New Superconducting Phases in Field-Induced Organic Superconductor λ-(BETS)$_2$FeCl$_4$

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We derive the parallel upper critical field, H_{c2}, as a function of the temperature T in quasi-2D organic compound λ-(BETS)$_2$FeCl$_4$, accounting for the formation of the nonuniform Larkin-Ovchinnikov-Fulde-Ferrell (LOFF) state. To further check the 2D LOFF model, we propose to study the $H_{c2}(T)$ curve at low T in tilted fields, where the vortex state is described by the high Landau level functions characterized by the index n. We predict a cascade of first-order transitions between vortex phases with different n, between phases with different types of the symmetry at given n and the change of the superconducting transition from the second order to the first order as FeCl$_4$ ions are replaced partly by GaCl$_4$ ions.

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Very recently, magnetic-field-induced superconductivity has been observed in the quasi-two-dimensional (2D) organic conductor λ-(BETS)$_2$FeCl$_4$ [where BETS stands for Bis(ethylenedithio)tetraselenafulvalene] [1]. At zero magnetic field, the antiferromagnetic ordering of Fe^{3+} moments in this compound gives rise to a metal-insulator transition at temperatures around 8 K. A magnetic field above 10 T restores the metal phase. A further increase of the magnetic field induces the superconducting transition at $B \approx 17$ T. As it has been revealed in the very high magnetic field experiments [2], the maximum critical temperature $T_c \approx 4$ K is reached at $B_0 \approx 33$ T and $T_c(B)$ drops to 2 K at $B = 42$ T. Such an unusual behavior was interpreted in Refs. [1,2] as a manifestation of the Jaccarino-Peter (JP) effect [3], when the exchange field of aligned Fe^{3+} spins compensates the external field in their combined effect on the electron spins. The JP compensation effect has already been proven to be responsible for the magnetic-field-induced superconductivity in pseudoternary Eu-Sn molybdenum chalcogenides [4] and in CePb$_3$ [5]. In contrast to λ-(BETS)$_2$FeCl$_4$, in Eu-Sn molybdenum chalcogenides the superconducting transition also exists in the absence of a magnetic field, and, as the magnetic field increases, it first destroys superconductivity, but further restores it in the range of fields 4 T $< B <$ 22 T at very low temperatures [4]. In CePb$_3$ in zero magnetic field, the heavy-fermion antiferromagnetic ground state was found [5]. Similarly to λ-(BETS)$_2$FeCl$_4$, the magnetic field destroys the antiferromagnetic ordering and induces superconductivity in fields higher than 14 T.

High-field superconductivity exists in all these compounds not only due to the JP effect, but also because of strong suppression of the orbital effect of the external field. In CePb$_3$ and Eu-Sn molybdenum chalcogenides, the orbital effect is weak due to a very short superconducting coherence length in the presence of impurities. In contrast, in the clean λ-(BETS)$_2$FeCl$_4$ superconductor, strong quasi-2D anisotropy leads to a negligible orbital effect for the field applied parallel to the layers. Here the parallel upper critical field is controlled by the spin effect only. Then the temperature dependence of H_{c2} may be well described by the quasi-2D (Josephson-coupled-layers) BCS model [6]. In this model at low temperatures $T < 0.55T_c$, the Larkin-Ovchinnikov-Fulde-Ferrell (LOFF) state is a correct superconducting phase [7,8]. We note that previous attempts to identify unambiguously the LOFF state were unsuccessful because in 3D crystals the orbital effect dominates over the spin effect, while quasi-2D systems, such as intercalated dichalcogenides, were not clean enough to allow for the LOFF state. The very clean 2D organic crystal λ-(BETS)$_2$FeCl$_4$ with clear evidence for dominant spin effect is the most favorable system to detect the LOFF state unambiguously.

