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LETTER TO THE EDITOR

Angle dependence of the upper critical field in the layered organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (BEDT-TTF $\equiv$ bis(ethylene-dithio)tetrathiafulvalene)

M-S Nam†, J A Symington†, J Singleton†, S J Blundell†, A Ardavan†, J A A J Perenboom‡, M Kurmoo§ and P Day‖

† University of Oxford, Department of Physics, Clarendon Laboratory, Parks Road, Oxford OX1 3PU, UK
‡ Laboratorium voor Hoge Magneetvelden, Toernooiveld 1, NL 6525ED, The Netherlands
§ IPCMS, 23 rue de Loess, BP 20/CR, 67037 Strasbourg, France
‖ The Royal Institution, 21 Albemarle Street, London W1X 4BS, UK

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Abstract. We have performed detailed studies of the angle- and temperature-dependent resistive upper critical fields in the layered organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. With the magnetic field lying in the conducting planes, our measurements show an upper critical field which comfortably exceeds the Pauli-paramagnetic limit in this material. We find no azimuthal angle dependence of the critical field, in spite of recent evidence that this material has gap nodes characteristic of d-wave superconductivity. We propose that the large critical fields may be due to a Fulde–Ferrell–Larkin–Ovchinnikov state which can exist in exactly in-plane fields because of the nature of the Fermi surface of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.

The family of superconducting charge-transfer salts κ-(BEDT-TTF)$_2$X, where X can, for example, be Cu(NCS)$_2$, Cu[N(CN)$_2$]Br or I$_3$, has attracted considerable recent attention. A variety of experiments have suggested that the superconducting gap function may contain nodes at certain points on the Fermi surface; e.g. the ^{13}C NMR spin–lattice relaxation rate [1] varies as T^3 and the thermal conductivity [2] is proportional to T below the superconducting critical temperature T_c. In addition, microwave penetration-depth studies [3] show a non-BCS-like behaviour of the penetration depth as a function of T and the electronic component of the specific heat [4] has an unconventional field dependence below T_c. However, Shubnikov–de Haas [5–8], magnetic breakdown [7,9] and angle-dependent magnetoresistance oscillation [10, 11] experiments demonstrate that these salts have well-defined quasi-two-dimensional (Q2D) Fermi surfaces, indicating that the quasiparticles can be described by Fermi-liquid theory at low temperatures. Furthermore, it has been possible to fit experimental Fermi-surface-topology data to a simplified model of the tight-binding band structure (the so-called effective dimer model) to a good degree of accuracy [5, 12–14]. The combination of unconventional superconductivity and a tractable analytical representation of the band structure makes the κ-(BEDT-TTF)$_2$X superconductors attractive for theoretical studies, and a number of authors [12, 13, 15, 16] have explored the possibility of d-wave superconductivity mediated by spin fluctuations. Very recently, millimetre-wave magneto-optical experiments have shown that the superconducting order parameter in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ is very anisotropic within the highly conducting ***b–c*** planes, with nodes directed along the ***b***- and ***c***-directions and

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antinodes in between [17]; the consequent 'X' shape of the order parameter is very reminiscent of the predictions of Schmalian [13] and suggests that the superconductivity is indeed d-wave-like in nature.

It is natural to enquire whether the anisotropic nature of the order parameter is reflected in any of the other properties of the superconductor. In order to examine this question we have carried out detailed angle-dependent measurements of the transport properties of single crystals of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. We find that the upper critical field depends only on the angle θ between the applied magnetic field and the normal to the highly conducting $\boldsymbol{b}$–$\boldsymbol{c}$ planes; for $\theta = 90^\circ$, the upper critical field exceeds the Pauli-paramagnetic limit by $\sim$50%.

