Comparison of the normal-state properties of -(BEDT-TTF)$_2$Cu(NCS)$_2$ and its deuterated analogue in high magnetic fields and under high hydrostatic pressures

2002 J. Phys.: Condens. Matter 14 L495

(http://iopscience.iop.org/0953-8984/14/26/102)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **14** (2002) L495–L502 PII: S0953-8984(02)35147-6

LETTER TO THE EDITOR

Comparison of the normal-state properties of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and its deuterated analogue in high magnetic fields and under high hydrostatic pressures

Tim Biggs[1], **Anne-Katrin Klehe**[1], **John Singleton**[1,2,6], **David Bakker**[1], **Jane Symington**[1], **Paul Goddard**[1], **Arzhang Ardavan**[1], **William Hayes**[1], **John A Schlueter**[3], **Takehiko Sasaki**[4] and **Mohamedally Kurmoo**[5]

[1] Department of Physics, University of Oxford, The Clarendon Laboratory, Parks Road, Oxford OX1 3PU, UK
[2] National High Magnetic Field Laboratory, LANL, MS-E536, Los Alamos, NM 87545, USA
[3] Materials Science Division, Argonne National Laboratory, IL 60439, USA
[4] Institute for Materials Research, Tohoku University, Aoba Ku, Sendai, Miyagi 9808577, Japan
[5] IPCMS, 23 rue du Loess, BP 20/CR, 67037 Strasbourg Cedex, France

E-mail: j.singleton1@physics.ox.ac.uk

Received 22 March 2002
Published 21 June 2002
Online at stacks.iop.org/JPhysCM/14/L495

Abstract
Details of the Fermi-surface topology of deuterated κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (where BEDT-TTF $\equiv$ bis(ethylene-dithio)tetrathiafulvalene) have been measured as a function of pressure, and compared with equivalent measurements of the undeuterated salt. We find that the superconducting transition temperature is much more dramatically suppressed by increasing pressure in the deuterated salt. It is suggested that this is linked to pressure-induced changes in the Fermi-surface topology, which occur more rapidly in the deuterated salt than in the undeuterated salt as the pressure is raised. Our data suggest that the negative isotope effect observed on deuteration is due to small differences in Fermi-surface topology caused by the isotopic substitution.

(Some figures in this article are in colour only in the electronic version)

The nature of superconductivity in quasi-two-dimensional crystalline organic metals is the subject of current debate in the literature [1–4]. The close proximity of an antiferromagnetic to a superconducting ground state in the temperature–pressure phase diagram has spurred theoretical suggestions of d-wave Cooper pairing mediated by antiferromagnetic fluctuations [3–7]. Such an idea, which implies nodes in the superconducting order

[6] Author to whom any correspondence should be addressed.

parameter, is strongly supported by NMR (^{13}C [8–10] and ^{1}H [11]), tunnelling [12], thermal conductivity [13] and magnetic penetration depth experiments [14], and by the form of the superconducting phase diagram deduced from magnetometry and NMR [15]. The coupling of Raman modes to the antiferromagnetic fluctuations has also been observed [16], suggesting interactions between the lattice and the magnetic fluctuations. On the other hand, it has been suggested that specific heat measurements may be interpreted using a BCS-like model [17]. The observed hardening of low-energy, intramolecular vibrations at the superconducting transition in Raman [18, 19] and inelastic neutron scattering experiments [20] has been interpreted as further evidence for the involvement of phonons in superconductivity. However, similar phonon self-energy effects have also been observed in the non-BCS-like cuprate superconductors [21] and perhaps merely indicate very strong electron–phonon coupling.