In this Letter, we use a 2D LOFF model for the clean superconductor λ-(BETS)$_2$FeCl$_4$ to calculate the $H_{c2}(T)$ curve for the orientation of the magnetic field parallel to the layers, accounting for the exchange field induced by Fe^{3+} polarized magnetic moments. We show that accounting for the 2D LOFF state improves fitting at low temperatures in comparison with the 3D model as was also discussed in Ref. [2]. In addition to the results [2], we calculate H_{c2} for the magnetic fields tilted by angle θ with respect to the layers. We show that a quasiperiodiclike angular dependence of H_{c2} is a specific property of the vortex state, which originates from the 2D LOFF phase when the orbital effect, caused by the perpendicular component of the external field, is turned on as θ increases. This vortex structure is characterized by the discrete variable n, the Landau level index. Changes of n with θ lead to a cascade of first-order transitions of the vortex lattice. We argue also that partial replacement of FeCl$_4$ ions by nonmagnetic GaCl$_4$ ions should lead to the suppression of the LOFF state and to the first-order normal-to-superconducting (N-S) transition.

We consider first the $H_{c2}(T)$ curve for the parallel orientation of the external field. The total effective field acting on the electron spins is $H_{\rm eff} = B - I\langle S\rangle/\mu$, where $\mu \approx \mu_B$ is the electron magnetic moment, and I is the exchange integral for the interaction between the conduction electrons and Fe^{3+} magnetic moments. The negative sign implies the JP compensation effect. In the whole (B, T) region, where the field-induced superconductivity exists in λ-(BETS)$_2$FeCl$_4$, the Fe^{3+} moments are saturated, $\langle S \rangle = S_0$. The maximum $T_c(H)$ corresponds to $H_{\text{eff}} = 0$. Hence, the effective field acting on spins is simply $H_{\text{eff}} = B - B_0$, where $B_0 = IS_0/\mu$. The upper critical field is given by the solution of the linearized equation for the superconducting order parameter $\Delta(\mathbf{r})$, where $\mathbf{r} = (x, y)$ is the in-plane coordinate:

$$\Delta(\mathbf{r}) = \int K_0(\mathbf{r} - \mathbf{r}')\Delta(\mathbf{r}')\, d\mathbf{r}'. \tag{1}$$

For the nonuniform order parameter, $\Delta(\mathbf{r}) = \Delta \exp(i\mathbf{q} \cdot \mathbf{r})$, the kernel $K_0(\mathbf{r} - \mathbf{r}')$ takes the form [6,9]

$$K_0(\mathbf{q}) = 2\pi|\lambda|T \,\mathrm{Re} \sum_{\omega>0} \oint \frac{[2\pi|\mathbf{v}_F(l)|]^{-1}\, dl}{\omega + i\mu H_{\text{eff}} + i\mathbf{v}_F(l)\mathbf{q}/2}, \tag{2}$$

where ω denotes the Matsubara's frequencies, λ is the coupling parameter, the line integral over the coordinate l is along the 2D Fermi surface in the momentum space, and $\mathbf{v}_F(l)$ is the in-plane Fermi velocity.

As has been demonstrated by Larkin, Ovchinnikov, Fulde, and Ferrell [7], in magnetic fields above some critical value, the modulated superconducting phase with nonzero q gives higher T_c for singlet pairing. A uniform superconducting order parameter in the presence of uniform Zeeman splitting is unfavorable because electrons with opposite spins and momenta have different energies $\epsilon(k) \pm \mu H$, where $\epsilon(k)$ is the electron kinetic energy. Meanwhile, the Cooper instability towards formation of superconducting pairs is strongest when the energies of electrons in a pair are close to each other. Hence, pairing of electrons with momenta $\mathbf{k} \pm \mathbf{q}$ at $q \approx \mu H_{\text{eff}}/v_F$ and opposite spins is more favorable than at $q = 0$, because energies $\epsilon(\mathbf{k} + \mathbf{q}) - \epsilon_F - \mu H_{\text{eff}}$ and $\epsilon(\mathbf{k} - \mathbf{q}) - \epsilon_F + \mu H_{\text{eff}}$ are closer. Obviously, gain in the superconducting energy depends on the dimensionality of the electron motion. In a quasi–1D system, one can compensate Zeeman splitting almost completely, while in the 2D case compensation is only partial due to different orientations of the Fermi velocity; and in 3D crystals compensation is even less effective. Hence, H_{c2} is very sensitive to the geometry of the in-plane Fermi surface (FS).

