, considerable progress has been made in the field of organic superconductors with the discoveries of over 50 organic superconductors [1,2]. While the highest T_c (*ca.* 13 K) of an organic superconductor is still an order of magnitude lower than that of the oxide superconductors, similarities in their structural and physical properties have been recognized by several authors [3]. With the availabiliy of several organic superconductors with $T_c >$ 10 K, they are also being studied intensively by experimental solid state physicists in order to unravel the underlying physics of these novel materials. At present, one of the controversial issues pertaining to organic superconductors is the origin of the electron-pairing mechanism. Experimental evidence has been presented in support of both conventional (phonon-mediated, BCS, *s*-wave symmetry) and unconventional (electronically-mediated, non-BCS, *d*-wave symmetry) mechanisms. We have recently investigated, in a comprehensive manner, the effects of systematic isotopic substitution in both the organic donor component (BEDT-TTF labeled with ^{13}C, ^{34}S and ^{2}H isotopes) and the charge-compensating anion component $[Cu(NCS)_2]^-$ labeled with ^{13}C and ^{15}N isotopes] on the T_cs of organic superconductors to seek answers to the following questions: (i) Is the superconductivity phonon-mediated? (ii) Are the *intra*molecular symmetrical vibrational modes associated with the TTF skeleton responsible for electron-pairing? and (iii) Do the symmetrical vibrational modes associated with the anions mediate electron-pairing? Our results indicate that neither the *intra*molecular vibrational modes of the TTF skeleton nor those associated with the anion contribute to the pairing mechanism in any significant way [4–8,18]. Additionally, for the first time in any organic superconductor, we have obtained tenable experimental evidence for the existence of a genuine mass isotope effect, viz., lowering of T_c when labeled with higher mass isotopes, in κ-$(ET)_2Cu(NCS)_2$ [9]. While the latter result supports the conventional, phonon-mediated, BCS-like mechanism for the Cooper pair formation, it is pointed out by the *inverse* isotope effect when the hydrogen atoms on the ET molecule are replaced by deuterium isotopes that it may not be truly a simple BCS scenario.

2. Experimental methods

The seven different isotopically labeled ET derivatives synthesized for this study are depicted in Figure 1. These were synthesized according to the well-established literature procedures. In each case, we also synthesized a batch of unlabeled ET in strictly parallel experiments using the corresponding unlabeled precursors (CS_2 and 1,2-dibromoethane). Superconducting crystals of both labeled and unlabeled materials were grown by the electrocrystallization technique, again in strictly parallel experiments employing the same batches of solvent and electrolyte in each case.

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Superconducting transition temperatures were determined by AC susceptibility measurements on a large number, typically eight or more, of crystal specimens of each labeled and unlabeled materials. The large sampling was essential because organic superconductors generally exhibit considerable sample-to-sample variations in T_c within the same isotopic composition so that isotope shifts beyond the statistical variations could be determined with a reasonable degree of precision. AC susceptibility measurement methods and the methods of data analysis have been described in detail elsewhere [4–9].
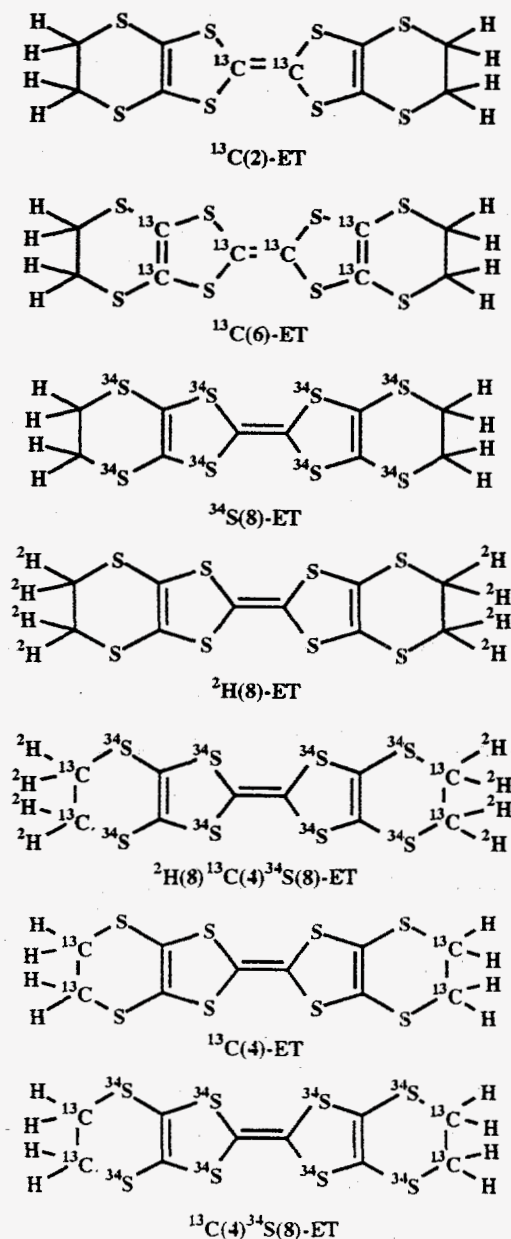