In this context, the observation of a 'negative isotope effect' in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ may be of great importance [22, 23]; on replacing the terminal hydrogens of the BEDT-TTF molecule in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ by deuterium, it was found that a small but consistent increase in the superconducting critical temperature T_c occurred [22, 23]. By contrast, isotopic substitutions of other heavier atoms in the BEDT-TTF molecule or in the anion layer exhibit respectively a very small, normal isotope effect or no significant isotope effect at all [23]. We have therefore studied the changes in Fermi-surface parameters of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ on deuteration using the Shubnikov–de Haas effect. Data were recorded both at ambient pressure and as a function of hydrostatic pressure. Taken in conjunction with very recent millimetre-wave magnetoconductivity experiments [26], our data suggest that it is primarily the changes in the detailed topology of the of the Fermi surface brought about by deuteration that cause the observed isotope effect. This would tend to support models for superconductivity involving pairing via electron–electron interactions [3–7].

The experiments involved single crystals of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ ($\sim$0.7 $\times$ 0.5 $\times$ 0.1 mm^3; mosaic spread $\lesssim 0.1°$), produced using electrocrystallization [22, 23]. In some of the crystals, the terminal hydrogens of the BEDT-TTF molecules were isotopically replaced by deuterium; we refer to these deuterated samples as d8, and conventional hydrogenated samples as h8. In order to check for extrinsic effects, independently prepared batches of both types of crystal were made at Argonne, Strasbourg and Sendai; no extrinsic effects were found. Note that, to all intents and purposes, the crystallographic unit cells of h8 and d8 seem to be indistinguishable in size and shape [23–25].

The magnetoresistance of the samples was measured using standard four-wire AC techniques (frequency $f = 15$–180 Hz, current $I = 1$–$20\ \mu$A) [2]. Contacts were applied to the upper and lower large surfaces of the crystals, so that the current was directed and the voltage measured in the interlayer direction; such a configuration gives a resistance which is accurately proportional to the interlayer component of the magnetoresistance, ρ_{zz} [2].

In the ambient-pressure experiments, crystals of d8 and h8 were simultaneously studied in a ^{3}He/^{4}He cryostat which allowed rotation of the samples to all possible angles in the magnetic field [28]. The magnetoresistance was measured with the samples at many orientations in the magnetic field, so that any errors due to slight differences of mounting of the d8 and h8 crystals could be eliminated; the quasiparticle effective masses and Shubnikov–de Haas oscillation frequencies discussed below are corrected to $\theta = 0$, where θ is the angle between the normal to the sample's conducting planes and the magnetic field. Temperatures were monitored using ruthenium oxide sensors, with additional checks carried out using the ^{3}He and ^{4}He vapour pressures. Quasistatic magnetic fields were provided by a 15 T superconductive magnet at Los Alamos and by the 45 T hybrid magnet at NHMFL Tallahassee.

The high-pressure experiments were carried out on three d8 crystals using a non-magnetic piston–cylinder cell [27]; the pressure medium was Fluorinert FC75. The exact crystal