Single crystals of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ ($T_c = 10.4$ K) of approximate size $1\times1\times0.1$ mm^3 were produced using electrocrystallization [18]. Electrical contacts were made to the upper and lower large faces of each crystal by attaching 12.5 μm platinum wires using graphite paint; the large faces are parallel to the $\boldsymbol{b}$–$\boldsymbol{c}$ planes. The resistivity was measured by driving a current between a contact on the upper surface and one on the lower surface; the voltage was measured on an adjacent pair of similar contacts. In such a configuration in anisotropic organic molecular metals, the measured resistance is very accurately proportional to the interplane resistivity component ρ_{zz} [19]. Typical contact resistances were less than 10 Ω; all four contacts had almost identical contact resistances, so possible artefacts due to unbalanced contacts were negligible. AC currents, 10–25 μA and 17–107 Hz, were used for the measurements, and the voltage was detected using a lock-in amplifier; great care was taken to ensure that the measured resistance was neither frequency nor current dependent and that no heating of the sample occurred. The samples were mounted in a cryostat which provided temperatures between 450 mK and 10 K and which allowed them to be rotated to all possible orientations in the magnetic field; the same equipment has been used to study angle-dependent magnetoresistance oscillations (AMROs) in organic molecular metals [10]. The angular coordinates of a sample in the magnetic field are defined by the polar angle θ and the azimuthal angle ϕ, where $\phi = 0$ represents a plane of rotation of the field containing $\boldsymbol{b}$ and the normal to the $\boldsymbol{b}$–$\boldsymbol{c}$ plane. Experiments were carried out on five individual crystals of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ using a 17 T superconducting magnet in Oxford, the 30 T hybrid magnet at the University of Nijmegen in the Netherlands and a 33 T resistive magnet in the National High Magnetic Field Laboratory in Tallahassee, USA. The five crystals gave identical results; in this letter we present data taken from one crystal.

Figure 1(a) shows the resistance of a crystal of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ in a constant magnetic field of 26.5 T as a function of the angle θ (T = 1.4 K). A series of AMROs are observed due to the varying electron orbits around the Fermi surface [10, 11, 20]. There is also a very sharp dip at $\theta = \pm90^\circ$, associated with the normal-to-superconducting transition; the upper critical field becomes very large when the field is almost exactly in-plane (see below), so the resistance suddenly decreases at this angle, even at 26.5 T. In order to get an accurate value for the in-plane critical field, we found that it is very important to accurately align the crystal to better than $\pm0.1^\circ$ using the sharp dip at $\theta = 90^\circ$; misalignment by a fraction of a degree can lower the measured critical field by $\sim$1–2 T.

Figure 1(b) shows the sample resistance as a function of magnetic field, and also gives various definitions of the resistive upper critical field; we define a junction B_j, a mid-point B_m, a zero-magnetoresistance extrapolation $B_{MR\rightarrow0}$ and a field B_h which will be discussed below.

A notable feature of the magnetoresistance data in figure 1(b) is the presence of a 'hump' in the resistance between the superconducting and normal behaviour. This effect has been seen in a number of Cu-containing κ-phase BEDT-TTF salts [6, 21, 22], and is most noticeable when the current is driven in the interplane direction [21, 22]. A weaker effect was observed when the current was driven in-plane, but was found to be suppressed when the number of defects