$^{13}C(2)$-ET

$^{13}C(6)$-ET

$^{34}S(8)$-ET

$^2H(8)$-ET

$^2H(8)$ $^{13}C(4)$ $^{34}S(8)$-ET

$^{13}C(4)$-ET

$^{13}C(4)$ $^{34}S(8)$-ET

Fig. 1. Seven different isotopically labeled ET derivatives synthesized for isotope effect studies.

3. Results and Discussion

3.1. Intramolecular vibrational modes

The possibility of electron-pairing in organic superconductors composed of TTF derivatives mediated by the *intra*molecular symmetrical vibrational modes involving C=C and C–S stretching vibrations in the TTF skeleton was originally proposed by Yamaji in 1987 [10]. This proposition was based on the large coupling constant (λ) calculated for the conduction electron-molecular vibration coupling (e-mv coupling) for the aforementioned vibrational modes. Experimentally, the e-mv coupling is manifested as a broad envelope in the 1200–1400 cm^{-1} region in the reflectance spectra of the organic superconducting crystals [11]. Although the initial experimental support for the Yamaji theory was provided by Merzhanov *et al.* [12] in their isotope effect studies of β^*-$(ET)_2I_3$ involving ^{13}C-labeling of the two carbon atoms in the central C=C bond, subsequent studies by us [5,8] and the Orsay group [13] indicated that the isotope shift is well within the relatively large ($\pm$ 0.2 K) sample-to-sample variations in T_c for the β^*-$(ET)_2I_3$ system. These studies further pointed out the importance of (i) large sampling of crystals in order to discern any isotope shifts beyond the sample-to-sample variations in T_c, (ii) the *ambient pressure* superconductors, such as κ-$(ET)_2Cu(NCS)_2$ and κ-$(ET)_2Cu[N(CN)_2]Br$, being the materials of choice for isotope effect studies, and (iii) the use of magnetic, rather than resistivity, measurements (such as AC susceptibility measurements) for the determination of T_cs.

Our isotope effect studies of the two ambient pressure superconductors κ-$(ET)_2Cu(NCS)_2$ (T_c = 9.6 K, inductive onset), and κ-$(ET)_2Cu[N(CN)_2]Br$ (T_c = 11.6 K, inductive onset) by use of ET molecules with ^{13}C-labeling at the central C=C bond as well as all three C=C bonds have revealed *no* discernable isotope shift beyond the sample-to-sample variations in T_c (*ca.* $\pm$ 0.1 K) [4,6]. The two labeling schemes give rise to nearly 2% and 4% frequency shifts, respectively, of the a_g vibrational modes involving C=C stretching vibrations of ET molecule at energies near 1500 cm^{-1}. The AC susceptibility in the 10–12 K temperature range of four crystals each of $^{13}C(6)$-labeled and unlabeled κ-$(ET)_2Cu[N(CN)_2]Br$ superconductor are shown in Figure 2. The two sets of curves clearly overlap over the same temperature range, elucidating the sample-to-sample variations in T_c and the absence of any discernible isotope shift. These results do not support the *intra*molecular C=C stretching modes of ET molecule being the *dominant* mediators of superconductivity.