In the following, we consider an isotropic in-plane electron spectrum and also the anisotropic one defined as

$$\epsilon(\mathbf{p}) = W(\cos p_x + \Gamma \cos p_y), \qquad \epsilon_F = 0, \tag{3}$$

where the parameter $\Gamma \leq 1$ accounts for the in-plane anisotropy. $T_c(B)$ for such a nonuniform state is defined by the equation $K(\mathbf{q}, B, T) = 1$. The wave vector $\mathbf{q}$ at the transition from the normal state to the LOFF state is that which gives a maximal H_{c2} at a given T. It depends on the v_F value, but H_{c2} does not. The corresponding $H_{c2}(T) = B_0 \pm H_{\text{eff}}$ curves for the 3D spherical FS, 2D circular FS and for the spectrum given by Eq. (3) at $\Gamma = 0.7$, calculated for $T_c = 4.3$ K, are shown in Fig. 1 together with the experimental data [2].

The common part of the $B_{c2}(T)$ curves corresponding to the transition into the uniform state is presented by the thin solid line. To give insight into the importance of the in-plane anisotropy, we calculate the critical value of $h = 2\mu H_{\text{eff}}/\Delta_0$ at $T = 0$ as a function of Γ. Here $\Delta_0 = 1.76T_c$ is the superconducting gap at $T = 0$. The upper critical value of h is given by the equation

$$\int_0^{\pi/2} du \frac{\ln|h^2 - q_x^2(1 - \Gamma^2 \cos^2 u)|}{\sqrt{1 - \Gamma^2 \cos^2 u}} = 0. \tag{4}$$

At $\Gamma = 0.7$, we obtain the upper critical value $h_{\text{cr}} = 2.64$ corresponding to $\mu H_{\text{eff}} = 1.32\Delta_0$. For comparison, we obtain $h_{\text{cr}} = 2$, corresponding to $\mu H_{\text{eff}} = \Delta_0$, in the case of a circular FS. In this approach, $h_{\text{cr}}(\Gamma)$ increases without saturation as Γ decreases.

To check whether the LOFF state is indeed realized in λ-(BETS)$_2$FeCl$_4$, a decisive experimental test is needed. Here we propose that such a critical experiment may be the study of the dependence $H_{c2}(T)$ for tilted-toward-the-plane field orientation. The perpendicular component of the magnetic field suppresses pairing by the orbital mechanism and leads to the formation of the vortex state on the already nonuniform LOFF background caused by the spin effect. The interplay between the orbital and the spin effects gives rise to a very peculiar upper-critical-field behavior [8,9] resulting from the solutions with higher Landau level functions for the superconducting order parameter in the vortex state.

To derive the $H_{c2}(T)$ curve at tilting angles θ, we account for the effect of the vector potential describing the

