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Determination of gap symmetry from angle-dependent H_{c2} measurements on $CeCu_2Si_2$

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The tetragonal heavy-fermion compound $CeCu_2Si_2$ exhibits a superconducting ground state (S type, $T_c = 0.67$ K) close to a magnetic instability. Here, we present angle-resolved resistivity measurements of the upper critical field H_{c2}. In-plane rotation of S-type $CeCu_2Si_2$ single crystals reveals a four-fold oscillation of H_{c2}. An extended weak-coupling BCS model for a d-wave symmetry including strong Pauli-limiting effects confirms the aforementioned angular dependence and points towards d_{xy} symmetry of the order parameter.

Unconventional superconductivity has been discovered in a number of systems whose magnetic ordering is suppressed to a magnetic instability at $T_N = 0$ K. Magnetic fluctuations are speculated to mediate the Cooper-pair formation for such superconductors [1]. $CeCu_2Si_2$ is one of the few stoichiometric compounds which exhibits superconductivity at ambient pressure in the vicinity of a magnetic instability [2]. However, the nature of its unconventional superconducting state remains still unraveled. The difficulties controlling the ground-state properties of $CeCu_2Si_2$ first prevented a systematic investigation of the superconducting phase [3]. Nowadays, large homogeneous single crystals with superconducting (S type), magnetically ordered (A type) and competing magnetic and superconducting phases (A/S type) are produced by slightly varying the Cu-to-Si ratio [2].

Recent neutron-diffraction experiments have shown that the magnetic A phase is formed due to strong nesting of the renormalized Fermi surface [4]. The nature of the long-range antiferromagnetic (AF) order was then determined as an incommensurate spin-density wave with small magnetic moment. Nearly stoichiometric A/S-type $CeCu_2Si_2$ lies close to an AF quantum critical point (QCP), at which the magnetic order is continuously suppressed to $T_N = 0$ K. The physical properties are well described within the spin-density-wave scenario with three-dimensional magnetic fluctuations [5]. Inelastic-neutron-scattering (INS) characterization of S-type $CeCu_2Si_2$ samples points towards a weak-coupling d-wave superconducting state [6]. Further theoretical analysis of such neutron-scattering data suggested a $d_{x^2-y^2}$ state symmetry [7]. Measurements of the NQR-relaxation rate [8, 9] and specific heat under pressure [10] have proven to be consistent with a d-wave pairing state, and even though indirect proof of $d_{x^2-y^2}$ symmetry has been deduced, the symmetry of the superconducting order parameter has not yet been unambiguously determined.

A variety of angle-resolved techniques have been successfully applied to determine the symmetry of the order parameter [11, 12]. For instance, angle-dependent resistivity measurements have helped to shed light onto the nature of the superconducting order parameter in heavy-fermion superconductors such as $CeCoIn_5$ (Ref. 13) and Sr_2RuO_4 (Ref. 14). Earlier angle-resolved studies of the upper critical field (H_{c2}) on $CeCu_2Si_2$ samples which showed pressure-induced superconductivity, pointed either towards a nodal line or fully-gapped superconductivity [15]. They remained inconclusive due to sample dependences and limited experimental resolution.

Here, we present resistive measurements of H_{c2} on high-quality single-crystalline S-type $CeCu_2Si_2$ samples upon rotation within the basal tetragonal plane. We compare the results to a weak-coupling BCS model for a d-wave superconductor, which takes into account Fermi-surface anisotropies as well as the strong Pauli-limiting effect present in $CeCu_2Si_2$ [16]. The model predicts a four-fold modulation of H_{c2} which is in good agreement with our experimental results, but with an unexpected finding of d_{xy} order-parameter symmetry.