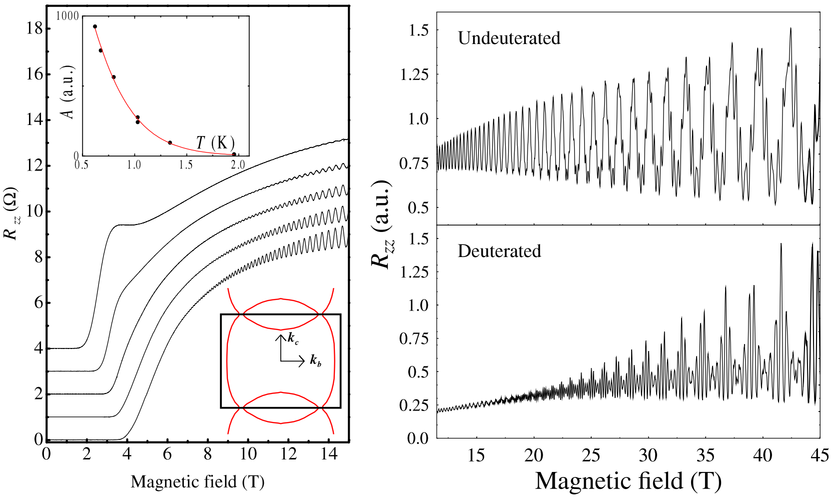

Figure 1. Left: interplane resistance $R_{zz}(\propto\rho_{zz})$ of h8 κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ at ambient pressure with the magnetic field applied perpendicular to the quasi-two-dimensional planes. Data for temperatures 1.96 K (uppermost trace), 1.34 K, 1.03 K, 800 mK and 620 mK (lowest trace) are shown; for clarity, the data have been offset by 1 Ω. The superconducting to normal transition is clearly visible, as are Shubnikov–de Haas oscillations due to the α-pocket of the Fermi surface. The upper inset shows a typical plot of the Fourier amplitude A of the Shubnikov–de Haas oscillations as a function of temperature; data are points and the curve is a fit of the Lifshitz–Kosevich formula [2]. The lower inset shows the Brillouin zone and Fermi-surface cross-section of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ with its closed α-pocket and quasi-one-dimensional sheets (based on parameters given in [28]). Right: comparison of the high-field interplane resistance R_{zz} of d8 (deuterated) and h8 (undeuterated) κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ ($T = 520$ mK). Note how the high frequencies caused by magnetic breakdown are much more dominant in d8.

orientation with respect to the field was determined by comparison with ambient-pressure data and corrections to the measured Shubnikov–de Haas frequency made accordingly [2]. The cell was placed in a large-volume ^{3}He cryostat capable of temperatures down to 700 mK within a 17 T superconductive magnet at Oxford. The pressure inside the cell was determined using a manganin wire [27]. Temperatures were measured with a Pt thermometer above 50 K and a ruthenium oxide thermometer at low temperatures. All pressures quoted were measured at 4.2 K. T_c was taken to be the resistive mid-point of the normal–superconducting transition during cool down.

The left-hand side of figure 1 shows typical low-field ambient-pressure magnetoresistance data for an h8 sample. Similar data were recorded simultaneously for a d8 sample. Shubnikov–de Haas oscillations caused by the quasi-two-dimensional α-pocket of the Fermi surface (see the lower inset of figure 1) are visible. At these low fields, the oscillatory magnetoresistance is much less than the non-oscillatory component, and magnetic breakdown is a relatively minor consideration [2]. Hence, the Lifshitz–Kosevich formula may be used to extract the effective mass m^* [2] from the temperature dependence of the oscillation amplitude A; a typical fit is shown as the upper inset in figure 1.

Data such as those in figure 1 suggest that the Fermi-surface α-pockets of h8 and d8 are rather similar; as an example, the magnetic quantum oscillation frequencies of the α-pocket at $\theta = 0$ were $F_\alpha = 600 \pm 1$ T (h8) and 597 ± 1 T (d8); the former is in good agreement with the accepted value [1]. Although the d8 and h8 frequencies are very close, consistently smaller values were obtained for the d8 samples, and so we believe that the stated difference is real. The corresponding α-pocket effective masses ($\theta = 0$) are $m^* = 3.5 \pm 0.1\ m_\mathrm{e}$ (h8) and $m^* = 3.4 \pm 0.1\ m_e$ (d8); the difference between the masses is around the experimental error. The average interlayer transfer integrals for d8 and h8 were measured in a separate experiment [28]; both were found to be close to 0.04 meV [28].

The only significant difference between the magnetotransport of d8 and h8 at ambient pressure occurs in the magnetic breakdown between the α-pocket and quasi-one-dimensional sheets, which gives rise to a semiclassical orbit with the same cross-sectional area as the Brillouin zone [29]. As shown in the right-hand side of figure 1, which displays magnetoresistance data recorded in the hybrid magnet, the breakdown is significantly stronger in d8, leading to a plethora of high-frequency oscillations in the magnetoresistance due to the Shiba–Fukuyama–Stark quantum interference effect [2]. Following the method set out in [29], analysis of the breakdown oscillations suggests a breakdown field of $B_0 = 30 \pm 5$ T in d8, compared to a value of $B_0 = 41 \pm 5$ T [29] in h8.