A similar study involving ^{34}S labeling of all eight sulfur atoms in the ET molecule was carried out to determine whether or not the a_g vibrational modes involving C–S stretching motions (~ 500 cm^{-1}) were responsible for electron-pairing [7]. The $^{34}S(8)$ labeling shifts the C–S vibrational modes by *ca.* 2.7% while concurrently increasing the mass of ET
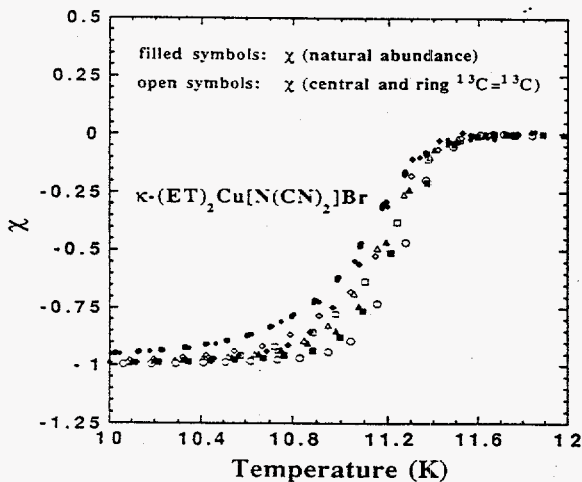
Fig. 2. Volume susceptibility χ' (corrected for demagnetization) of four crystals each of natural abundance (filled symbols) and $^{13}C(6)$-labeled (open symbols) κ-$(ET)_2Cu[N(CN)_2]Br$.

molecule by *ca.* 4%. This situation makes it rather difficult to ascertain unambiguously whether the isotope shift originates from the *intra*molecular or intermolecular, lattice phonon modes. Experimentally, for the κ-$(ET)_2Cu[N(CN)_2]Br$ superconductor we observed a small negative isotope shift ($\Delta T_c = -0.08 \pm 0.07$ K) barely above the experimental uncertainties, and for the κ-$(ET)_2Cu(NCS)_2$ we observed *no* isotope shift within the experimental uncertainties.

The above results led us to conclude that the *intra*molecular phonon modes involving C–S stretching motion are also not the *principal* mediators of electron-pairing. The small negative isotope shift observed in the case of κ-$(ET)_2Cu[N(CN)_2]Br$, which is about one-third of that expected for a conventional BCS mass isotope effect, assuming that the relevant mass entity is that of the ET molecule, can be understood as arising from strong Coulomb effects, a notable feature of organic superconductors [1,2].

It is, however, interesting to note that in alkali metal-C_{60} superconductors, the normal ^{13}C isotope effect and the observed line broadening below T_c of some peaks in their Raman spectra have been interpreted in terms of the involvement of *intra*molecular C=C stretching phonon modes (h_g symmetry) as well as the lattice phonon modes in the pairing mechanism [14].

3.2. Intermolecular (lattice) phonons

Next, we investigated the possibility of electron-pairing mediated by the lattice phonon modes by use of two labeled ET compounds, $^{13}C(4)^{34}S(8)$-ET and $^2H(8)^{13}C(4)^{34}S(8)$-ET in the superconductor κ-$(ET)_2Cu(NCS)_2$ ($T_c = 9.6$ K, inductive onset)

[9]. The first compound, $^{13}C(4)^{34}S(8)$-ET, provides the largest, practical isotopic mass increase (about 5%) for our purposes, without any interference from the inverse isotope effect previously reported for deuterium substitution. The latter compound, $^2H(8)^{13}C(4)^{34}S(8)$-ET, provides a second approach, wherein the mass isotope effect of $^{13}C(4)^{34}S(8)$-labeling would compete with the *inverse* isotope shift of deuterium substitution in κ-$(ET)_2Cu(NCS)_2$. This also required a reinvestigation, by employing a large sampling (typically 8 or more crystals of each composition), of the deuterium isotope effect, and the effect of $^{13}C(4)$-labeling in the superconductor κ-$(ET)_2Cu(NCS)_2$.

The experimentally observed isotope shifts for the four different labeling schemes discussed above are shown in Table 1. The previously reported *inverse* isotope effect for $^2H(8)$-labeling was confirmed in our studies, and we obtain a more *precise and definitive* value for this shift, $\Delta T_c = 0.30 \pm 0.07$ K, which is at the lower end of several reported values [15–17]. This result is graphically illustrated in Figure 3. In this figure, we show susceptibility curves after demagnetization corrections of four crystals each (among the 14 studied of each composition) of deuterated and non-deuterated samples of κ-$(ET)_2Cu(NCS)_2$. On the other hand, $^{13}C(4)$-labeling leads to *no* isotope shift, in contrast to the two conflicting reports, a small negative shift with large uncertainties (-0.1 ± 0.3 K) in one paper [16], and a large inverse shift ($+0.3$ K; no uncertainties reported) in another paper [17].

