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New Findings and Implications**

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On the “inverse” isotope effect in organic superconductors: new findings and implications

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Abstract

The “inverse” deuterium isotope effect, previously found in κ -(BEDT-TTF)₂Cu(NCS)₂, is also found in two other BEDT-TTF based superconductors with different packing motifs and different types of anions. Remarkably, the magnitude of the isotope shift is essentially identical in all three superconductors, *ca.* $+0.26 \pm 0.06$ K. These results, when taken together with the recent results of Lang et al. on the uniaxial pressure derivatives of T_c , suggest that the “inverse” isotope effect may not have a direct relationship to the pairing mechanism but instead is a reflection of the change in the “internal lattice pressure”.

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

1. Introduction

Despite intense research efforts towards understanding the nature of electron-pairing mechanism in organic superconductors, a consensus has not yet emerged. Experimental evidence has been presented in support of both conventional (phonon-mediated, BCS, *s*-wave order parameter symmetry) and unconventional (not phonon-mediated, non-BCS, *d*-wave order parameter symmetry) mechanisms [1]. Our comprehensive and carefully performed isotope effect studies have revealed two competing isotope effects in the ambient pressure organic superconductor κ -(BEDT-TTF)₂Cu(NCS)₂ — a “normal” isotope shift (lowering of T_c) when the largest possible mass increase of BEDT-TTF (hereafter ET) molecule is achieved by ³⁴S and ¹³C labelling and an “inverse” isotope shift (increase in T_c) when hydrogen (H) atoms in ET molecule are replaced by deuterium (D) [2]. While the former effect is a clear indication for the involvement of lattice phonon modes in electron-pairing, the latter effect can not be reconciled with any existing theoretical models. In this connection, we have continued our isotope effect studies to determine whether the “inverse” D isotope effect

is specific to κ -(BEDT-TTF)₂Cu(NCS)₂ or is more universal in nature. We have now found that it occurs in at least two other ET based superconductors, viz., κ_L -(ET)₂Ag(CF₃)₄(BDCE) where BDCE is 1-bromo-1,2-dichloroethane [3] and β'' -(ET)₂SF₅CH₂CF₂SO₃. Furthermore, the magnitude of the isotope shift is essentially the same ($+0.26 \pm 0.06$ K) in all three superconductors (with T_c 's ranging from 2.9 to 9.2 K), irrespective of the donor packing motifs (κ or β'') or the nature of the counter anions (polymeric or discrete or organometallic). In the meantime, Müller, Lang and coworkers have determined uniaxial pressure coefficients of T_c in κ -(ET)₂Cu(NCS)₂ and β'' -(ET)₂SF₅CH₂CF₂SO₃ by high-resolution measurements of the coefficients of thermal expansion, and have found a large negative uniaxial stress effect perpendicular to the conducting planes in both superconductors [4]. These two results, when taken together, strongly suggest that the “inverse” D isotope shift may not be directly related to the electron-pairing mechanism, but rather to the change in “internal lattice pressure”.

2. Results and Discussion

As a continuation of our isotope effect studies [2,3], we have recently determined the effect of D substitution in the ET portion of β'' -(ET)₂SF₅CH₂CF₂SO₃. The same preparative, measurement and data analysis protocols as used previously by us were employed, and they are described in detail elsewhere [5]. An “inverse” isotope shift of $+0.27 \pm 0.06$ K was found for this completely

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Table 1

Summary of H-to-D isotope shifts and uniaxial pressure derivatives (perpendicular to conducting planes) in three superconductors

| Superconductor | T_c (K) | ΔT_c (K) | $(\partial T_c / \partial p)_\perp$ (K/kbar) |
|--|-------------|------------------|--|
| κ_L -(ET) ₂ Ag(CF ₃) ₄ (BDCE) | 2.90 ± 0.04 | 0.21 ± 0.06 | — |
| β'' -(ET) ₂ SF ₅ CH ₂ CF ₂ SO ₃ | 4.34 ± 0.05 | 0.27 ± 0.06 | -5.9 ± 0.25 |
| κ -(ET) ₂ Cu(NCS) ₂ | 9.20 ± 0.05 | 0.30 ± 0.07 | -6.2 ± 0.25 |

organic superconductor. In Figure 1, we graphically illustrate the "inverse" isotope effect found so far in three different superconductors, which are of essentially the same magnitude within experimental uncertainties (see also Table 1).