We now turn to the high-pressure experiments. Figure 2(a) shows the pressure dependence of the effective mass m^*_α of the d8 Fermi-surface α-pocket, extracted from the temperature dependence of the Shubnikov–de Haas oscillations [2]. At pressures of less than 0.25 GPa, m^*_α decreases very sharply with increasing pressure P ($\mathrm{d}m^*_\alpha/\mathrm{d}P \approx -10\, m_e\mathrm{GPa}^{-1}$); above this pressure, the mass decreases much more gently as P is raised. The d8 masses are compared with the h8 data of Caulfield *et al* [30] in figure 2(a); note that the initial rate of decrease of m^*_α with P is significantly less in h8, but that the variations of m^*_α are very similar in h8 and d8 at higher P.

Figure 2(b) shows the superconducting critical temperature T_c of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ as a function of P for both d8 (this work) and h8 [30]. In the case of d8, T_c is very rapidly suppressed with increasing P($\mathrm{d}T_c/\mathrm{d}P \approx 80$ K GPa^{-1}). By contrast, $\mathrm{d}T_c/\mathrm{d}P \approx 30$ K GPa^{-1} for h8 [30]. As in the case of the effective mass, the pressure seems to have a much more marked effect for d8 than for h8.

Weiss *et al* suggested that there may be some universal relationship between T_c and m^*_α in κ-phase BEDT-TTF superconductors [31] (see also [30, 32]). Figure 2(c) shows such a plot for d8 (this work) and h8 [30]. Whilst the data for the two salts vary in a qualitatively similar fashion, the slope of T_c versus m^*_α seems to be somewhat steeper for d8.

Figures 3(a) and (b) show the pressure dependence of the Shubnikov–de Haas oscillation frequencies for d8 and h8. As has been mentioned above, the β-orbit frequency F_β (figure 3(b)) reflects the size of the Brillouin zone in the conducting bc-plane; it is therefore a direct measure of the in-plane compressibility. Figure 3(b) shows that the pressure dependences of F_β are almost identical in h8 and d8. This suggests that any lattice softening effects due to deuteration do not affect the intraplane compressibility, and are thus, if present, only effective in the interplane direction. By contrast, the Fermi-surface α-pocket frequency grows much more quickly with P in d8 than in h8 (figure 3(a)); interestingly, T_c tends to zero in *both* d8 and h8 at pressures where the α-orbit frequencies reach approximately the same value, $F_\alpha \approx 770 \pm 15$ T.

To examine the effect of pressure more deeply, we turn to the *effective dimer model* which has been shown to represent the intralayer quasiparticle dispersion $E(\boldsymbol{k}_\parallel)$ in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ accurately (see [28] and references therein);

$$E(\boldsymbol{k}_\parallel) = \pm 2\cos\left(\frac{k_b b}{2}\right)\sqrt{t_{c1}^2 + t_{c2}^2 + 2t_{c1}t_{c2}\cos(k_c c)} + 2t_b\cos(k_b b). \tag{1}$$

Here k_b and k_c are the intralayer components of $\boldsymbol{k}$ (see figure 1, inset) and t_b, t_{c1} and t_{c2} are effective interdimer transfer integrals[7]; the + and − signs result in the quasi-one-dimensional

[7] Recent fits of this model to de Haas–van Alphen data at ambient pressure have produced the values $t_b = 15.6$ meV, $t_{c1} = 24.2$ meV and $t_{c2} = 20.3$ meV [28]. Note that these t are *effective* transfer integrals, as opposed to the bare, unrenormalized transfer integrals used in a band-structure calculation; instead, as they are based on parameters from de Haas–van Alphen data, they will include the effects of electron–electron and electron–phonon interactions [33].