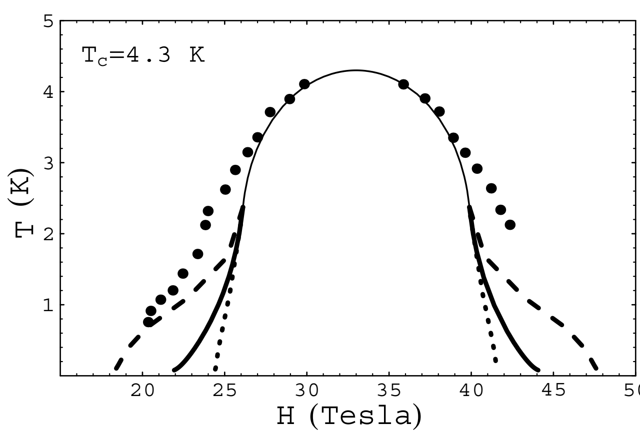

FIG. 1. The dependence of the critical temperature on the magnetic field parallel to the layers in the presence of the Jaccarino-Peter effect. The thin solid curve is the transition from the normal metal to the uniform superconducting state. The dotted (thick) line is the transition to the LOFF state in the isotropic 3D (2D) system, and the dashed line is for the in-plane anisotropic 2D system. Dots are experimental data obtained by resistivity measurements [2].

perpendicular component of the magnetic field, $\mathbf{B}_\perp$, in addition to the spin effect of $B_\parallel$ and of the exchange field. Now, in Eq. (1), the kernel is given as

$$K(\mathbf{r},\mathbf{r}') = K_0(\mathbf{r} - \mathbf{r}')\exp\left[2ie/\hbar c \int_{\mathbf{r}}^{\mathbf{r}'} \mathbf{A}(\mathbf{s})\, d\mathbf{s}\right], \quad (5)$$

for an isotropic 2D FS, and the in-plane vector potential is $\mathbf{A} = -(\mathbf{B}_\perp \times \mathbf{r})/2$, with $B_\perp = B\sin\theta$ [10]. Following Refs. [8,9], general solutions of the integral equation for the order parameter are the Landau level functions:

$$\Delta_n(\mathbf{r}) = \exp(-in\varphi - \rho^2/2)\rho^n, \quad (6)$$

where $\rho = r\sqrt{eB_\perp/\hbar c}$ and φ is the polar angle.

When the orbital effect dominates, it is the zero Landau level function which gives the solution corresponding to the highest magnetic critical field. However, if the spin effect is strong and the electron mean free path is much bigger than the superconducting correlation length (i.e., in the clean limit), the higher Landau level functions for a superconducting nucleation give higher H_{c2}, because they provide rapid spatial variations of the superconductor order parameter needed to compensate Zeeman splitting of electrons in a singlet pair. Discontinuous adjustments of the discrete variable n to the change of the angle θ give rise to unusual quasioscillatory angular and temperature dependence of H_{c2} (see Refs. [8,9]). The general expression for H_{c2} is given by the equation

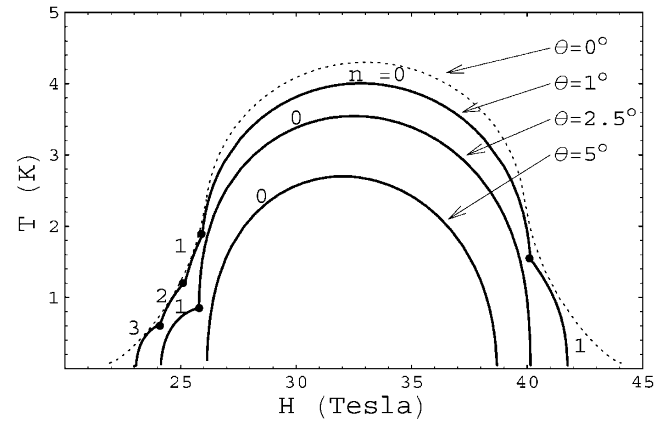

FIG. 2. The dependence of the upper critical magnetic field on T at different tilt angles θ for an isotropic 2D Fermi surface. Different parts of curves correspond to different Landau level functions characterized by the index n.

$$\ln(T/T_c) = \pi T \mathrm{Re} \sum_{\omega>0} \left\{ \int_0^\infty \frac{(-1)^n L_n(x)\exp(-x/2)\, dx}{[(\omega + i\mu H_{\mathrm{eff}})^2 + x v_F^2 eB_\perp/4\hbar c]^{1/2}} - \frac{2}{\omega} \right\}, \quad (7)$$

where $L_n(x)$ are the Laguerre polynomials. In Fig. 2 we show the expected behavior of H_{c2} for different tilting angles θ for the model with isotropic 2D FS. In these calculations, we take the value 5 T for the orbital magnetic critical field at $T = 0$ as was obtained for λ-$(BETS)_2GaCl_4$ with similar conducting layers [1]. The behavior of the system in the quasi-1D limit may be calculated in the same way based on the results of Ref. [11].