In Table 1, we have also included the uniaxial pressure coefficients of T_c for κ -(ET)₂Cu(NCS)₂ and β'' -(ET)₂SF₅CH₂CF₂SO₃ perpendicular to the conducting planes. These were obtained from high resolution measurements of the coefficient of thermal expansion, $\alpha = \Gamma^{-1} \times (\partial \Gamma / \partial T)$, on single crystals of the two superconductors, which show large and highly anisotropic phase transition anomalies at T_c [4]. By combining the thermal expansion data with the literature results on the specific heat and by use of the Ehrenfest equation, the uniaxial pressure coefficients were obtained. The most notable finding is that the uniaxial pressure derivatives perpendicular to the conducting plane, i.e., along a^* in κ -(ET)₂Cu(NCS)₂ and c in β'' -(ET)₂SF₅CH₂CF₂SO₃, are rather large and of nearly the same magnitude, -5.9 ± 0.25 and -6.2 ± 0.25 K/kbar respectively. The essentially similar and large negative values of the uniaxial pressure derivative in two different superconductors now provide new insights into why the D isotope effect is "inverse" and is of the same magnitude.

In this connection, it is necessary to know what if any changes in the lattice parameters are caused by the H-to-D substitution in these materials, because it has been argued that the inverse isotope shift could be an outcome of changes in the lattice parameters and consequently the band structure. Watanabe et al. have showed by four-circle single crystal x-ray diffraction (300–12K) studies that the H-to-D isotopic substitution in both κ -(ET)₂Cu(NCS)₂ and κ -(ET)₂Cu[N(CN)₂]Br results in no significant changes in the lattice parameter perpendicular to the conducting planes, although measurable changes occur in other lattice parameters at low temperatures [6]. Since C–H(D) bonds in ET-based superconductors are oriented perpendicular to the planes, and C–D bonds have a smaller zero point displacement compared to C–H bonds, H-to-D substitution should result in longer (or softer) intermolecular contacts with the atoms in the anion and with other donor molecules [7]. In other words, the "internal lattice pressure" perpendicular to the planes becomes smaller as a result of the H-to-D substitution, and this change is expected to be of the same magnitude irrespective of the anion or the packing motif within the conducting plane. Since the large

negative pressure derivative of T_c in the direction perpendicular to the planes is the same for the two superconductors, it therefore follows that the observed isotope shift is merely an outcome of the lowering of the "internal lattice pressure".

Finally, we note that the "inverse" D isotope effect is a clear indication of the importance of interlayer coupling in layered organic superconductors, and may not be directly linked to what mediates electron-pairing. Whangbo et al. have suggested that within the framework of the generalized BCS model and the McMillan equation, the H-to-D substitution should result in a "softer" lattice and a larger λ (electron-phonon coupling constant), and hence a higher T_c [7,8].

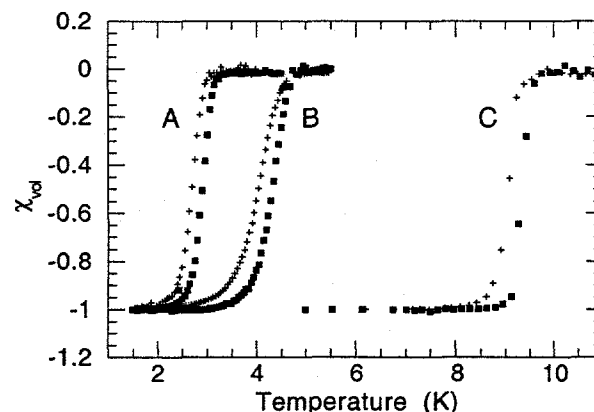


Fig. 1. Representative superconducting transition curves (by a.c. susceptibility) of (A) κ_L -(ET)₂Ag(CF₃)₄(BDCE), (B) β'' -(ET)₂SF₅CH₂CF₂SO₃ and (C) κ -(ET)₂Cu(NCS)₂. Plus symbols = H; filled squares = D.

3. References

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