Paramagnetism and Reentrant Behavior in Quasi-1D Superconductors at High Magnetic Fields

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ABSTRACT

The thermodynamics of quasi-one-dimensional superconductors in the presence of large magnetic fields is studied. When the quantum effects of the magnetic field are taken into account, several reentrant phases persist at very high fields. In the last reentrant phase, the free energy, the specific heat jump and the excess magnetization are estimated near the critical temperature. In particular, the excess magnetization is found to be paramagnetic as opposed to *diamagnetic* (in weak fields) and its sign is found to be controlled by the slope of H_{c_2}. This result is further generalized to the entire phase diagram (including *all* quantum phases) and to different physical systems using general thermodynamic relations which show that the *sign* of the excess magnetization ΔM near $H_{c_2}(T)$ follows $dH_{c_2}(T)/dT$. These relations provide a scenario for the evolution of the *sign* of ΔM from weak fields to strong fields.

1. Introduction

In recent years quasi-one-dimensional (quasi-1D) conductors with open fermi surfaces have received a lot of attention[1] because of their unusual properties in the presence of a magnetic field. The most representative conductors of this class are the Bechgaard salts which exhibit Field Induced Spin Density Waves (FISDW) phases at high magnetic fields due to a quantized nesting mechanism[1,2]. These organic salts have a very rich phase diagram and are also known to be superconducting. It is then very natural to ask what will be the effect of large magnetic fields in systems that are superconducting at zero magnetic field.

High magnetic fields usually tend to destroy superconductivity because of orbital frustration effects that raise the free energy and suppress the coherence of the superconducting state. This picture usually emerges in the framework of a Ginzburg-Landau theory, where the semiclassical approximation is used and the quantum effects of the magnetic field are completely neglected.

In the normal state of quasi-1D superconductors, the Fermi surface is open, i.e, has two disconnected branches and as a result the semiclassical orbits of motion in a magnetic field are also open. Considering the quantum effects of the magnetic field, Lebed[3] was the first to propose that quasi-1D superconductors may exhibit a strong reentrant phase in high magnetic fields. More recently, though, Dupuis, Montambaux and Sá de Melo[4] have shown that the phase diagram originally proposed by Lebed[3] was incomplete. Provided that the system is in the clean limit, many additional intermediate reentrant phases exist between the semiclassical and the extreme quantum

regimes. These phases are separated by first order transition lines corresponding to structural phase transitions between laminar lattices with different periods. The laminar lattices are characterized by two indices, Q and M; Q is a modulation wavevector along the direction of largest hopping (x direction) and M is the periodicity of the laminar lattice along the direction of smallest hopping (z direction). The periodicity M is commensurate with the underlying crystalline lattice.

Here, we will be concerned mostly with laminar lattices of rectangular symmetry. Moreover, we will mainly discuss the high field (extreme quantum limit, $M = 1, Q = 0$) phase[4], where many analytical approximations can be made to calculate the free energy, the change in specific heat and the excess magnetization close to the critical temperature $T_c(H)$. In particular, we show that the excess magnetization in the last reentrant phase is *paramagnetic* due to *localization* and *quantum* effects as opposed to *diamagnetic* in weak fields. We further generalize this result to *all* quantum phases by means of *general* thermodynamic relations which indicate that the *sign* excess magnetization ΔM of the superconducting state near $H_{c_2}(T)$ follows $dH_{c_2}(T)/dT$. In addition, these relations provide a scenario for the evolution of the *sign* of ΔM from weak fields to strong fields.