A Cu self-flux approach combined with a Bridgman cooling technique has been used to grow single crystals in Al_2O_3 crucibles [17]. The obtained samples are thoroughly characterized via wavelength-dispersive X-ray spectroscopy (WDX) revealing a slightly enhanced Cu-to-Si ratio, which is characteristic of an S-type crystal. A plate-like sample ($\sim$3 mm $\times$ 1 mm $\times$ 0.2 mm) has been carefully oriented by using Laue diffraction. A state-of-the-art uniaxial rotor has been adapted to a dilution refrigerator, allowing an external magnetic field $\boldsymbol{B}$ to be used as a directional probe. An optical measuring system detects angular steps as small as 0.001° and allows free rotation from 0 to 180°. The single crystal is thermally and mechanically coupled onto a silver sample holder which remains fixed upon rotation of the magnetic field. The position of the sample holder with respect to the external field has been carefully determined with the aid of a Hall sensor. A low-frequency, four-point ac technique is used in order to measure the electrical resistivity, where low-temperature transformers are employed to enhance the signal-to-noise ratio. Electrical contacts were made of silver paint, allowing the current $\boldsymbol{j}$ to flow along the [100] direction. Upon rotation, both current and magnetic field remain within the basal plane.

Resistivity measurements as a function of field and temperature for $CeCu_2Si_2$ are shown in the insets of Fig. 1. The jump in $\rho(H,T)$ indicates the onset of superconductivity which shifts to lower T as the magnetic field is increased. Sharp transitions into the normal state indicate good crystal quality. H_{c2} has been estimated as the 50% value of the superconducting transition. The resulting $H - T$ phase diagram constructed from such field- and temperature-dependent resistivity measurements for the case $\boldsymbol{B} \| [100]$ is shown in Fig. 1(a). The obtained $T_c = 0.67$ K and $H_{c2} = 1.96$ T are in good agreement with previous studies on $CeCu_2Si_2$ single crystals [16].

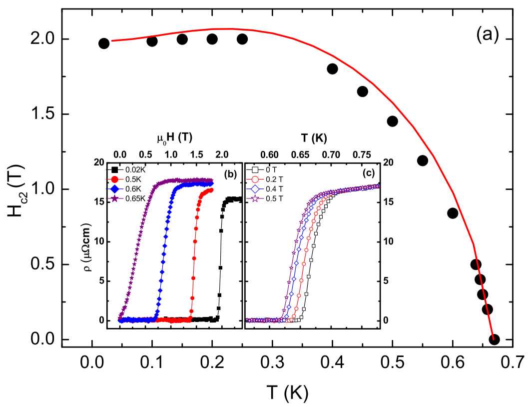

FIG. 1: a) $H-T$ phase diagram for $CeCu_2Si_2$. The solid red curve indicates the theoretical calculation for a d-wave symmetry (see text). Note the non-monotonicity of H_{c2} at lower temperatures, both in the data and the fit, due to the Pauli limiting effect [16]. Resistivity ρ as a function of magnetic field H (b) and temperature T (c) for S-type $CeCu_2Si_2$ from which the $H-T$ diagram was obtained.

Figure 2 shows the electrical resistivity of S-type $CeCu_2Si_2$ as a function of magnetic field, at constant temperature (40 mK) and for different field orientations. Here, θ represents the angle between $\boldsymbol{B}$ and the [100] direction (see sketch).

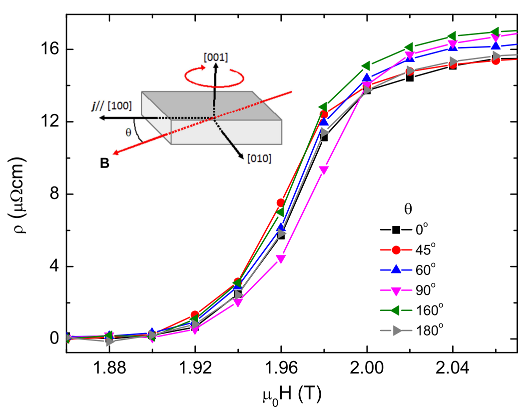

FIG. 2: Resistivity ρ as a function of field H for different angles at 40 mK. Here θ is the angle between the magnetic field and the crystalline a-axis.

A 2π-period component due to a 5° out-of-plane misalignment has been determined as our experimental error. In figure 3 the angular dependence of H_{c2} is displayed after subtracting the aforementioned misalignment. $H_{c2}(\theta)$ exhibits a small variation (∼0.6%) upon rotation. A clear four-fold symmetry with local minima around 45° and 135° is detected.

By choosing the aforementioned geometry (sketch Fig. 2), where the external field $\boldsymbol{B}$ is always perpendicular to the sample's smallest dimension [001], demagnetization effects are considerably reduced. The angle dependence for such a shape anisotropy is known to behave as $cos^2\theta/(1-D_a) + sin^2\theta/(1-D_b)$, where D_a and D_b are the demagnetization factors along the [100] and [010] directions, respectively (e. g. Ref. 18). Such angle variation neither mimics nor masks our experimental observation, which in turn is only consistent with the anticipated gap symmetry of an unconventional d-wave superconductor and disagrees with a fully gapped s-wave superconductor.