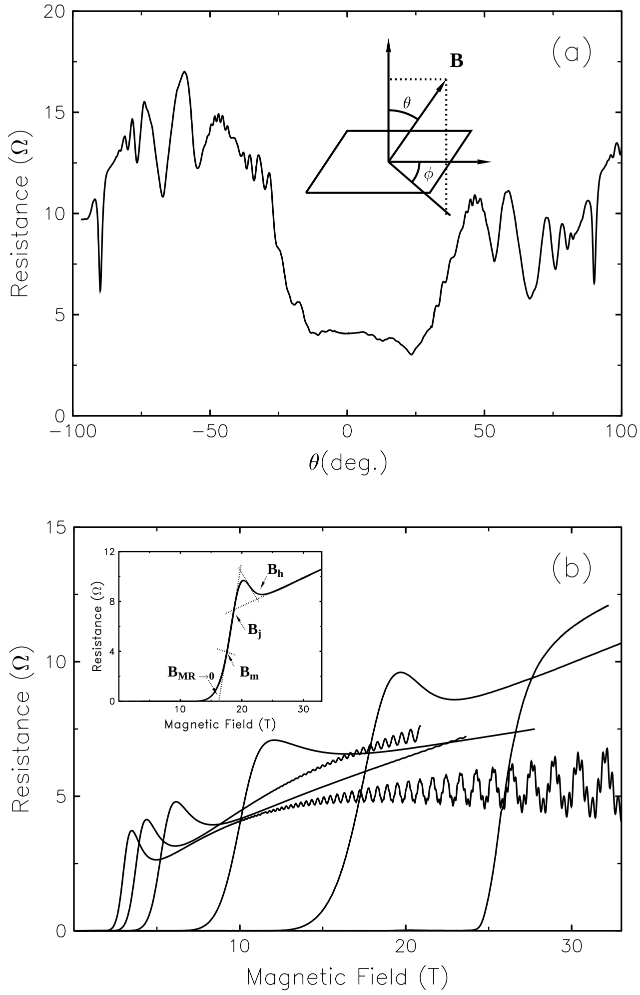

Figure 1. (a) Angle dependence of the resistance of a single crystal of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ at $\phi = 150°$ and $B = 26.5$ T and $T = 1.45$ K. (b) Resistance versus magnetic field B for angles $\theta = 3.01°$, 35.9°, 55.3°, 74.5°, 84.2° and 90°; $T = 1.45$ K and $\phi = 150°$. Note the Shubnikov–de Haas oscillations and the presence of the 'hump'. The diagram also defines the critical fields used in this letter.

in the samples was reduced [23, 24]. By contrast, the 'hump' was found to be largest when the current is in the interplane direction for very pure samples [26], so it may be an intrinsic feature of these layered materials [26]. The hump has been attributed to a number of effects, including dissipation due to superconducting weak links in inhomogeneous samples [22], a resistance-shunted Josephson-junction model [23, 25], magnetoresistance due to thermal fluctuations associated with lattice distortions caused by coupling to the quantized vortices [27] and dissipation caused by fluctuations characteristic of a d-wave superconductor [16]. In the context of the current letter it is necessary to be aware of two things. Firstly, we note that the 'hump' disappears in in-plane fields ($\theta = 90°$), indicating that it is associated in some way with the arrangement of the vortices relative to the crystal structure. This may favour the Josephson-junction model [23, 25], since this involves a noise voltage associated with thermal fluctuations which disrupts the phases of the order parameter between adjacent Josephson-coupled planes; it will only be operative when the vortex cores traverse those planes. It has been already been established that because κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ is a very anisotropic superconductor, the vortex lattice is no longer a system of rigid rods but consists of a weakly coupled stack of 'pancake' vortices, each one confined to a superconducting plane, with the coupling due to Josephson or electromagnetic effects [28, 29]. Secondly, the fact that the proposed mechanisms all regard the 'hump' as an artefact of the *mixed state*, rather than the *normal state*, means that the fields B_j, B_m and $B_{MR\to 0}$ will all be *underestimates* of the true upper critical field B_{c2}. In order to allow for this, we have also evaluated a magnetic field B_h (see figure 1(b)) which denotes the high-field limit of the 'hump' feature.

Figure 2 (upper part) shows the ϕ-dependence of $B_{MR\to 0}$ for $\theta = 90^\circ$ at 4.2 K and 1.45 K, illustrating the fact that the critical field is very insensitive to ϕ. Similar behaviour holds for B_m and B_j (B_h is not defined at $\theta = 90^\circ$ as there is no 'hump'); we find that $B_{MR\to 0} = 25.5\pm 0.1$ T, $B_j = 28.5\pm 0.1$ T and $B_m = 27.0\pm 0.1$ T at 1.45 K independently of ϕ. $B_{MR\to 0} = 17.1\pm 0.1$ T at 4.2 K for all ϕ. The lack of azimuthal dependence of $B_{MR\to 0}$ which we observe reflects the dominance of the effect of the layered structure. Since the interlayer coupling is weak, the interplane velocities are small. Hence the orbital pair-breaking effect due to a magnetic field, reflecting an average over electron orbits, is strongly dependent on the ratio of in-plane to interplane velocity contribution but largely independent of the in-plane anisotropy [13, 17].