2. Background

To understand the properties and the nature of the superconducting state of quasi-1D superconductors in the presence of magnetic fields it is important to understand first the normal state. We choose the branch dispersion $\varepsilon_{\alpha,\sigma}(\mathbf{k}) = v_F(\alpha k_x - k_F) + t_y \cos(k_y b) + t_z \cos(k_z c) - \sigma g \mu_B H$ and take advantage of the largest (E_F) and smallest (t_z) scales, $E_F \gg t_y \gg t_z$, in the problem at zero field by applying the magnetic field along the y direction ($\mathbf{H} = H\hat{y}$). We will concentrate here only on the quantum aspects of the problem. Using the Landau gauge $\mathbf{A} = (Hz, 0, 0)$ where k_x, k_y and α are good quantum numbers, while k_z is not, the eigenfunctions of $H_0(\mathbf{k} - e\mathbf{A}) = \varepsilon_{\alpha,\sigma}(\mathbf{k}) + \alpha \omega_c z/c$ are $\Phi_{k_x,k_y,N,\alpha,\sigma}(x, y, z = nc) = \exp[i(k_x x + k_y y)]J_{N-n}(\alpha t_z/\omega_c)$ and the eigenvalues $\epsilon_{k_x,k_y,N,\alpha,\sigma} = \varepsilon_{\alpha,\sigma}(\mathbf{k}_\rho) + \alpha N \omega_c$ where $J_p(u)$ is the Bessel function of integer order p and argument u and $\varepsilon_{\alpha,\sigma}(\mathbf{k}_\rho) = v_F(\alpha k_x - k_F) + t_y \cos(k_y b) - \sigma g \mu_B H$ is a 2D dispersion, with $\omega_c = v_F G$ and $G = |e|Hc$. G is the characteristic magnetic wavenumber, g is the gyromagnetic factor and ω_c is the frequency of the periodic motion along the z direction (analogous to the *cyclotron* frequency for isotropic systems), i.e., the frequency at which the electrons traverse the Brilouin zone in the z direction. Notice that the eigenfunctions for the quasi-1D case become localized when $\omega_c \gg t_z$ in the planes $z = Nc$, i.e., xy plane, via the argument of the Bessel function in agreement with the semiclassical condition that the amplitude of motion in the z direction $z_A \ll c$.[3,4] The physical interpretation is even more transparent when we analyse in addition the energetics; the energy barrier for an electron to tunnel from plane $z = nc$ to plane $z = (n+1)c$ is ω_c, hence when the energy barrier becomes large

in comparison to the hopping t_z, the electrons are essentially confined to their initial planes. As a result the magnetic field induces a dimensional crossover between highly anisotropic 3D ($t_z \gg \omega_c$) system to a highly anisotropic 2D ($t_z \ll \omega_c$) system. This dimensional crossover has a dramatic impact upon the superconducting state. For instance, the previous analysis already suggests that when $t_z \ll \omega_c$, pairing occurs essentialy within a given plane and paired electrons may tunnel from planes $z = Nc$ to neighboring planes $z = (N \pm 1)c$. At all values of the magnetic field the instability of the normal state towards superconductivity arises from pairing electrons between the different magnetic subbands $\epsilon_{k_x,k_y,N,\alpha,\sigma}$.

