1. Introduction

Ideal diamagnetism is one of the most striking properties of superconductors. It is manifested by the Meissner effect, the complete expulsion of a magnetic field from the volume of a superconductor. Conversely, magnetic fields with relatively large values can destroy superconductivity. In most real (type II) superconductors, it may take place in two ways—through orbital or paramagnetic effects. The orbital pair breaking is connected with the rise of the Abrikosov vortex state in superconductors, while paramagnetic pair breaking originates from the Zeeman splitting of electronic energy levels. Both effects determine the upper critical magnetic field, in which the relative importance of the orbital and paramagnetic effects in the suppression of the superconductivity is described by the Maki parameter \( \alpha = \frac{\sqrt{2} H_{c2}^{orb} H_{c2}^{P}}{H_{c2}^{P}} \) and the ratio of the critical magnetic fields at zero temperature \( H_{c2}^{orb} \) and \( H_{c2}^{P} \), derived from the orbital and diamagnetic effects, respectively.

In most superconductors, the orbital pair-breaking effects are more disruptive than the diamagnetic ones, thus \( H_{c2}^{P} \) is usually larger than \( H_{c2}^{orb} \) \( (\alpha \ll 1) \) and superconductivity disappears when vortex cores begin to overlap. When \( \alpha \gg 1 \), superconductivity is destroyed by the Zeeman effect (Pauli paramagnetism), and systems exhibiting this property are called Pauli-limited materials.

In the absence of an external magnetic field, superconductors are found in the Bardeen–Cooper–Schrieffer (BCS) state \([2, 3]\), where superconductivity is formed by Cooper pairs with total momentum equal to zero. However, in Pauli-limited superconductors, the external field can lead to interesting phenomena near or above the critical magnetic field \( H_{c2}^{P} \), such as the transition to the Fulde–Ferrell–Larkin–Ovchinnikov (FFLO) phase \([4, 5]\). In contrast to the BCS state, the Cooper pairs are now formed between the spin-up and spin-down sheets of the split Fermi surface with non-zero total momentum. Moreover, this phase exhibits a spatially oscillating superconducting order parameter (SOP) in real space and spin polarization.

Although the FFLO phase had already been described theoretically in the 1960s, the experimental search is still ongoing and riddled with difficulties. This is a consequence of the physical properties of this inhomogeneous phase: it can only occur in Pauli-limited superconductors at a low temperature and high magnetic field (LTHM) regime. Only in the last decade have systems appeared in which we expect an experimental verification of this phase, such as heavy-fermion superconductors.
IBSC are chemical compounds possessing a layered structure, with a characteristic Fermi surface (FS). In order to explain the FS features in IBSC, various two-orbital [46], three-orbital [47, 48] and five-orbital [49, 50] tight-binding models have been proposed. The abundance of available models is induced by the relatively complicated band structure of IBSC materials, which is strongly dependent on the chemical doping [51]. To describe e.g. FeAs layers realistically, five 3d orbitals of iron ions need to be retained in the model. However, the band structure calculations suggest the importance of itinerant electrons from the $d_{xz}$ and $d_{yz}$ orbitals. The $d_{xy}$ orbitals are also influential in the formation of the FS. For this reason, we use the three-band model proposed by Daghofer et al [47, 48] in our calculations for simplicity. Although this model was initially proposed to determine the FS of LaOFeAs, it reproduces the characteristic FS of IBSC: a hole-like Fermi pocket around the Γ-point and electron-like Fermi pockets around the $M$-point of the first Brillouin zone.

In general, the momentum-dependent tight-binding non-interacting Hamiltonian of the multi-orbital IBSC in orbital space is given by:

$$H_0 = \sum_{\alpha, \beta, k} (T_{k}^{a\beta} - (\mu + \sigma h) \delta_{\alpha\beta}) c_{\alpha k\sigma}^\dagger c_{\beta k\sigma},$$  

(1)

where $c_{\alpha k\sigma}$ ($\bar{c}_{\alpha k\sigma}$) annihilates (creates) an electron with momentum $k$ and spin $\sigma$ in the orbital $\alpha$. The hopping matrix elements $T_{k}^{a\beta}$ correspond to the kinetic energy of a particle with momentum $k$ changing the orbital from $\beta$ to $\alpha$; they are given by the effective tight-binding model of the two-dimensional FeAs planes in the selected model. We use the model of IBSC proposed by Daghofer et al in [47] and improved in [48]. Beyond the $d_{xz}$ and $d_{yz}$ orbitals, the model also accounts for the $d_{xy}$ orbital:

$$T_{11}^{k} = 2t_2 \cos k_x + 2t_1 \cos k_y + 4t_3 \cos k_x \cos k_y + 2t_4 (\cos(2k_x) - \cos(2k_y)) + 4t_5 \cos(2k_y),$$  

