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LETTER TO THE EDITOR

Has the Fulde–Ferrell–Larkin–Ovchinnikov state been observed in the organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$?

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Abstract. We compare the theoretical anisotropic upper critical field $H_C(\Theta, T)$ of a quasi-two-dimensional d-wave superconductor with recent H_{c2}-data for the layered organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (BEDT-TTF $\equiv$ bis(ethylene-dithio)tetrathiafulvalene). We find agreement as regards both the angular and the temperature dependence of H_C. This supports the suggestion that the Fulde–Ferrell–Larkin–Ovchinnikov (FFLO) state exists in this material for exactly plane-parallel orientation of the magnetic field. Indications of precursor states, occurring for small deviations from the plane-parallel field direction, are also pointed out and further measurements for confirming the existence of the FFLO state are proposed.

If the superconducting state in high magnetic fields is limited by paramagnetic pair breaking alone, the transition from the homogeneous superconducting state to the normal-conducting state may proceed either directly, at the Pauli limiting field H_P, or via an interposed inhomogeneous superconducting state predicted in 1964 by Fulde and Ferrell [1] and by Larkin and Ovchinnikov [2] (the FFLO state). The latter state, which stabilizes as a consequence of spin polarization, has attracted considerable interest over the years, but has, despite this, not yet been definitely verified experimentally.

Favourable conditions for observing the FFLO state are found in clean superconductors with orbital critical fields much larger than H_P. In practice, it seems always necessary to reduce the orbital pair-breaking effect by using layered superconductors with nearly decoupled planes or extremely thin films (quasi-two-dimensional superconductors) and applying the magnetic field in a direction parallel to the conducting planes. Several classes of superconducting materials with favourable conditions for observing the FFLO state do exist. These include the 'classical' intercalated transition metal dichalcogenides as well as more exotic materials like high-T_c compounds and organic superconductors.

In this letter we refer to a recent measurement of the upper critical field H_{c2} in the organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ [3]. This layered material shows strong anisotropy of the superconducting properties as regards out-of-plane directions. In addition, a number of experiments listed in reference [3] are interpreted in terms of a strong in-plane anisotropy, of d-wave type, of the gap parameter. The coherence length $\xi_\perp$ perpendicular to the layers of this clean material is smaller than the interlayer spacing d and one expects an extreme reduction of orbital pair breaking for plane-parallel applied field. The angular dependence of H_{c2} was measured in reference [3] both with respect to the angle Θ between the applied magnetic field

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and the direction normal to the conducting planes and with respect to the azimuthal angle ϕ, which denotes the direction of the magnetic field lying within the plane. The results showed, as expected, a strong variation of H_{c2} with Θ. On the other hand, no dependence on ϕ was observed. The maximal value of H_{c2} at the plane-parallel position $\Theta = \pi/2$ was of the order of, but 50% higher than, the Pauli paramagnetic limit H_P. These facts led the authors of reference [3] to propose that their in-plane critical field is the phase boundary between the normal-conducting state and the FFLO state of a d-wave superconductor.

We examined this question by calculating the angular and temperature dependences of the theoretical phase boundary $H_C(\Theta, T)$ between the normal-conducting state and the superconducting states of a quasi-two-dimensional d-wave superconductor. Comparison with the data of reference [3] showed good agreement, supporting the hypothesis that in this experiment the phase boundary of a FFLO state (for d-wave superconductors) has been observed for the first time.

We assume that the coupling between the conducting planes of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ can be neglected, making our problem effectively two dimensional. Then, if the field has both a perpendicular and a parallel component, the superconducting state is limited by both orbital and paramagnetic pair breaking. For an exactly plane-parallel magnetic field the FFLO phase should be realized below a reduced temperature ($t = T/T_c$) of $t \approx 0.4$ [4]. Such a situation, with competition between the two pair-breaking effects, was studied first by Bulaevskii [5]. His treatment was later generalized to arbitrary temperatures and d-wave superconductors by Shimahara and Rainer [6]. Below the stability limit of the normal-conducting state, which will be referred to as $H_C(\Theta, T)$, a series of different inhomogeneous superconducting states, depending on Θ, appear. For s-wave superconductors each one of these states relates to a particular value of Landau's quantum number n, which takes integer values $n = 0, 1, 2, \ldots$. These states are (for the s wave) the following:

- The vortex state for small Θ relating to $n = 0$.
- A series of inhomogeneous states for Θ near $\pi/2$, each one characterized by a single value of $n > 0$, with n increasing with increasing Θ.
- The FFLO state for $\Theta = \pi/2$, which may be characterized by $n \to \infty$.