3. Reentrant Behavior

To study the instability of the normal state we consider the cases of singlet superconductivity (SS) and triplet superconductivity (TS) within a functional integral approach[5]. Here, we consider only the situation where $t_z \gg T_c^{(\eta)}(0)$, with $\eta = SS, TS$, which guarantees that there is no Josephson coupling ($\xi_z(0) \gg c$) in the superconducting state between different xy planes at zero magnetic field. First we analyse the upper critical field $H_{c_2}(T)$ or $T_c(H)$. In weak magnetic fields where both the quantum effects of the magnetic field $\omega_c \ll 2\pi T$ and the Zeeman splitting can be neglected the semiclassical approximation can be used to obtain $H_{c_2}(T) = \phi_0/2\pi\xi_x(T)\xi_z(T)$ leading to $T_c^{(\eta)}(H) = T_c^{(\eta)}(0) - \kappa t_z \omega_c/T_c^{(\eta)}(0)$ with $\kappa = 7\sqrt{2}\zeta(3)/16\pi^2$, where $T_c^{(\eta)} = 2\omega_D\gamma/\pi \exp\left[-1/N(E_F)\lambda_\eta\right]$ and $\omega_D \sim E_F$. In the limit of high magnetic fields $\omega_c \gg 2\pi T$ the quantum effects and localization induced by the magnetic field play an important role in the determination of $T_c(H)$ as well as the Zeeman splitting. In the case of singlet pairing or opposite spin triplet pairing the Zeeman term partially suppresses the transition to the superconducting state. In contrast, for singlet pairing with $g = 0$ (SP0) or equal spin triplet pairing (ESTP) the Zeeman splitting does not play any important role and $T_c(\infty) \to T_c^{(2D)}(0)$ since the electronic motion is confined to the xy planes which are parallel to the direction of the applied magnetic field, i.e., the orbital frustration that destroys superconductivity is suppressed. In the SP0 and ESTP cases for $\omega_c \gg t_z \gg T_c(H)$ we obtain the critical temperature $T_c^{(TS)}(H) \simeq T_c^{(2D)}(0)\left[1 - (t_z/\omega_c)^2 \ln\left[\gamma\omega_c/\pi T_c^{(2D)}(0)\right]\right]$, a limiting result first obtained by Lebed[3].

4. Thermodynamics

The thermodynamics of the superconducting state in high magnetic fields for the case of singlet pairing with $g = 0$ (SP0)[6] and order parameter $\Delta(r)$ can be obtained from the total free energy[5]

$$F = F_0 + F_1 + F_2 + F_3 + F_4 + F_B \tag{1}$$

near $T_c(H)$, where F_0 is the free energy for $\Delta(r) = 0$, $F_B = \int dr\, [B(r)]^2/8\pi$ is the

magnetic field energy with $\mathbf{B}(\mathbf{r}) = \mathbf{H} + \mathbf{h}_s(\mathbf{r})$. The terms F_i ($i = 1, 2, 3, 4$) are defined below.

In the SP0 state the non-uniform order parameter has the form $\Delta(\mathbf{r}) = \Delta_0 + 2\Delta_2 \cos(2Gx)$, expected to be valid in the last reentrant phase $M = 1, Q = 0$, which has periodicity $l_x = \pi/G$ and $l_z = c$ and holds a flux quantum inside the plaquette (l_x, l_z), i.e., $Hl_xl_z = \phi_0$.

In the range of fields we are interested here $\omega_c \gg t_z$, $\Delta_0 \gg \Delta_2$ and the free energies F_i have the form, $F_1 \simeq -(1/\lambda_{TS})(\Delta_0^2 + 2\Delta_2^2)$; $F_2 \simeq B_{20}\Delta_0^2 + B_{11}\Delta_0\Delta_2 + B_{02}\Delta_2^2$; $F_3 \simeq D_{20}\Delta_0^2 + D_{11}\Delta_0\Delta_2 + D_{02}\Delta_2^2$; $F_4 \simeq (1/2)(C_{40}\Delta_0^4 + C_{31}\Delta_0^3\Delta_2 + C_{22}\Delta_0^2\Delta_2^2)$.

From the saddle point condition $\delta F/\delta\Delta_0 = 0$, $\delta F/\delta\Delta_2 = 0$, and the Maxwell's equation $\nabla \wedge \mathbf{h}_s(\mathbf{r}) = 4\pi\mathbf{j}_s(\mathbf{r})$ ($\delta F/\delta\mathbf{a}_s = 0$ and $\mathbf{h}_s(\mathbf{r}) = \nabla \wedge \mathbf{a}_s(\mathbf{r})$), we find $\Delta_0^2 \simeq [8\pi^2/7\zeta(3)]\, T_c(H)\, [T_c(H) - T]\, [1 + (t_z/\omega_c)^2]$ and $\Delta_2 \simeq (t_z/\omega_c)^2\Delta_0/2$ (for $E_F \gg \omega_c$).