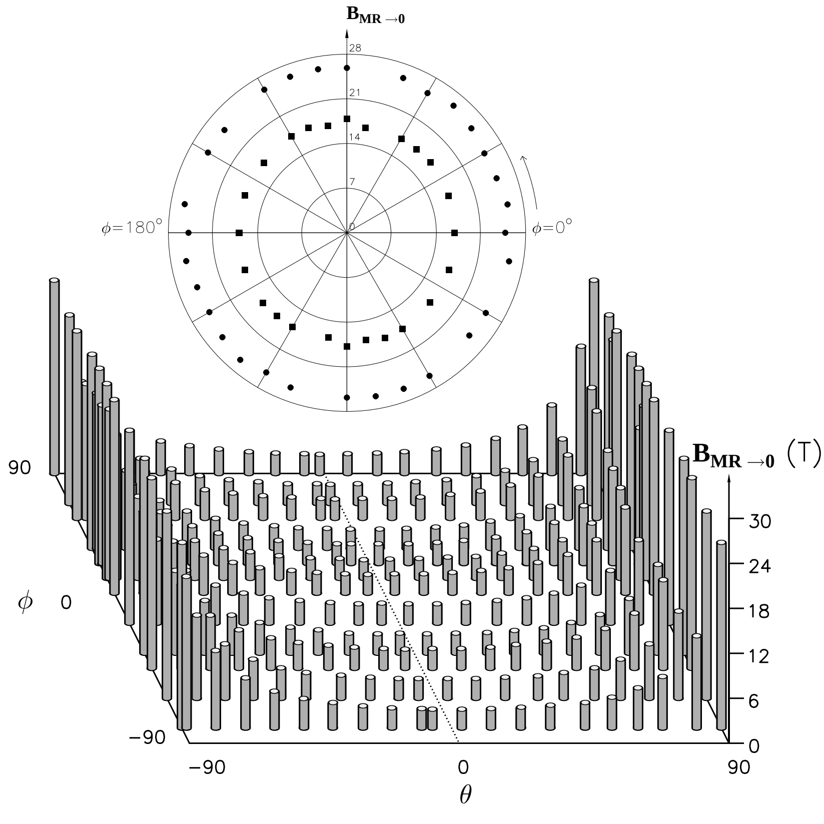

Figure 2. Upper part: azimuthal angle dependence of in-plane $B_{MR\to 0}$ at $T = 4.2$ K (filled squares) and 1.45 K (filled circles). Lower part: the full angle dependence of $B_{MR\to 0}$ at $T = 1.45$ K.

Figure 2 (lower part) also shows the full polar (θ) and azimuthal (ϕ) angle dependence of $B_{\mathrm{MR}\to 0}$ at 1.45 K, again illustrating the ϕ-independence. (The angle dependences of B_{j}, B_{m} and B_{h} show similar behaviour to $B_{\mathrm{MR}\to 0}$ but are increased by ≈11%, ≈6% and ≈45% respectively.) The ratio between the resistive critical fields for $\theta = 90°$ and $\theta = 0$ is about 10 for each of $B_{\mathrm{MR}\to 0}$, B_{j} and B_{m}.

Figure 3 shows the temperature dependence of $B_{\mathrm{MR}\to 0}$, for an in-plane field ($\theta = 90°$) parallel to $\boldsymbol{b}$ ($\phi = 0$). Since $B_{\mathrm{MR}\to 0} \approx 28.9$ T in this orientation and at 450 mK, our maximum field of 33 T is insufficient for extracting B_{j} and B_{m} at this temperature. Note that although the onset of superconductivity occurs in our samples at $T_{\mathrm{c}} = 10.4$ K, zero resistance is not obtained until $T \approx 9.5$ K.

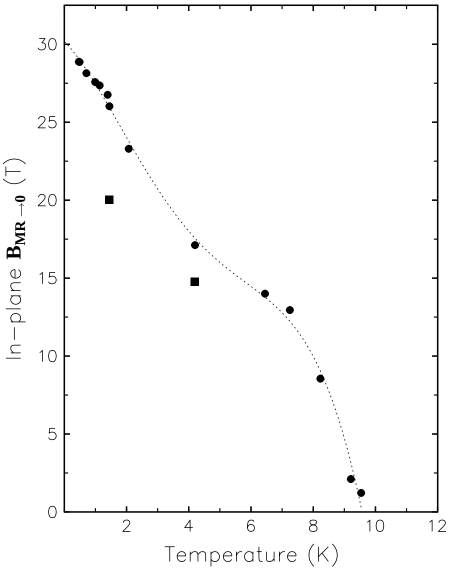

Figure 3. Temperature dependence of in-plane ($\theta = 90°$) values of $B_{\mathrm{MR}\to 0}$; filled circles are data and the dotted line is a guide for the eye. The filled squares are values of B_{spin} from table 1.