The structure of the higher Landau level states, for $n > 0$, has been calculated recently for s-wave superconductors by minimizing the quasiclassical free energy [7]. For d-wave superconductors [6] a state below $H_C(\Theta, T)$ is characterized no longer by a single value of n but rather by an infinite subset $\{n_0, n_0 \pm 4, n_0 \pm 8, \ldots\}$. However, the dominant contribution may still be characterized by a single number n, which increases again with increasing Θ and approaches infinity in the FFLO limit. Thus, basically the above classification scheme remains valid for d-wave symmetry. The phase boundary of the 'pure' FFLO state for d-wave superconductors (the curve $H_C(\pi/2, T)$) has been calculated by Maki and Won [4].

The linearized gap equation to be solved is given by [5, 6]

$$-\log\left(\frac{T}{T_c}\right)\Delta(\vec{r}) = \pi k_B T \int_0^\infty \frac{\mathrm{d}s}{\sinh(\pi k_B T s)} \int_0^{2\pi} \frac{\mathrm{d}\phi'}{2\pi} \left[\gamma(\hat{p}')^2\right] \times \left[1 - \cos\left[s\left\{\mu_0 H - \frac{1}{2}\vec{v}_F' \cdot \vec{\Pi}\right\}\right]\right]\Delta(\vec{r}). \tag{1}$$

We consider a cylindrical Fermi surface, appropriate for the present two-dimensional problem, with the Fermi velocity $\vec{v}_F = v_F(\vec{e}_x \cos\phi + \vec{e}_y \sin\phi)$. The gap parameter is given by

$$\Delta(\vec{r}, \hat{p}) = \Delta(\vec{r})\gamma(\hat{p})$$

where $\gamma(\hat{p}) = 1$ for the s wave, and

$$\gamma(\hat{p}) = \sqrt{2}(\hat{p}_x^2 - \hat{p}_y^2) = 1 + \cos(4\phi)$$

for d-wave pairing. The canonical momentum is defined by

$$\vec{\Pi} = \frac{\hbar}{\mathrm{i}}\left(\vec{\nabla} - \mathrm{i}\frac{2e}{\hbar c}\vec{A}\right).$$

The magnetic field $\vec{H}$ is assumed to lie in the yz-plane, with $H_y = H_\parallel = H \sin\Theta$ and $H_z = H_\perp = H\cos\Theta$. We use the following gauge for the vector potential: $A_x = H_\parallel z - H_\perp y$ and $A_y = A_z = 0$. Paramagnetic pair breaking enters via the term $\mu_0 H$ in (1); the electron's magnetic moment is $\mu_0 = -g_L\mu_B/2$, with the Landé factor $g_L \approx 2$ and the Bohr magneton $\mu_B = \hbar e/(2mc)$. The method of reducing equation (1) to a set of algebraic equations follows exactly reference [6] and need not be repeated here. As a first check of our numerical method we compared our results with reference [6] and found complete agreement whenever the same set of input parameters was used.

Let us proceed to a comparison of the solutions H_C of equation (1) with the H_{c2}-data reported in reference [3]. The first point to address is the independence of H_{c2} on the azimuthal angle ϕ. Such a dependence may easily be incorporated in the present model by replacing $\vec{v}_F'$ in (1) by $v_F\left[\vec{e}_x\cos(\phi'+\phi) + \vec{e}_y\sin(\phi'+\phi)\right]$. As long as orbital pair breaking is present for a parallel field component, the symmetry-breaking term $A_x = H_\parallel z$ has to be kept in (1). If, on the other hand, complete decoupling of the (infinitely thin) conducting planes can be assumed, the term $H_\parallel z$ can be dropped and H_C becomes independent of ϕ, as can be explicitly confirmed numerically. In this context, we recall that a three-dimensional d-wave superconductor shows anisotropy of the upper critical field [8]. Thus, the observed independence of H_{c2} on ϕ is in agreement with the present model and, in particular, with the assumption of quasi-two-dimensional superconductivity.