The upper critical field as a tool to access the symmetry of the superconducting order parameter has been extensively discussed. In particular, it is possible to derive the angular dependence of H_{c2} for an unconventional superconductor within the framework of the weak-coupling BCS theory by assuming, for instance, d-wave symmetry [19, 20].
Following Luk'yanchuk and Mineev's approach [21], the order parameter for the vortex state can be expanded as:

$$|\Psi\rangle = \cos(2\phi)\left[1 + C\left(a^{\dagger}\right)^{2}\right]|0\rangle\,, \tag{1}$$

where $|0\rangle$ is the Abrikosov state for an s-wave superconductor [22], $a^{\dagger}$ is the raising operator of the Landau wave function, and C the corresponding admixture parameter of the Landau levels. A quasi-2D cylindrical Fermi surface for a clean-limit superconductor with strong Pauli limiting has been assumed, for which a $d_{x^2-y^2}$ order parameter has been taken as a first *ansatz*. The angular dependence of the upper critical field is

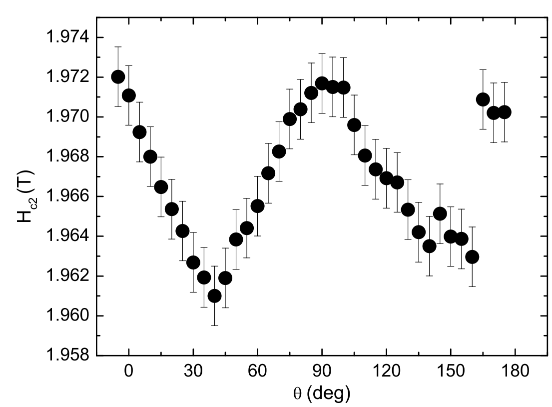

FIG. 3: Angular dependence of the upper critical field H_{c2} at 40 mK after subtraction of a 5°-misalignment component

then determined from the linearized gap equation:

$$-\ln t = \int_0^\infty \frac{du}{\sinh hu}\left\{1 - \left\langle[1+\cos(4\theta_0)cos(4\theta)]e^{-pu^2|s|^2}\cos(hu)[1+2Cpu^2s^2]\right\rangle\right\} \tag{2}$$

$$-C\ln t = \int_0^\infty \frac{du}{\sin hu}\left\{C - \left\langle[1+\cos(4\theta_0)\cos(4\theta)]e^{-pu^2|s|^2}\cos(hu)[pu^2s^2 + C(1-4pu^2\mid s\mid^2 + 2p^2u^4\mid s\mid^4)]\right\rangle\right\}, \quad (3)$$

where $t \equiv T/T_c$, $h \equiv (g\mu_B H)/(2\pi T)$, $s = \sin\chi + i\sin\theta$, and $p \equiv (v_a v_c eH)/(8\pi^2 T^2)$. Here, v_a (v_c) are the components of the Fermi velocity within (perpendicular to) the basal plane. θ_0 is the angle of the magnetic field with respect to the antinodal direction, θ the angle between v_a and the antinodal direction, $\chi = ck_z$, and $\langle ... \rangle$ is the average over θ and χ.
Both the Fermi velocity and the gyromagnetic ratio g can be used as fitting parameters. For the case of a d-wave state, only the $N = 0$ and $N = 2$ levels are allowed, based on symmetry arguments [19]. By solving Eqs. (2) and (3) with the constraint for a unique solution, the admixture of the Landau levels (represented by C) and the angular dependence $H_{c2}(\theta)$ are calculated.