(2)

$$T_{22}^{k} = 2t_1 \cos k_x + 2t_2 \cos k_y + 4t_4 \cos k_x \cos k_y - 2t_4 (\cos(2k_x) - \cos(2k_y)) + 4t_5 \cos(2k_y),$$  

(3)

$$T_{33}^{k} = 4t_3 \cos k_x \cos k_y + 4t_5 \cos k_x \cos k_y + 4t_6 \cos(2k_x) + \cos(2k_y)),$$

(4)

$$T_{12}^{k} = T_{21}^{k} = 4t_4 \sin k_x \sin k_y, $$  

(5)

$$T_{13}^{k} = T_{31}^{k} = 2it_7 \sin k_x + 4it_8 \sin k_y, $$  

(6)

$$T_{23}^{k} = T_{32}^{k} = 2it_7 \sin k_y + 4it_8 \sin k_x,$$

(7)

where $\alpha, \beta = 1, 2, 3$ denote the $d_{xz}$, $d_{yz}$ and $d_{xy}$ orbitals respectively. In [48] the hopping parameters are given in electron volts as: $t_1 = -0.08$, $t_2 = 0.1825$, $t_3 = 0.08375$, $t_4 = -0.03$, $t_5 = 0.15$, $t_6 = 0.15$, $t_7 = -0.12$, $t_8 = 0.06$, $t_9 = 0.0$, $t_{10} = -0.024$, $t_{11} = -0.01$, $t_{12} = 0.0275$ and $\epsilon_0 = 0.75$. The average number of particles in the system $n = 4$ is attained for $\mu = 0.4748$.

The band structure of the IBSC model can be reconstructed from the kinetic tight-binding Hamiltonian in the orbital representation $H_0$ via the unitary transformation $H'_{0} = U^\dagger H_0 U$ [47]. Then $H'_{0} = \sum_{\alpha, \kappa, \sigma} E_{\alpha\kappa\sigma} d_{\alpha\kappa\sigma}^\dagger d_{\alpha\kappa\sigma}$. Here $d_{\alpha\kappa\sigma}$ ($d_{\alpha\kappa\sigma}^\dagger$) annihilates (creates) an electron in band $\epsilon$. The total number of particles in the system $\sum_{\alpha, \kappa, \sigma} c_{\alpha\kappa\sigma}^\dagger c_{\alpha\kappa\sigma} = \sum_{\alpha, \kappa, \sigma} d_{\alpha\kappa\sigma}^\dagger d_{\alpha\kappa\sigma}$ is adjusted by the chemical potential $\mu$. We neglect orbital effects, which is equivalent to assuming that the external magnetic field $h$ is parallel to the FeAs layers.

We assume a unique phase throughout the system for simplicity, although it should be kept in mind that in many IBSC systems superconductivity can coexist with magnetic order [52]. In this paper, we introduce a superconducting pairing between the quasi-particles in bands $\epsilon$, which
is a good approximation in the limit of weak or vanishing inter-band pairing [53], without specifying the mechanisms responsible for the formation of the superconducting phases. Superconductivity with non-zero Cooper pairs total momentum (CPTM) can be described by the phenomenological effective Hamiltonian:

$$H'_{\text{SC}} = \sum_{k} \{ \Delta_{\pm} d_{\pm k}^\dagger d_{\mp -k+q} + H.c. \},$$

(8)

where $\Delta_{\pm} = \Delta_{\pm} \eta(k)$ is the SOP in band $\epsilon$ for the CPTM $q$, and amplitude $\Delta_{\pm} = U\langle d_{\pm,-k+q} d_{\mp k} \rangle$. $U$ is the effective pairing interaction in band $\epsilon$ and can be found by imposing the disappearance of the SOP at the critical temperature $T_{C}$. The structure factor given by $\eta(k)$ captures the symmetry of the SOP, related to the effective interaction in real space [30, 54], and it equals 1 for s-wave symmetry, $4\cos(k_x)\cos(k_y)$ for s$\pm$-wave and $2(\cos(k_x) - \cos(k_y))$ for d-wave symmetry. $H'_{\text{SC}}$ in band space is the reformulation of the interacting Hamiltonian in orbital space [47]. Similarly to the two-band model, the SOP in the band representation can be transformed into an orbital one [55]. Moreover, the interband SOPs with different values of $\Delta_{\pm}$ in every band $\epsilon$ correspond to the existence of the intra- and interorbital SOPs in the system.