If T is measured in units of T_c and H in units of $\mu\Delta_0$ (where Δ_0 is the BCS gap at $T = 0$), the present model requires only one single parameter k_BT_c/E_F to be fitted. This parameter is proportional to the 'bulk' ratio of the orbital and spin critical fields $\hbar c/(2e\xi_0^2)$ and k_BT_c/μ_0 respectively. In the present anisotropic model the actual ratio of spin and orbital pair breaking depends on Θ and may be written in the form $k_BT_c/(E_F\cos\Theta)$. The best fit to the Θ-dependence of H_{c2} at $T = 1.45$ K (see figure 4 of reference [3]) has been obtained for $k_BT_c/E_F = 0.058$. This value of k_BT_c/E_F is consistent with a critical temperature $T_c = 10.4$ K of the sample studied in reference [3], and a Fermi energy of the order of 100 K as estimated from several experiments [9]. Using this value we found very good agreement between H_C and the data of reference [3], as shown in figure 1. The theoretical curves in figure 1 have been calculated assuming d-wave symmetry; the difference between d-wave and s-wave results was found to be small except very close to $T = 0$ K and $\Theta = 90°$.

The H_{c2}-data show a small but clearly visible kink near the plane-parallel orientation, at $\Theta \approx 87°$. A similar feature is also found in the theoretical phase boundary $H_C(\Theta)$, as shown in figure 1 (where the square of the critical fields has been plotted in order to make this discontinuous change in slope more visible). This kink indicates the transition from the vortex state, with $n = 0$, to the first of the above-mentioned FFLO precursor states, with $n = 1$. Still closer to $\Theta \approx 90°$, equation (1) yields additional transitions corresponding to $n = 2, 3$, which are still visible in figure 1 in the theoretical curve but not in the data points. The H_C-curves describing the $n = 0, 1, 2$ transitions, for the same material but higher T, are shown on a larger scale in figure 2. The order parameter structure of the precursor phases, where pairing takes place in Landau levels n with $n > 0$, has been investigated recently for s-wave superconductors [7]. Two types of such precursor states have been found:

(i) quasi-one-dimensional states, which may be considered as mixtures of rows of vortices and one-dimensional FFLO-type oscillations; and

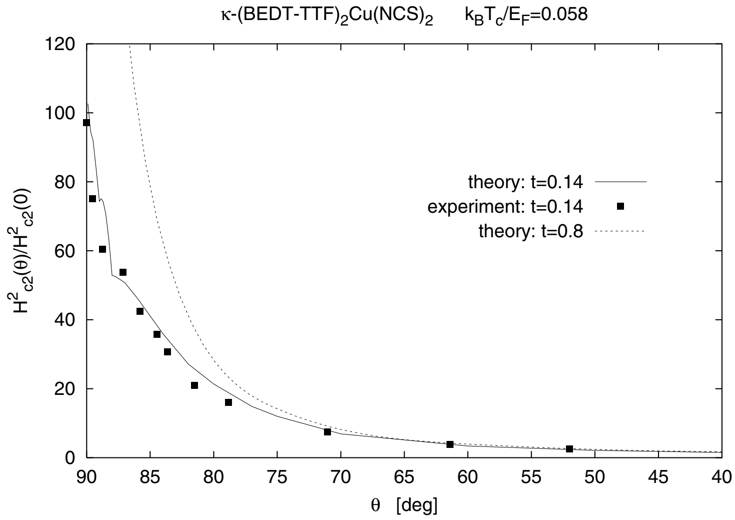

Figure 1. The square of the upper critical field, normalized to its value at $\Theta = 0$, as a function of Θ. Full squares: data from reference [3] at $t = T/T_c = 0.14$. Full line: the theoretical result for the Bulaevskii–Shimahara–Rainer phase boundary for $t = 0.14$. Dashed line: the theoretical result for $t = 0.8$.