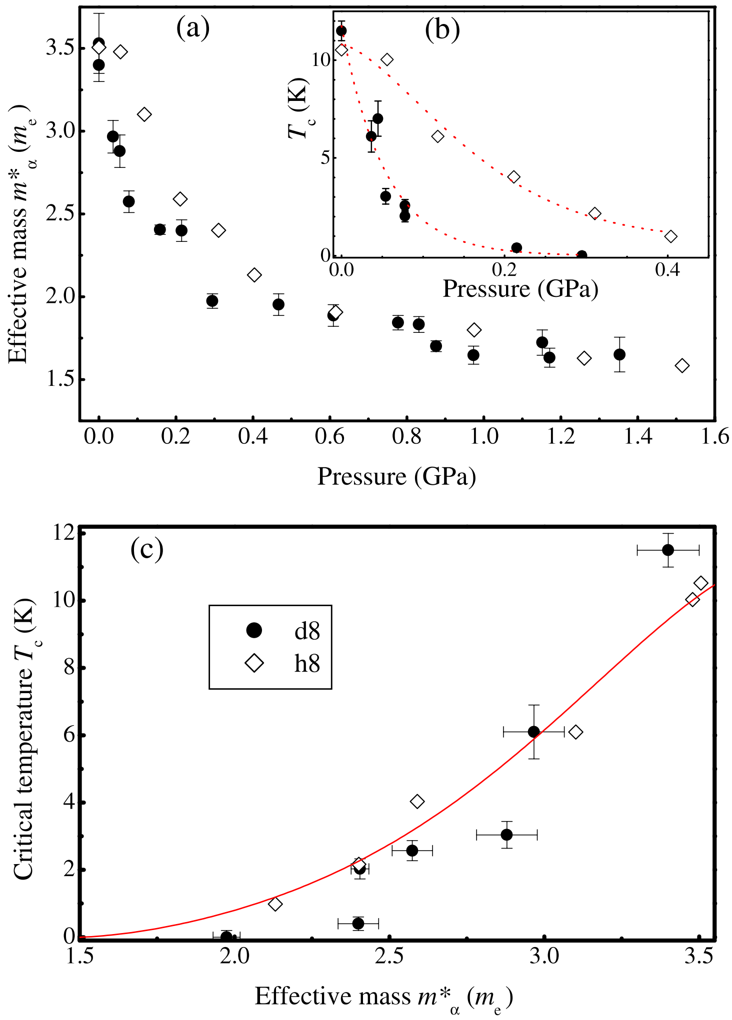

Figure 2. (a) Pressure dependence of the effective mass m^*_α of the Fermi-surface α-pocket of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ as a function of pressure P. Data for d8 (this work) are filled circles; data for h8 [30] are hollow diamonds. (b) Variation of superconducting critical temperature T_c of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ as a function of P; filled circles: d8 (this work); hollow diamonds: h8 [30]. (c) T_c versus m^*_α for h8 (filled circles) and d8 (hollow diamonds). The curve is the linearized Eliashberg solution from [7].

sheets and the α-pocket of the Fermi surface respectively. The cross-sectional area of the α-pocket is determined by the ratio t_b/t_c, where t_c is the mean of t_{c1} and t_{c2} [28]. Using this approach [30], we can convert the frequencies F_α from figure 3(a) into values of t_b/t_c; the result is shown for both h8 and d8 as the inset in figure 3(a). The inset shows that t_b/t_c increases with P more rapidly in d8 than in h8.

Reference [30] shows that an increase of t_b/t_c elongates the overall Fermi-surface cross-section in the k_c-direction by 'fattening' the α-pocket. As a consequence, the corrugation of the quasi-one-dimensional sheets changes somewhat; the regions next to the breakdown gap become slightly more pointed, whilst away from the gap, the sheets flatten slightly. Our data suggest that these changes occur much more rapidly with increasing pressure in d8 than in h8.