Volovik and Gor'kov have shown that for a tetragonal structure as $CeCu_2Si_2$, both singlet and triplet phases are possible [23]. It has been already discussed that the enhanced Pauli susceptibility in heavy-fermion compounds leads to strong Pauli limiting of the superconducting state [24]. In the case of $CeCu_2Si_2$, Pauli paramagnetism basically excludes triplet states [25]. An estimation of the orbital critical field is obtained via $H_{c2}^{\rm orb} = 0.746\, T_c \left|\frac{dH}{dT}\right|_{T_c} = 8.3$ T, where the large slope $\left|\frac{dH}{dT}\right|_{T_c} = 17$ T/K is a signature of the heavy quasiparticles involved in the superconducting state [16, 25]. In turn, the Pauli limiting field [26] $H_{c2}^{\rm Pauli} = 2.25 T_c = 1.5$ T is closer to the measured value of H_{c2}.
The superconducting coherence length has been estimated from $H_{c2}^{\rm orb} = \frac{\phi_0}{2\pi\xi_0^2}$ as $\xi_0 \approx 60$ Å. From $\xi_0 = 0.18\frac{\hbar v_F}{k_B}T_c$, $m^* = \frac{\hbar k_F}{v_F}$ and assuming $k_F = 10^{10}$ m, we obtain $v_F \approx 2923$ m/s and $m^* \approx 396 m_e$, both in agreement with previous studies of the upper critical field [25]. Following the same approach as Orlando et al. [27], the electronic mean free path can be estimated from $\ell = \frac{1.00965*10^{-12}}{\rho\xi_0\gamma_N T_c}$[cm]. Specific heat measurements on the same sample (not shown) reveal a normal-state Sommerfeld coefficient $\gamma_N = 0.726$ J/mol K^2 at T_c. Using the aforementioned parameters, the mean free path yields $\ell \approx 100$ Å. Consequently, $CeCu_2Si_2$ can be considered a clean-limit superconductor ($\ell > \xi_0$). The ratio $\frac{\Delta C}{\gamma_N T_c} = 1.43$ denotes the weak-coupling limit for an s-wave BCS superconductor, but this ratio is smaller for anisotropic, nodal superconductors. In the case of $CeCu_2Si_2$, $\frac{\Delta C}{\gamma_N T_c} = 1.16$, in fair agreement with the prediction of 0.95 for a two-dimensional weak-coupling d-wave superconductor [28] . It is therefore reasonable to assume that $CeCu_2Si_2$ lies within the weak-coupling regime.
Our model based on a d-wave character can be already applied for the case θ_0=0 (antinodal direction) as a function of temperature, as shown in Fig. 1a (solid curve). Our calculation gives a very reasonable description of the $H - T$ phase diagram in the whole temperature range, where only the product $v_a v_c$ and g were used as free parameters (see below). Strong Pauli paramagnetism is mainly responsible for the weakening of the superconducting state at lower temperatures. A decrease of the upper critical field for $T < 0.2$ K has been observed as a signature of the enhanced Pauli susceptibility [16]. It is worth mentioning that such non-monotonicity of H_{c2} at lower temperatures is recovered by our model. This is a direct result of the comparatively large value (1.06) of g required to fit the data. In the calculations, the Fermi velocity term $v_a v_c$ is generally determined by the slope of H_{c2} near T_c (where the Pauli limiting is of no importance), while g is chosen to match the value of H_{c2} as $T \to 0$. If a significantly smaller g, such as 0.7, is employed the non-monotonicity disappears, and it becomes impossible to fit the data both near T_c and at low temperature.

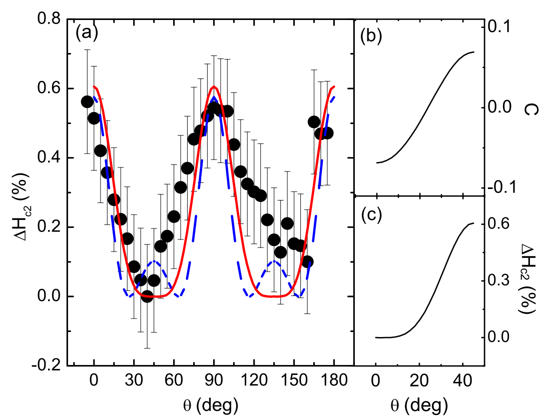

FIG. 4: a) In-plane angular dependence of H_{c2} normalized with respect to the upper critical field along [110]. The theoretical model for a d_{xy} wave superconductor at 100 mK is presented with (solid red curve) and without Fermi velocity anisotropy (dashed blue curve). The four-fold modulation and the amplitude of the oscillation is well reproduced by the calculation. b) The admixing parameter C as a function of θ (anisotropic case). c) In-plane angular dependence of H_{c2} when assuming a $d_{x^2-y^2}$ symmetry (anisotropic case). Note the 45° shift compared to the experimental data