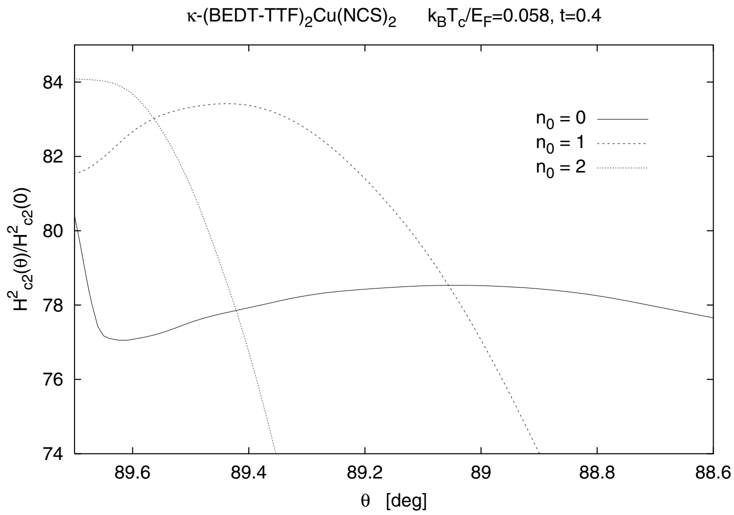

Figure 2. The branches $n_0 = 0, 1, 2$ of the upper critical field, as calculated from equation (1), are plotted in more detail, using the same value of $k_B T_C/E_F$ as in figure 1 but a higher temperature $t = 0.4$.

(ii) two-dimensional lattices with several zeros of the order parameter with different vorticity [7].

Such unusual states (of type (ii)) have been predicted to occur in the extremely high-field region where quantization of single-electron levels becomes important [10]. The present arrangement might provide a relatively feasible way of observing such vortex structures. It should be mentioned, however, that for d-wave superconductors neither the equilibrium structure of the FFLO state nor that of the $n > 0$ states has been calculated so far.

The shape of the $H_C(\Theta)$ curve depends distinctively on temperature, as shown by the plot (dashed line) of $H_C(\Theta)^2$ at $t = 0.8$ in figure 1. The reason for the enhancement at higher T is, of course, that paramagnetic pair breaking becomes less effective at higher temperature. Data at higher T have not been reported in reference [3] but would be useful for checking the present interpretation. Looking for similar measurements, we found old data given by Morris and Coleman [11] for intercalated transition metal dichalcogenide TaS_2-(pyridine) samples. In this material, which represents a nearly perfect realization of two-dimensional superconductivity, an unexplained anomaly with regard to the behaviour of the upper critical field at different T has been reported (figure 10 of reference [11]). We find excellent agreement (see figure 3) comparing the data of reference [11] with the solutions of equation (1) for an s-wave superconductor. Again, a single parameter has been adjusted ($k_B T_c/E_F = 0.024$) to obtain both of the theoretical curves shown in figure 3. The resistance data reported in reference [11] show a non-monotonic behaviour near the plane-parallel field orientation (see figure 3 of reference [11]), which may be due to transitions to the $n > 0$ states. The latter states are discussed in more detail in reference [7].