Next, we discuss the vortex lattice originating from the LOFF state due to the orbital effect of $\mathbf{B}_\perp$. Inside the superconducting phase, the order parameter must form a lattice, and without the spin effect it is a triangular Abrikosov vortex lattice made of $n = 0$ Landau level functions. In such a standard vortex lattice, the number of zeros of the superconducting order parameter coincides with number of quantized vortices; i.e., there is one zero per unit cell. However, for higher Landau level solutions, the number of zeros exceeds the number of quantized vortices determined by the component $B_\perp$, and only a fraction of the zeros coincides with the centers of quantized vortices. Respectively, zeros become inequivalent; they form a lattice determined by two length scales, the average distance between quantized vortices, $a = (\Phi_0/B_\perp)^{1/2}$, and the LOFF period determined by the effective field, $\ell = \hbar v_F/\mu H_{\mathrm{eff}}$. This leads to a large variety of exotic vortex lattices as has been predicted in Refs. [12,13].

To determine the equilibrium vortex structure we minimize the free energy. In Ref. [12], the generalized Ginzburg-Landau (GL) functional has been derived to describe the LOFF state near the tricritical point, $H_{\mathrm{eff}}^* = 1.07T_c/\mu$, $T^* = 0.55T_c$, for isotropic FS:

$$\frac{\mathcal{F}}{N(0)T_c^2} = 0.86\frac{B - H_{\mathrm{eff}}(T)}{H_{\mathrm{eff}}^*}|\Delta|^2 + 0.15\frac{T - T^*}{T^*}|\Delta|^4 + 0.011|\Delta|^6 + 3.0\frac{T - T^*}{T^*}\xi_0^2|\tilde{\nabla}\Delta|^2 + 3.1\xi_0^4|\tilde{\nabla}^2\Delta|^2$$
$$+ 0.85\xi_0^2\left\{|\Delta|^2|\tilde{\nabla}\Delta|^2 + \frac{1}{8}[(\Delta^*\tilde{\nabla}\Delta)^2 + (\Delta\tilde{\nabla}\Delta^*)^2]\right\}, \quad (8)$$

where $N(0)$ is the density of states at the Fermi level, $\tilde{\nabla} = \nabla - (2ie/\hbar c)\mathbf{A}$, and $\xi_0 = \hbar v_F/2\pi T_c$ is the superconducting correlation length. Note that we need to include in the functional the second-order derivative term $\sim|\tilde{\nabla}^2\Delta|^2$ due to the negative sign of the first-derivative term. Similarly, we add the sixth order term $\sim|\Delta|^6$ [14]. Strictly speaking, the derived functional is valid near the tricritical point only, but we may expect that it describes qualitatively correctly (as the standard GL functional) the LOFF state at all temperatures. Extending the analysis of the vortex lattice structure [15] to this new functional, one can calculate the structures of possible new vortex lattices. It turns out that the N-S transition becomes of the first order in some temperature and angle intervals [12],