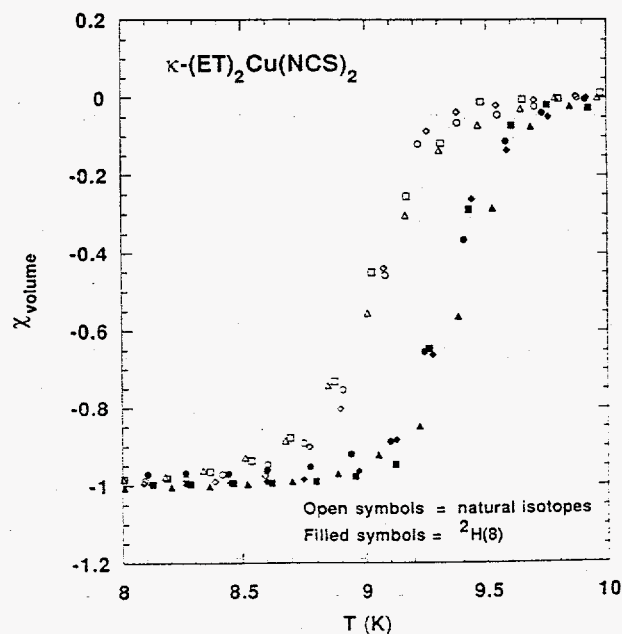

Fig. 3. Susceptibility curves (corrected for demagnetization) of four crystals each of natural abundance (open symbols) and $^2H(8)$-labeled (filled symbols) κ-$(ET)_2Cu(NCS)_2$.

Table 1
Summary of isotope shifts (ΔT_c) for κ-(ET)$_2$Cu(NCS)$_2$ crystals for four different isotopic substitutions in the ET molecule

Isotopic substitution	ΔT_c
^{13}C(4)^{34}S(8)	-0.12 ± 0.08
^{13}C(4)	0.00 ± 0.09
^{2}H(8)^{13}C(4)^{34}S(8)	0.15 ± 0.08
^{2}H(8)	0.30 ± 0.07

The isotope shift we observed for ^{13}C(4)^{34}S(8)-labeling in κ-(ET)$_2$Cu(NCS)$_2$, $\Delta T_c = -0.12 \pm 0.08$ K, is the *first* definitive, BCS-like, mass-related isotope effect reported for any organic superconductor. This value was obtained following measurement of T_cs of 19 crystals each of natural abundance and ^{13}C(4)^{34}S(8)-labeled κ-(ET)$_2$Cu(NCS)$_2$. The isotope shift is graphically represented in Figure 4, which shows the susceptibility data after demagnetization corrections belonging to four crystals of each isotopic composition. Each set of curves, despite being spread over a temperature region of 0.1–0.15 K, shows a clean separation illustrating our conclusion. This result is further substantiated by the smaller *inverse* isotope shift, $\Delta T_c = 0.15 \pm 0.08$ K, determined for ^{2}H(8)^{13}C(4)^{34}S(8)-labeling (see Figure 5). Evidently, the *inverse* isotope shift of ^{2}H(8)-labeling is partially cancelled out by the normal isotope shift originating
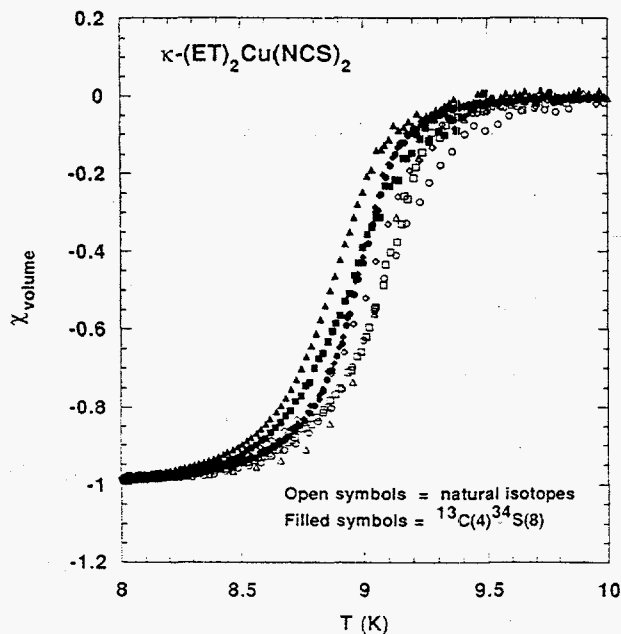
from ^{13}C(4)^{34}S(8)-labeling. If we compare the average T_cs of ^{2}H(8)-labeled and ^{2}H(8)^{13}C(4)^{34}S(8)-labeled κ-(ET)$_2$Cu(NCS)$_2$ samples, we obtain an isotope shift of $\Delta T_c = -0.11 \pm 0.07$ K for ^{13}C(4)^{34}S(8)-labeling in deuterated salts, in excellent agreement with the isotope shift in non-deuterated salts, $\Delta T_c = -0.12 \pm 0.08$ K .