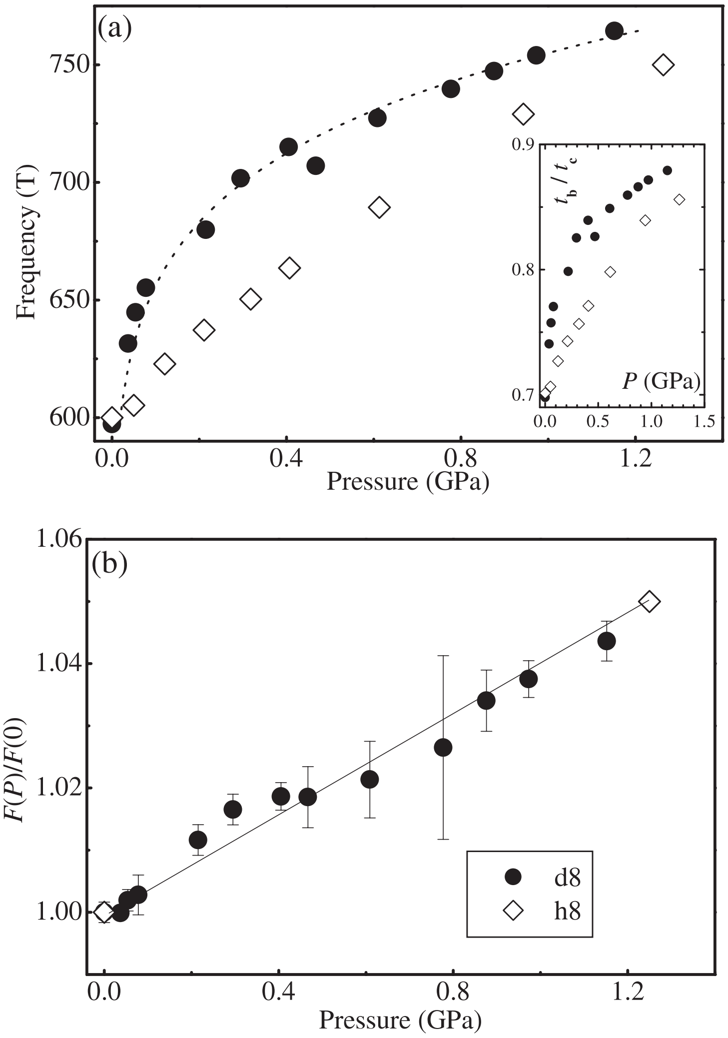

Figure 3. (a) Shubnikov–de Haas oscillation frequency for the Fermi-surface α-pocket as a function of pressure P for d8 (filled circles; this work) and h8 (hollow diamonds, [30]). The inset shows t_b/t_c versus pressure, where the t are effective transfer integrals defined in equation (1). (b) An equivalent plot for the β-breakdown frequency, but with the frequencies normalized to the ambient-pressure value.

With this in mind, we suggest that the more rapid suppression of superconductivity in d8, compared to h8, is linked to the fact that the Fermi-surface topology changes more drastically with pressure in d8 (figure 3). This strongly suggests that the superconducting mechanism is very sensitively influenced by the exact topology of the Fermi surface, and hence that this effect is also responsible for the inverse isotope effect in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ observed on deuteration. Additional support for this proposal is provided by the difference in magnetic breakdown strength seen in d8 and h8 at ambient pressure (figure 1), suggesting slightly different Fermi-surface topologies for the two salts.

An alternative explanation for the inverse isotope effect invokes a softening of the bonds upon deuteration and a concurrent increase in the electron–phonon interaction [23].

Comparative Raman studies on deuterated and undeuterated κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ may also be interpreted in this way [34]. It might also be possible to simulate the size and direction of change of T_c experienced upon deuteration from the anisotropic compressibility [24, 35] of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, and the strongly anisotropic uniaxial pressure dependence of its superconducting transition temperature [36, 37][8]. However, neither of these explanations can shed any light on the very obvious relationship between the details of the Fermi-surface shape and T_c, shown by our data (figures 2 and 3).