The total Hamiltonian $H = H_{0} + H'_{\text{SC}}$ formally describes a system with three independent bands. For this reason, the eigenvalues of $H$ in the band representation are given by the standard Bogoliubov transformation [56, 57]:

$$\lambda_{\pm}^\pm = \tilde{\omega}_{k} \pm \sqrt{\left(\tilde{\omega}_{k}^2 \mp |\Delta_{\pm}|^2 \right)} \quad \forall \; k, \epsilon$$

(9)

where $\tilde{\omega}_{k}^\pm = (E_{\pm k} \pm E_{\mp -k+q})/2$. The grand canonical potential can be calculated explicitly from its definition $\Omega = k_{B}T\ln\{\text{Tr}[\exp(-H/k_{B}T)]\}$, which for given (fixed) parameter $h$ and $T$ can be treated as a function of the SOP $\Delta_{\pm}$ and CPTM $q_{\epsilon}$ in each band.

2.1. The entropy and specific heat calculation

In the case of intraband superconductivity, the grand canonical potential is given as $\Omega = \sum_{\epsilon,\alpha} \Omega_{\epsilon}$, where:

$$\Omega_{\epsilon} = -k_{B}T\sum_{k} \ln \left[ 1 + \exp \left( \frac{\lambda^{\pm}_{\epsilon k}}{k_{B}T} \right) \right] + \sum_{k} \left( E_{\pm k} - |\Delta_{\pm}|^2 / U_{\epsilon} \right).$$

(10)

detailed calculations can be found in [30, 55–57]. From the thermodynamical potential, we can determine the entropy $S = -\sum \Omega / d\Omega$ and superconducting specific heat at temperature $T$ as $C = -T\partial^2 \Omega / \partial T^2$, where $\Omega$ is the grand canonical potential. The entropy [58] is $S = -\sum \Omega / d\Omega$, where:

$$\frac{d\Omega}{dT} = \sum \left[ \frac{\partial \Omega}{\partial T} \right] + \sum \left[ \frac{\partial \Omega}{\partial \Delta_{\pm}} \frac{\partial \Delta_{\pm}}{dT} + \frac{\partial \Omega}{\partial q_{\epsilon}} \frac{\partial \Delta_{\pm}}{dT} \right],$$

(11)

where the subscript $\epsilon$ labels the equilibrium values of the SOPs $\Delta_{\pm}$ and CPTMs $q_{\epsilon}$. From the equilibrium condition, we have: $\partial \Omega / \partial \Delta_{\pm} = 0$ for all $\epsilon$, since $\Omega (\Delta_{\pm},q_{\epsilon})$ is at a minimum. Hence $S = -\sum c \partial \Omega / \partial T |_{\epsilon}$ or a priori:

$$S = \sum \left[ \frac{\lambda^{\pm}_{\epsilon k}}{T} f(\lambda^{\pm}_{\epsilon k}) + k_{B} \ln \left( 1 + \exp \left( \frac{\lambda^{\pm}_{\epsilon k}}{k_{B}T} \right) \right) \right],$$

(12)

where $f(E)$ is the Fermi-Dirac distribution. The specific heat is then defined in the usual manner by:

$$C = TdS/dT|_{\text{in,T},\epsilon} \equiv -T\partial^2 \Omega / \partial T^2|_{\epsilon}. \quad \text{It should be noted that the grand potential (and also the SOPs and CPTMs) depends on temperature in a non-trivial manner, which forces the calculation of $S$ and $C$ to be carried out by numerical derivatives.}

3. Numerical results and discussion

The global ground state can be obtained at fixed values of the parameters (temperature $T$ and magnetic field $h$) from the minimization of the grand canonical potential $\Omega$ with respect to the SOP $\Delta_{\pm}$ and CPTM $q_{\epsilon}$, while at the same time determining the optimal values of the latter parameters. All calculations have been performed on NVIDIA GPUs, in momentum space on a square lattice grid $k_{x} \times k_{y} = 10000 \times 10000$, using the algorithm described in [57]. The following are predictions for the s-wave symmetry of the SOP, however other symmetries generate analogous results.

We assume a different effective attractive intraband pairing in each band. It is found by seeking the simultaneous disappearance of the superconducting BCS phase at critical temperature $T_{C}$, equal to 55 K ($\sim$5 meV). For this set of parameters, the BCS critical magnetic field $h_{\text{BCS}}$ is also uniform in the bands, with a value of about 100 T ($\sim$6 meV). Although these relatively large values can be found in some classes of IBSC [59], we focus on the generic features of IBSC in the LTHM regime.

Above $h_{\text{BCS}}$, at temperatures below some characteristic $T'$, the FFLO phase arises [6]. In this phase the SOPs decrease with increasing external magnetic field (figures 1(a)–(c)). Moreover, in general the CPTM depend on the size of the splitting between the Fermi surfaces for electrons with spin up and down, the source of which is the Zeeman effect. Raising the external magnetic field increases the splitting, which leads to greater CPTM (figures 1(d)) [55], which is also true in other systems [60]. The CPTM dependence on the temperature is, however, weak.