3.3. Anion phonon modes

Finally, we have addressed the question of whether or not the symmetrical vibrational modes of the charge-compensating anions are involved in the electron-pairing mechanism of organic superconductors by synthesizing κ-(ET)$_2$Cu(^{15}N^{13}CS)$_2$ and the corresponding unlabeled material in strictly parallel experiments. Although this labeling gives rise to large shifts (*ca.* 75 cm^{-1}) in the Raman frequencies (near 2000 cm^{-1}) of the anion, there was *no* discernible isotope shift within the standard deviation ($\pm$ 0.12 K) in our measurements involving 12 crystal specimens each of labeled and unlabeled κ-(ET)$_2$Cu(NCS)$_2$ [18]. These results are graphically shown in Figure 6.

4. Concluding Remarks

Our isotope effect studies with isotopic labeling at various specific sites within the ET molecule represent the most comprehensive investigations of isotope shift performed

Fig. 4. Susceptibility curves (corrected for demagnetization) of four crystals each of natural abundance (open symbols) and ^{13}C(4)^{34}S(8)-labeled (filled symbols) κ-(ET)$_2$Cu(NCS)$_2$.
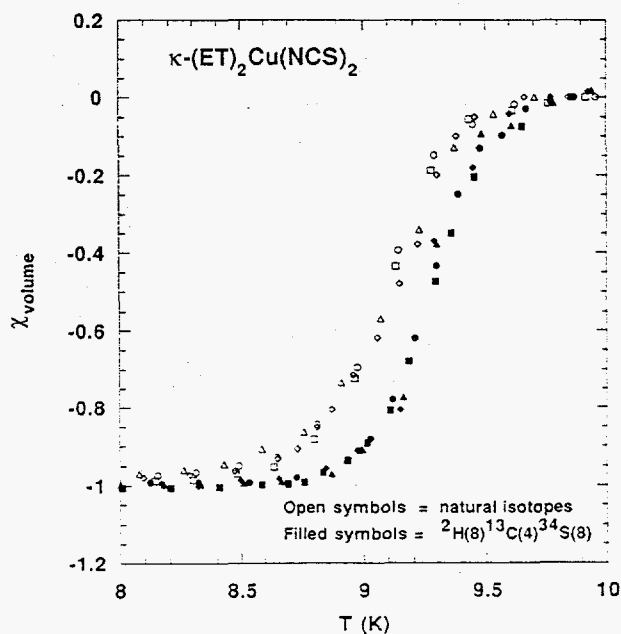

Fig. 5. Susceptibility curves (corrected for demagnetization) of four crystals each of natural abundance (open symbols) and ^{2}H(8)^{13}C(4)^{34}S(8)-labeled (filled symbols) κ-(ET)$_2$Cu(NCS)$_2$.
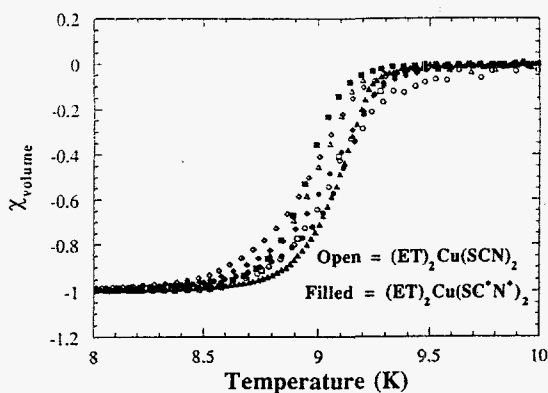
Fig. 6. Susceptibility curves (corrected for demagnetization) of four crystals each of natural abundance κ-$(ET)_2Cu(NCS)_2$ (open symbols) and κ-$(ET)_2Cu(^{15}N^{13}CS)_2$ (filled symbols) .