Table 1. Parameters derived from fits of equation (3) to $B_{\mathrm{MR}\to 0}$ versus θ data (such as those in figure 4) compared to values of $B_{\mathrm{MR}\to 0}$ at $\theta = 0$ and 90°. The fits were performed over the angular range $|\theta| \leqslant 86°$.

Temperature (K)	$B_{\mathrm{MR}\to 0}(\theta = 90°)$ (T)	B_{spin} (T)	α^{-1}	$B_{\mathrm{MR}\to 0}(\theta = 0)$ (T)
1.45	25.5 ± 0.1	20.0 ± 0.1	7.73	2.60 ± 0.05
4.2	17.1 ± 0.1	14.8 ± 0.1	17.2	0.86 ± 0.02

Figure 4 shows the detailed θ-dependence of $B_{\mathrm{MR}\to 0}$ at fixed ϕ and temperature $T = 1.45$ K. The data in figure 4 are at first sight qualitatively similar to the predictions of the Ginzburg–Landau anisotropic effective-mass approximation [30–32]:

$$B_{\mathrm{c2}}(\theta) = \frac{B_{\mathrm{c2}}(\theta = 0)}{\sqrt{\cos^2(\theta) + \gamma^{-2}\sin^2(\theta)}} \tag{1}$$

in which the superconductivity is destroyed by orbital effects; here γ is the square root of the ratio of the effective masses for interplane and in-plane motion respectively. (In addition, γ can be defined in terms of the penetration depths as $\gamma = \lambda_{\perp}/\lambda_{\parallel}$.)

However, whilst equation (1) has a similar form to the data in figure 4, it cannot reproduce the detailed angle dependence of the data. Moreover, another serious failure of this approach

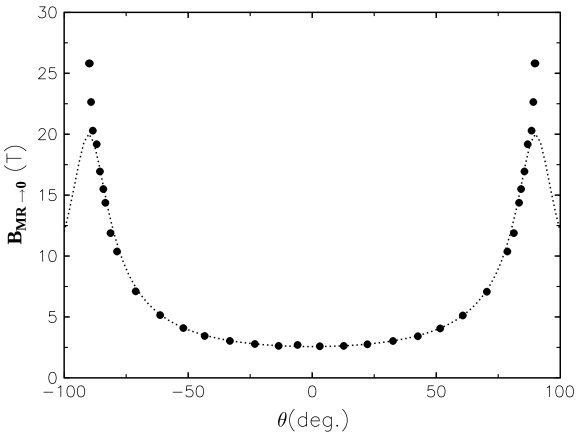

Figure 4. Detailed θ-dependence of $B_{MR\to 0}$ at $\phi = 150^\circ$ and $T = 1.45$ K. The dotted line is a fit to equation (3).

becomes apparent when one compares the value $\gamma \approx 10$ obtained by fitting the data in figure 4 to equation (1) with the accepted value of $\gamma \sim 160$–350 obtained from very careful measurements of the penetration depths [29].

The large values of γ measured in reference [29] occur because the coherence length perpendicular to the conducting layers, $\xi_\parallel$, is smaller than the interlayer distance a. The intralayer overlap of electron wavefunctions in the superconducting state is very weak because $\xi_\parallel$ is shorter than the Josephson tunnelling length $l_J = \eta a$ (η is a constant) between Josephson vortices in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ [29]. In sufficiently high magnetic fields parallel to the layers, flux lines will be trapped inside the layers; in such a limit, the compressing effect of the magnetic field on the Cooper-pair wavefunction [33, 34] exactly compensates the increasing flux density, potentially leading to a very high in-plane upper critical field [35] if orbital effects are the limiting mechanism. This is obviously *not* observed in our data; some other mechanism therefore seems to be limiting the upper critical field close to $\theta = 90^\circ$.