Instead, our data support models for exotic d-wave superconductivity in the organics which invoke electron–electron interactions depending on the topological (i.e. nesting) properties of the Fermi surface [3–6]. Similar interactions probably contribute to the relatively large values of the quasiparticle mass observed in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ [1]. Hence, the changes in Fermi-surface topology may cause *both* the suppression of the superconducting transition temperature and that of the effective mass (see figure 2); the causal relationship between T_c and m^* suggested in earlier works [30–32] is perhaps an oversimplification.

Support for our interpretation comes from recent millimetre-wave magnetoconductivity experiments which give information about the corrugations of the quasi-one-dimensional sheets of the Fermi surface [26] in the *interlayer* direction. It was found that the corrugations on the Fermi sheets of h8 (lower T_c) were relatively large compared to those on the sheets of d8 (higher T_c). This again suggests that it is primarily details of the Fermi-surface topology, and in particular its nestability, that determine T_c.

In summary, we have measured details of the Fermi-surface topology of deuterated κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ as a function of pressure, and compared them with equivalent measurements of the undeuterated salt. We find that the superconducting transition temperature is much more dramatically suppressed by increasing pressure in the deuterated salt. This may be linked to pressure-induced changes in the Fermi-surface topology, which occur more rapidly in the deuterated salt as the pressure is raised. Our data support models for exotic d-wave superconductivity in the organics which invoke electron–electron interactions depending on the topological properties of the Fermi surface.

The work was supported by EPSRC (UK). We should like to thank Steve Blundell and Ross McDonald for stimulating discussions.

References

[1] Singleton J and Mielke C 2002 *Contemp. Phys.* **43** 150
[2] Singleton J 2000 *Rep. Prog. Phys.* **63** 1111
[3] Schmalian J 1998 *Phys. Rev. Lett.* **81** 4232
[4] Kuroki K, Kimura T, Arita R, Tanaka Y and Matsuda Y 2001 *Preprint* cond-mat 0108506
[5] Charfi-Kaddour S, Ben Ali A, Héritier M and Bennaceur R 2001 *J. Supercond.* **14** 317
Louati R, Charfi-Kaddour S, Ben Ali A, Bennaceur R and Héritier M 1999 *Synth. Met.* **103** 1857
Louati R, Charfi-Kaddour S, Ben Ali A, Bennaceur R and Héritier M 2000 *Phys. Rev.* B **62** 5957
[6] Kuroki K and Aoki H 1999 *Phys. Rev.* B **60** 3060
[7] Lee W-M 1998 *Solid State Commun.* **106** 601
[8] Kanoda K, Miyagawa K, Kawamoto A and Nakazawa Y 1996 *Phys. Rev.* B **54** 76
[9] Mayaffre H, Wzietek P, Jérome D, Lenoir C and Batail P 1995 *Phys. Rev. Lett.* **75** 4122
[10] de Soto S M, Slichter C P, Kini A M, Wang H H, Geiser U and Williams J M 1996 *Phys. Rev.* B **54** 16 101
[11] Lefebvre S, Wzietek P, Brown S, Bourbonnais C, Jérome D, Mézière C, Fourmigué M and Batail P 2000 *Phys. Rev. Lett.* **85** 5420
[12] Arai T, Ichimura K, Nomura K, Takasaki S, Yamada J, Nakatsuji S and Anzai H 2001 *Phys. Rev.* B **63** 104518

[8] Reference [36] does not distinguish between d8 and h8 samples. The pressure dependence of T_c for the d8 salt extracted from thermal expansion data [36] does not agree with the current direct measurement.