in organic superconducting systems. The most significant finding in these studies, which is relevant to the electron-pairing mechanism, is the normal, BCS-like mass isotope effect for $^{13}C(4)^{34}S(8)$-labeling in κ-$(ET)_2Cu(NCS)_2$. While the isotope shift is of the correct sign, its magnitude is somewhat lower than that predicted by the simple BCS formula ($T_c \propto M^{-\alpha}$) assuming ET as the relevant mass entity. As we have pointed out previously [9], this assumption may not be necessarily valid in organic molecular superconductors where the role of anions cannot be ignored. On the other hand, the smaller isotope shift may also be a reflection of ubiquitous Coulomb interactions in this class of materials. Nevertheless, by use of the experimental isotope shift and assuming that ET is the relevant mass entity, we obtain $\alpha = 0.26 \pm 0.11$ for $T_c \propto M^{-\alpha}$. It will be interesting to see if the normal, BCS-like mass effect is found in other organic superconductors belonging to different structural types and with different anions. Such studies are currently ongoing in our laboratory.

The *inverse* isotope effct upon deuteration does not appear to be unique to κ-$(ET)_2Cu(NCS)_2$. We have very recently performed deuterium isotope effect studies on the ambient pressure superconductor κ_L-$(ET)_2Ag(CF_3)_4$(1-bromo-1,2-dichloroethane), belonging to the newly discovered family of superconductors with large, discrete, non-polymeric anions [19]. In this superconductor, T_c was found to increase from 2.90 ± 0.04 K to 3.11 ± 0.04 K upon deuterium substitution in the ET molecule. Inverse isotope effects were also reported previously in κ-$(ET)_2Cu[N(CN)_2]Cl$, which requires a mild pressure (0.3 kbar) to become superconducting [20], and in β-$(ET)_2I_3$ [21].

Remarkably, at least in κ-$(ET)_2Cu(NCS)_2$, two isotope shifts of opposite sign are found in the same superconductor depending on which atoms in the ET donor molecule are isotopically labeled. Given the layered structure of organic superconductors, even more remarkable is the finding that a

mass-related, normal isotope effect (suggesting phonon-mediated electron-pairing) is observed in the conducting layer, and the *inverse* isotope effect (suggesting an unconventional mechanism for electron-pairing) is seen in the non-conducting layer (Figure 7). The latter result is likely related to the inter-layer coupling involving electronic tunneling, as a consequence of the quasi-two-dimensionality of the system.
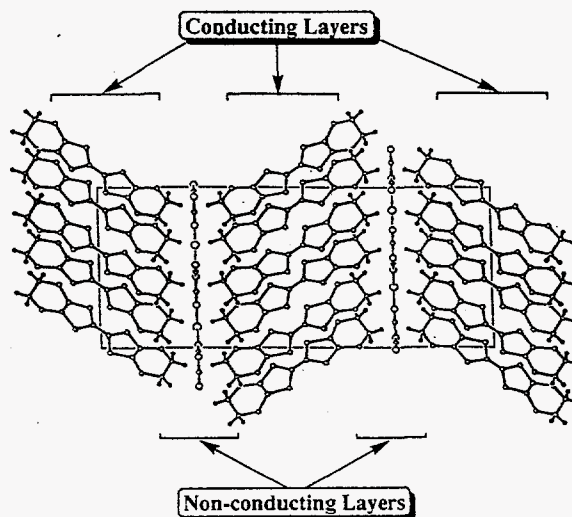

Fig. 7. Alternating conducting (with normal isotope shift) and non-conducting (with inverse isotope shift) layers in a layered organic superconductor such as κ-$(ET)_2Cu(NCS)_2$

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