As a result, the order parameter $\Delta(\mathbf{r}) = \Delta_0[1 + (t_z/\omega_c)^2 \cos(2Gx)]$, and the supercurrents $j_x(\mathbf{r}) \simeq 0$; $j_y(\mathbf{r}) = 0$; $j_z(\mathbf{r}) \simeq j_0(T, H)\sin(2Gx)$ with $j_0(T, H) = 8|e|(t_z/\omega_c)^2 cN(E_F)\ln[\gamma\omega_c/\pi T_c(H)]\Delta_0^2$, where all expressions are correct to order $(t_z/\omega_c)^2$. Here, $j_z(\mathbf{r})$ corresponds to a Josephson current coupling neighboring planes $z = Nc$ and $z = (N+1)c$. This *magnetic field induced* Josephson coupling $j_0(T, H)$ is a consequence of the localization ($\omega_c \gg t_z$) and quantum effects ($\omega_c \gg 2\pi T$) of the magnetic field and it is absent in weak fields in the regime we have considered here given that there is no Josephson coupling in zero magnetic field ($t_z \gg T_c(0)$, i.e., $\xi_z(0) \gg c$). As a result the normal state in high fields becomes unstable towards a *weakly coupled* quasi-2D superconductor with a *magnetic field induced* Josephson coupling between different xy planes.

The local excess magnetization per plaquette is $\Delta\mathbf{M}(\mathbf{r}) = \Delta M(\mathbf{r})\hat{y}$ and can be calculated from $\nabla \wedge \mathbf{h}_s(\mathbf{r}) = 4\pi\mathbf{j}_s(\mathbf{r})$ since $\Delta M(\mathbf{r}) = \mathbf{h}_s(\mathbf{r})/4\pi$. Hence the net excess magnetization per plaquette $\Delta M = j_0(T, H)/2G$ is *paramagnetic*, i.e., $\Delta M > 0$, a rather surprising result at first when contrasted with the usual *diamagnetism* in weak fields. Here, the diamagnetic contributions to ΔM are of order $(t_z/\omega_c)^4$.

This result can verified directly from the free energy difference $\Delta F = F_s - F_n$, between the superconducting and normal states. The saddle point ΔF is given by $\Delta F \simeq -[8\pi^2/7\zeta(3)]\, N(E_F)\, [T - T_c(H)]^2 + F_b$, where $F_b = \int dr\, [h_s(\mathbf{r})]^2/8\pi$ where only the terms correct to order $(t_z/\omega_c)^2$ should be considered for consistency. The total excess magnetization can be calculated from ΔF from the thermodynamic relation $\Delta\mathbf{M} = \mathbf{B}/4\pi - \partial\Delta F/\partial\mathbf{B}$ which leads to

$$\Delta\mathbf{M} \simeq [16\pi^2/7\zeta(3)]\, N(E_F)\, [T_c(H) - T]\, [dT_c(H)/dH]\,\hat{y} \qquad (2)$$

and implies that the *sign* of the excess magnetization is controlled by the slope of $T_c(H)$. The excess magnetization calculated from the free energy and from the induced supercurrents are the same to the order of the approximation $(t_z/\omega_c)^2$ considered here, as expected. This confirms the paramagnetic behavior obtained from the supercurrents and further associates the predicted paramagnetism with the reen-

trant behavior in large fields, i.e., $dT_c(H)/dH > 0$. In addition, the excess entropy is negative as it must be, $\Delta S \simeq - [16\pi^2/7\zeta(3)] \, N(E_F) \, [T_c(H) - T]$, since the superconducting state is more ordered than the normal state. A direct calculation of specific heat jump ΔC from ΔF leads to $\Delta C \simeq [16\pi^2/7\zeta(3)] \, N(E_F) T_c(H)$, which deviates from the BCS expression only through $T_c(H)$.