In the case of BCS, we can find a typical $h$–$T$ phase diagram (figure 2(a)), in which the superconductivity in every band disappears at the same external magnetic field [55]. Conversely, for the FFLO phase a different critical magnetic field $h_{\text{FFLO}}$ [30, 57] determines the superconducting behavior in each band, as shown in figure 2(a). Because of this, calorimetric experiments in the LTHM regime should display multiple phase transitions, in the form of a group of peaks at specific heat, shown as arrows in figure 2(b). The first group (or extended peak) can be connected with the transition from the BCS to the FFLO phase (first arrow from the left in figure 2(b)), while the second group arises due to transitions inside the FFLO phase (blue and green lines in figure 2(a)), and because of the final transition from the superconducting to the normal state (red line in figure 2(a)). To conclude, the measured total specific heat is characterized by a multiply
discontinuous shape, the black line in figure 2(b). It should be noted that similar effect can be found in systems with relatively significant finite-size effects \[61–63\]. However, multiple phase transitions in this case (and the relative discontinuities in the specific heat) are due to abrupt changes in the CPTM \(\varepsilon\) and are not the result of the disappearance of the FFLO phase in consecutive bands. This same effect can be expected in two-dimensional square lattices, where a growing magnetic field favors FFLO phases with a greater number of inequivalent momenta entering the CPTM \[64\].

Usually the superconductivity in IBSC is described by an \(\pm s\)-wave symmetry, where the gap changes its sign between the hole and electron pockets of the Fermi surface \[65, 66\]. However, \(d\)-wave symmetry can be also observed \[67, 68\]. Hole doping of IBSC can lead to the transition of the gap symmetry from \(s\)-wave to \(d\)-wave \[69–72\]. Our main result is not affected, with there being similar results for symmetries other than \(s\)-wave—the FFLO is the ground state in the LTHM regime in every band. However, a different SOP symmetry could influence the shape of specific heat as a function of the temperature (figure 2). Moreover, because the band structure of the IBSC depends strongly on doping, more realistic results require specific models for the chemical compound.

For different compounds, the quantity of specific heat peaks can depend on the number of bands forming the Fermi surface and supporting the FFLO state in the LTHM regime, with the detailed band structure only influencing the jump heights quantitatively.

3.1. Final remarks

It should be kept in mind that the results here have been obtained in the mean field approximation, but they are still significant as a qualitative result. In the context of Pauli-limited superconductors, we can speak about two scales of temperature. The former is the critical temperature \(T_C\), at which the superconductivity vanishes in zero external magnetic field. The latter is the temperature \(T^+\), in which phase transitions from the superconducting to normal state change kind, from first to second order. For comparison, the temperature \(T_C\) is reported as 2.3 K and 3.5 K for CeCoIn\(_5\) and KFe\(_2\)As\(_2\), respectively, while in both cases \(T^+\) can be approximated as 0.31 \(T_C\) \[8, 25\]. However, in CeCoIn\(_5\) the specific heat displays an additional anomaly within the superconducting state at a temperature \(\sim 300\) mK \(\sim 0.12 T_C\) \[7\]. These experimental results are interpreted as evidence for the existence of the FFLO phase. Similar behavior is observed in organic superconductors \[16\]. Relevant experimental data have been presented in the literature for KFe\(_2\)As\(_2\) \[73, 74\], but not at sufficiently low temperatures.

Iron-based KFe\(_2\)As\(_2\) Pauli-limited superconductors have a critical magnetic field near 5 T \[25\]. For fields above this value,
an anomalous shape for the specific heat can be observed in the LTHM regime for temperatures below 1 K [73, 74]. The authors explain these anomalies as being related to a metamagnetic transition in high-field heavy-fermion CeIrIn5 [75]. However, in the context of the existence of FFLO in heavy-fermion and IBCS, we must remember the mutual enhancement of magnetism and the FFLO phase. Under particular conditions, the magnetic and superconducting orders can cooperate in the sense that the presence of superconductivity can enhance the tendency towards the formation of magnetic order, and the presence of magnetic order can enhance the tendency towards Cooper pair formation [76]. It was experimentally observed in heavy-fermion CeCoIn5, where the additional phase transition in the LTHM regime inside the superconducting phase can be the manifestation of the emergence of the incommensurate spin density wave (ICSDW) [77]. In relation to this situation, in multiband materials we can expect a similar formation of ICSDW or a modification of the existing SDW in the presence of the FFLO phase. To verify this hypothesis, more accurate calorimetric measurements are required in the LTHM regime and further theoretical studies are underway.

4. Summary

In this paper we show that the presence of the FFLO phase in multiband materials such as IBCS can be experimentally ascertained through the appearance of multiple phase transitions, which are in turn manifested by multi-discontinuities in the shape of the specific heat in the low temperature and high magnetic field regime. This result can be instrumental in the experimental verification of the FFLO phase in Pauli-limited multiband materials.

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