A possible candidate is the Pauli-paramagnetic limit (PPL), also known as the Clogston–Chandrasekhar limit [36–38]. This occurs when the magnetic energy associated with the spin susceptibility in the normal state exceeds the condensation energy in the superconducting state; for isotropic s-wave superconductors it is given by

$$B_{PPL}(T = 0) = 1.84\ T_c. \qquad (2)$$

The PPL mechanism should be roughly isotropic (as the electron g-factor in organic superconductors is within a few per cent of 2 for all field orientations [39]). Therefore, in the spirit of the Ginzburg–Landau approximation (equation (1)), which is a vector sum of two competing critical fields, we propose the following empirical description of the critical field in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, which represents an anisotropic orbital limiting mechanism, dominant at lower values of θ, combined with an isotropic PPL-type mechanism which limits the critical field close to $\theta = 90^\circ$:

$$B_{c2}(\theta) = \frac{B_0}{\sqrt{\cos^2(\theta) + \alpha^2}}. \qquad (3)$$

Here $B_0 = (1 + \alpha^2) B_{c2}(\theta = 0)$ and $\alpha = B_0/B_{spin}$, with B_{spin} the limiting field due to the spin susceptibility.

Equation (3) provides a good fit to the θ-dependences of $B_{MR\to 0}$, B_j, B_m and B_h for angles $|\theta| \leqslant 86^\circ$ (see figure 4); parameters for fits to $B_{MR\to 0}$ data over this angular range at temperatures of 1.45 K and 4.2 K are tabulated in table 1 and shown in figure 3. However, the data for $|\theta|$ closer to 90° do not follow the same dependence, and experimental values of $B_{\mathrm{MR}\to 0}(\theta = 90^{\circ})$ comfortably exceed the fitted B_{spin} at both 1.45 K and 4.2 K (see figure 4 and table 1). Whereas the fitted B_{spin} at 1.45 K is of a similar size to the theoretical PPL for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ ($B_{\mathrm{PPL}}(T = 0) = 19.3$ T using $T_c = 10.4$ K [39]), $B_{\mathrm{MR}\to 0}(\theta = 90^{\circ})$ is ~25% larger at this temperature (see table 1) [40, 41]; the difference between $B_{\mathrm{MR}\to 0}$ and B_{PPL} becomes even more extreme (~50%) at lower temperatures (see figure 3). Therefore it appears that an additional enhancement of the critical field occurs when the field is in-plane.

An intriguing possibility is the existence of a Fulde–Ferrell–Larkin–Ovchinnikov (FFLO) [42, 43] state in high in-plane fields and at low temperatures. To induce a FFLO state one needs a very efficient suppression of interactions involving the orbital moment, a Fermi-surface shape conducive to nesting and a low impurity scattering rate (clean limit). The first criterion may well be achieved in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ in an *exactly* in-plane magnetic field because virtually all of the possible quasiparticle paths on the Fermi surface will be open orbits [20]. Furthermore, a number of authors have pointed out that the Fermi surfaces of κ-phase BEDT-TTF salts are prone to nesting [12, 13, 15]. Finally, consideration of the scattering rates and band parameters of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ has led to the suggestion that it is in the clean limit [30]. Calculations have shown that the existence of the FFLO state in organic superconductors might lead to an enhancement of B_{spin} to between 1.5 and 2.5 times B_{PPL}, the exact value depending on the details of the pairing [44, 45]. This produces the enhancement required to explain our data, although no direct evidence for a first-order transition to a FFLO state has yet been observed in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.

In summary, we have measured the angle dependence of the resistive upper critical field in the layered superconductor, κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. No azimuthal (ϕ) dependence of the critical field was observed, in spite of strong evidence for in-plane gap nodes [13, 17] in this material. The θ-dependence of the measured critical fields can be described by an empirical formula which represents an anisotropic orbital limiting mechanism, dominant at lower values of θ, combined with an isotropic Pauli-paramagnetic-limit-type mechanism which limits the critical field close to the in-plane geometry, $\theta = 90^{\circ}$. However, in exactly in-plane magnetic fields, a further enhancement of the measured critical field appears to occur, and values can exceed the Pauli-paramagnetic (Clogston–Chandrasekhar) limit by ~50%. This may indicate the existence of a Fulde–Ferrell–Larkin–Ovchinnikov state in this material in in-plane fields.

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