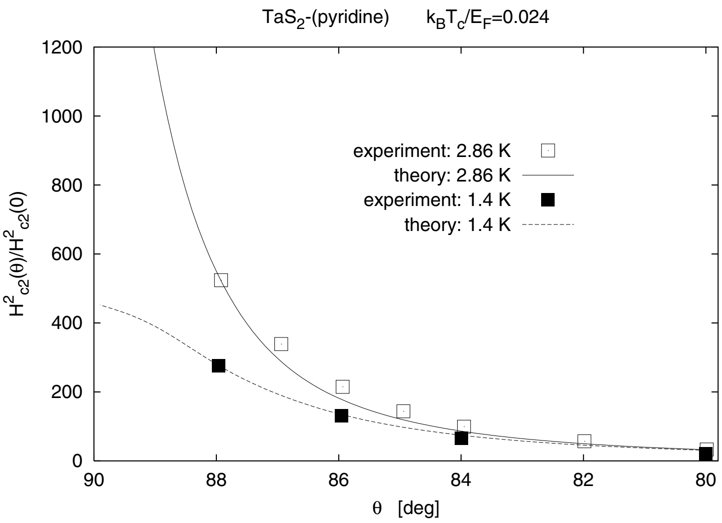

Figure 3. Comparison of the Θ-dependence of the upper critical field of TaS_2-(pyridine), as reported in reference [11], with the solutions of equation (1) for s-wave superconductivity at $t = 2.86$ and $t = 1.4$.

Finally, let us compare the measured temperature dependence of H_{c2} for the plane-parallel field orientation (figure 3 of reference [3]) with $H_C(\pi/2, T)$. According to our interpretation of these data, the states below $H_{c2}(\pi/2, T)$ should be a d-wave version of the FFLO state for $T < T^* \cong 0.4\ T_c$, and the homogeneous superconducting state for $T > T^*$. This phase boundary was first calculated by Maki and Won [4]. The Shimahara–Rainer d-wave phase boundary must agree with reference [4] in the limit $\Theta \to \pi/2$. We found agreement, except for the steep rise of $H_C(\pi/2, T)$ below $0.05T_c$ reported in reference [4] (a possible reason for this discrepancy is the slow convergence of our numerical method for low T and high n). The comparison between theory [4] and experiment [3] depicted in figure 4 shows again fairly good agreement. A characteristic difference between the temperature variations above and below T^* is visible in the data points, although it is less pronounced than in the theoretical curve. The difference in critical field between the s-wave and d-wave cases is again rather small; at $T = 0.05\ T_c$, the lowest temperature for which measurements for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

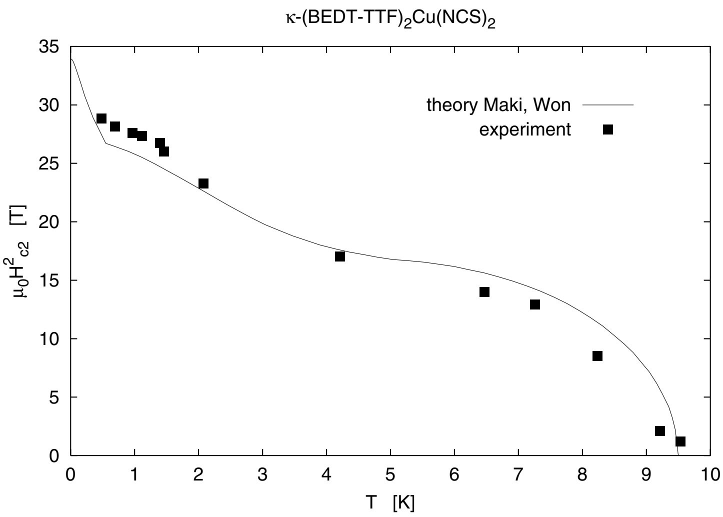

Figure 4. Comparison of the temperature dependence of the plane-parallel upper critical field reported in reference [3] with the theoretical result reported in reference [4].

have been reported [3], both are approximately given by the standard 2D result [12] for the FFLO state, $\mu_0 H_C = \Delta_0$, which exceeds the Pauli limiting field by $\cong$40%. Thus, these numbers do also fit well into the FFLO interpretation of the phase boundary for plane-parallel field orientation.

Summarizing, the proposal of Nam *et al* [3], that upper-critical-field data for a plane-parallel field orientation in the layered organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ should be interpreted in terms of a FFLO state, has been supported by our calculations. The data agree with the predictions of a model of a quasi-two-dimensional superconductor as regards both the angular and the temperature dependence of the critical field. Further confirmation of this interpretation could be obtained by means of measurements at higher temperatures, where paramagnetic pair breaking is strongly reduced. If this interpretation is correct, precursor states with interesting properties should appear for applied fields close to the plane-parallel orientation.

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