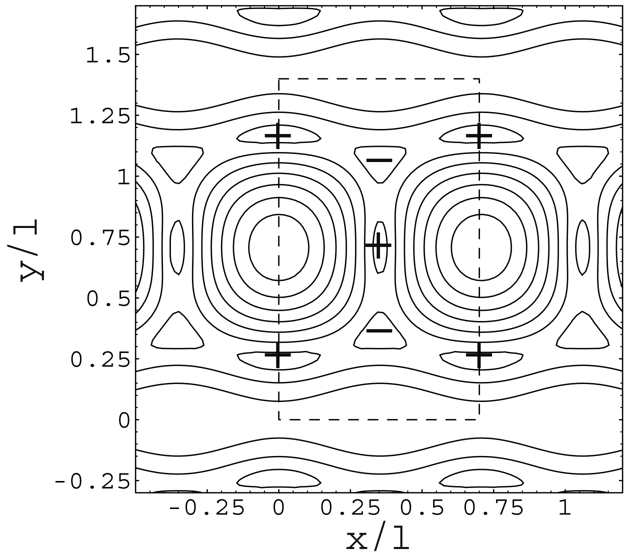

FIG. 3. Square asymmetric vortex lattice described by the Landau level functions $n = 2$ formed in the presence of orbital and spin effects. The profiles of the amplitude of the superconducting order parameter are shown. The dashed line represents the unit cell with five zeros. Their winding numbers, ± 1, are shown. There is one flux quantum per unit cell.

and the lattice structure exhibits zeros with positive and negative winding numbers w, $|w| \geq 1$, as well as strongly anisotropic structures. In Fig. 3, we present as an example the square asymmetric vortex lattice obtained numerically by use of the functional (8). It corresponds to the Landau level function $n = 2$ and have five zeros in the unit cell. Two of them have $w = -1$, while three have $w = +1$, so that there is one flux quantum per unit cell. Note that zeros are positioned inequivalently and that different types of symmetry in their positions as well as different indices n lead to a variety of vortex lattices and first-order phase transitions between them.

Let us discuss now the anticipated behavior of the system λ-$(BETS)_2(FeCl_4)_{1-x}(GaCl_4)_x$ using information [16] on $H_{c2}(T)$ at $x = 1$. Replacing the Fe^{3+} ion randomly by nonmagnetic Ga^{3+} reduces the average exchange field as $B_0(1 - x)$. Additionally, a random exchange field leads to electron scattering with rate of order $\mu B_0 x$. It causes suppression of the LOFF state at $x \approx 1/2$, when the scattering rate becomes comparable with Δ_0. Hence, as x increases, while remaining small, in Figs. 1 and 2 the curves $T(H)$ scale as $(1 - x)H$, while the thick lines and the dashed lines approach the dotted line due to the suppression of the LOFF state. At $x \approx 1/2$, we anticipate that due to strong exchange scattering the LOFF state vanishes, and the first-order superconducting transition takes place near the dotted line, at $H_{\mathrm{eff}} = \Delta_0/\mu\sqrt{2}$ at low T. Observation of the change of the transition type with x would confirm unambiguously existence of the LOFF state at $x = 0$. Interestingly, as x tends to unity, the system becomes clean again, and the LOFF state may reappear. In fact, at $x = 1$ the value of $H_{c2} \approx 14$ T at low T is close to that anticipated for the 2D LOFF state. We note that T_c increases slightly from 4.3 K at $x = 0$ to 5.5 K at $x = 1$. Additionally, anisotropy probably drops with x, but even at $x = 1$ the system remains close to 2D, because the interlayer correlation length is about the same as the interlayer spacing [16]. Hence, both effects do not change our qualitative predictions.

In conclusion, in λ-$(BETS)_2FeCl_4$ we anticipate first-order phase transitions between the superconducting phases corresponding to different higher Landau level states and between lattices with different symmetry. We anticipate also the change of the S-N transition from second order to first order as x approaches 1/2 in the system λ-$(BETS)_2(FeCl_4)_{1-x}(GaCl_4)_x$. These phase transitions may be detected by magnetization and specific heat measurements. We think that neutron scattering, μSR, and NMR measurements may be used additionally to reveal the structure of peculiar vortex phases formed due to the interplay of competing spin and orbital effects induced by the external and exchange fields.

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