[13] Izawa K, Yamaguchi H, Sasaki T and Matsuda Y 2002 *Phys. Rev. Lett.* **88** 027002
[14] Carrington A, Bonalde I J, Prozorov R, Giannetta R W, Kini A M, Schlueter J, Wang H H, Geiser U and Williams J M 1999 *Phys. Rev. Lett.* **83** 4172
[15] Lefebvre S, Wzietek P, Brown S, Bourbonnais C, Jérome D, Mézière C, Fourmigué M and Batail P 2000 *Phys. Rev. Lett.* **85** 5420
[16] Eldridge J E, Lin Y, Wang H H, Williams J M and Kini A M 1998 *Phys. Rev.* B **57** 597
[17] Elsinger H, Wosnitza J, Wanka S, Hagel J, Schweitzer D and Strunz W 2000 *Phys. Rev. Lett.* **84** 6098
Wosnitza J 1999 *Physica* C **317–8** 98
[18] Pedron D, Visentini G, Bozio R, Williams J M and Schlueter J A 1997 *Physica* C **276** 1
[19] Foulques E, Ivanov V G, Mézière C and Batail P 2000 *Phys. Rev.* B **62** R9291
[20] Pintschovius L, Rietschel H, Sasaki T, Mori H, Tanaka S, Toyota N, Lang M and Steglich F 1997 *Europhys. Lett.* **37** 627
Toyota N, Lang M, Ikeda S, Kajitani T, Shimazu T, Sasaki T and Shibata K 1997 *Synth. Met.* **86** 2009
[21] MacFarlane R M, Rosen H J, Engler E M, Lee V Y and Jacowicz R D 1988 *Phys. Rev.* B **38** 284
[22] Kini A M, Carlson K D, Wang H H, Schlueter J A, Dudek J D, Sirchio S A, Geiser U, Lykke K R and Williams J M 1996 *Physics* C **264** 81
[23] Schlueter J A, Kini A M, Ward B H, Geiser U, Wang H H, Montasham J, Winter R W and Gard G L 2001 *Physica* C **351** 261
[24] Watanabe Y, Shimazu T, Sasaki T and Toyota N 1997 *Synth. Met.* **86** 1917
[25] Schlueter J A and Geiser U 2002 unpublished
[26] Edwards R S *et al* 2002 *Phys. Rev. Lett.* submitted
[27] Eremets M 1996 *High Pressure Experimental Methods* (Oxford: Oxford University Press)
[28] Singleton J, Goddard P A, Ardavan A, Harrison N, Blundell S J, Schlueter J A and Kini A M 2002 *Phys. Rev. Lett.* **88** 037001
[29] Harrison N, Caulfield J, Singleton J, Reinders P H P, Herlach F, Hayes W, Kurmoo M and Day P 1996 *J. Phys.: Condens. Matter* **8** 5415
[30] Caulfield J M, Lubczynski W, Pratt F L, Singleton J, Ko D Y K, Hayes W, Kurmoo M and Day P 1994 *J. Phys.: Condens. Matter* **6** 2911
[31] Weiss H, Kartsovnik M V, Biberacher W, Steep E, Janssen A G M and Kushch N D 1997 *JETP Lett.* **66** 202
Weiss H, Kartsovnik M V, Biberacher W, Steep E, Balthes E, Janssen A G M, Andres K and Kushch N D 1999 *Phys. Rev.* B **59** 12 370
[32] Brooks J S *et al* 1995 *Phys. Rev.* B **52** 14 457
[33] Harrison N, Rzepniewski E, Singleton J, Gee P J, Honold M M, Day P and Kurmoo M 1999 *J. Phys.: Condens. Matter* **11** 7227
[34] Pedron D, Bozio R, Schlueter J A, Kelly M E, Kini A M and Williams J M 1999 *Synth. Met.* **103** 2220
[35] Chasseau D, Gaultier J, Rahal M, Ducasse L, Kurmoo M and Day P 1991 *Synth. Met.* **41** 2039
Rahal M, Chasseau D, Gaultier J, Ducasse L, Kurmoo M and Day P 1997 *Acta Crystallogr.* B **53** 159
[36] Müller J *et al* 2000 *Phys. Rev.* B **61** 11 739
[37] Sadewasser S, Looney C, Schilling J S, Schlueter J A, Williams J M, Nixon P G, Winter R W and Gard G L 1997 *Solid State Commun.* **104** 571