The numerical calculation in the whole angular range is plotted in Figure 4a together with the experimental data. Two different calculations are depicted: one including the effects of Fermi velocity anisotropy across the entire three dimensional Fermi surfaces as given in the tight-binding fit of Ref. 7 (solid red curve); and one without this (dashed blue curve). As observed, when no anisotropy is included a fair agreement between theory and experiment is reached, where both four-fold oscillations show an amplitude of 0.6% of the total value of H_{c2}. Including the effect of Fermi velocity anisotropy improves the fit substantially, with the local maximum around $\theta_0 = 45^o$ removed. Quantitatively we find that a Fermi velocity anisotropy of the form $v(\theta, \chi) = v_0(1 - 0.57 \sin(2\theta) \cos(\chi/2))$ provides a reasonable fit to the tight-binding calculation (which is itself an approximation); a somewhat smaller anisotropy ($0.57 \rightarrow 0.43$) fits the tight-binding fit somewhat better but produces a larger (0.9%) H_{c2} angular modulation. With this caveat, we note that unlike the previous work [13], here the magnitude of the angular dependence of H_{c2} is quantitatively reproduced without any adjustable parameters (such as a θ_0-dependent g), as the fitting parameters g and $v_a v_c$ were chosen uniquely to reproduce the temperature dependence from $T = 0$ K to $T = T_c$; the angular dependence is determined only by these parameters and the anisotropy.

The admixing parameter C is shown in Fig. 4(b). A monotonic increase as a function of angle is observed, as well as a sign change around 23°. The original calculation for the $d_{x^2-y^2}$ symmetry *ansatz* (i.e. antinodal direction along the a axis) is presented in Fig. 4(c). It can be seen that the position of the maximum and minimum with respect to the experimental data are shifted by 45°. This strongly suggests that the order parameter present in $CeCu_2Si_2$ has a d_{xy} rather than $d_{x^2-y^2}$ character. The unusual result of the calculation that H_{c2} is *largest* for the field along the *nodal* direction (i.e., the a-axis for d_{xy} symmetry) is a direct result of the strong Pauli limiting; in the earlier work [13, 29] a smaller g was used resulting in the conventional H_{c2} maximum for the field along the antinodal direction. We note in passing that unlike the earlier d-wave model calculations for $CeCoIn_5$ [13], here no assumption of an FFLO [30, 31] state has been made, as there is no evidence for such a state in $CeCu_2Si_2$.

Our main result - that the H_{c2} data point towards d_{xy} symmetry - is generally at odds with the result of Ref. 7, where $d_{x^2-y^2}$ symmetry was inferred from the existence of a "sharp resonance" in the INS data [6, 32], that is, as a result of the implied sign change in the order parameter over the spin-density-wave ordering wave vector connecting large portions of the renormalized Fermi surface. However, such a sharp resonance occurs in response to the superconducting state in predominantly *two-dimensional* superconductors and is, therefore not expected for the (anisotropic) *three-dimensional* superconductor $CeCu_2Si_2$. Instead of a *sharp* resonance, the INS spectra of S-type $CeCu_2Si_2$ below T_c show a spin-excitation gap forming out of a *broad* magnetic response, which extends to more than ten times the gap energy [32]. The opening of the spin gap results in a shifting of spectral weight from below to above the gap energy such that, below T_c, an inelastic line occurs above the gap edge. With this in mind, we suggest that the attribution of the inelastic line in the INS spectra uniquely to a $d_{x^2-y^2}$ state is premature.

To conclude, in this work we have shown that the upper critical field H_{c2} of the heavy-fermion superconductor $CeCu_2Si_2$ can be described by the anisotropic weak coupling theory as formulated by Luk'yanchuk and Mineev, with the inclusion of strong Pauli limiting in the calculation. The calculation reproduces quantitatively the temperature dependence of H_{c2} within the basal plane; in particular the non-monotonicity of H_{c2} is well captured. Using as inputs from the temperature calculation the fitted values of the Fermi velocity and gyromagnetic ratio g, we find a good description of the angular-dependent data with no adjustable parameters, and ultimately a surprising conclusion: that the order parameter has d_{xy} symmetry.

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