General thermodynamic relations in the vicinity of a second order phase transition, imply that $\Delta C = T \, [dH_{c2}(T)/dT]^2 \, (\partial \Delta M/\partial H)_T$ and that $(\partial \Delta S/\partial H)_T = -dH_{c2}(T)/dT(\partial \Delta M/\partial H)_T$. Our results for ΔC and ΔM do obey these general thermodynamic relations, but most interestingly is the relation

$$\Delta S = -(\alpha_m/\alpha_s)(dH_{c_2}(T)/dT)\Delta M, \qquad (3)$$

with $\alpha_s > 0$ and $\alpha_m > 0$, which shows that if $\Delta S < 0$ the product $(dH_{c_2}(T)/dT)\Delta M > 0$, i.e., a *diamagnetic (paramagnetic)* excess magnetization $\Delta M < 0 \; (\Delta M > 0)$ is always linked to a decrease (increase) in $H_{c_2}(T)$, $dH_{c_2}/dT < 0 \; (dH_{c_2}/dT > 0)$. Conversely, when $T_c(H)$ decreases (increases) with H there is a *diamagnetic (paramagnetic)* excess magnetization. The last relation is derived from the simple observation that in a second order phase transition ΔM and ΔS must vanish at H_{c_2} (from below), hence in the vicinity of H_{c_2} $\Delta M = M_0(1 - H/H_{c_2})^{\alpha_m}$ and $\Delta S = S_0(1 - H/H_{c_2})^{\alpha_s}$. Our results also satisfy this relation with $\alpha_m = \alpha_s = 1$, since the saddle point approximation is a mean field theory. Furthermore, the results are also valid even when fluctuation effects around the mean field theory are considered, provided that the system is in thermodynamic equilibrium. Fluctuations only affect equation (3) numerically, i.e., via the ratio $\alpha_m/\alpha_s \; (> 0)$ of the critical exponents. In addition, we should emphasize that the pure thermodynamic derivation given in this paragraph does not invoke any particular microscopic or phenomenological model as an approximation to the free energy in order to establish the relation between the *sign* of ΔM and the slope of $T_c(H)$, which is valid over the *entire* phase diagram.

5. Discussion

To make contact with experiments we should emphasize that the excess magnetization ΔM is the magnetization arising only from the superconducting part of the entire system. Therefore, to measure ΔM, the additional contributions to the total magnetization must be removed by an extraction method. Furthermore, the expected *paramagnetism* in the last reentrant phase of the quasi-1D Bechgaard salts should be measurable for temperatures $T < 2K$ and fields $H > 10T$, when the parameters $t_z = 20K$, $T_c = 2K$ are used.

We have also analysed the laminar phases $M = 2, Q = G$ for the rectangular lattice, $M = 2, Q = 0$ for the triangular lattice. In both cases supercurrents flow along x direction and the z direction and the period of the Josephson vortex lattice in the z direction is $2c$. The form of the order parameter does not change within a given

phase, but its magnitude and phase along the plaquette are magnetic field dependent. This magnetic field dependence is also transfered to the local supercurrents, which in turn present both *paramagnetic* and *diamagnetic* flows within a given plaquette. It is the competition between these current flows as a function of H that determines the net ΔM which is positive (*paramagnetic*) or negative (*diamagnetic*) depending on the slope of $T_c(H)$ as if the dominant charge carriers were Cooper pairs of holes or electrons respectively. With the aid of relation (3) we can extend this scenario to the *entire* phase diagram and, in particular, to *all* intermediate quantum phases of quasi-1D superconductors. There, the *sign* of ΔM has an oscillatory behavior governed by $dH_{c_2}(T)/dH$ as the magnetic field is increased. For instance, in a given phase the *sign* of ΔM changes continously following the *slope* of $H_{c_2}(T)$, while the *sign* of ΔM changes discontinuously between consecutive phases since $H_{c_2}(T)$ has cusps with slopes of *opposite* signs.

To conclude, we must say that in the quasi-1D superconductors like Bechgaard salts, the possible reentrant intermediate phases even for the best situation are in the very low temperature regime $T_c(H) \ll T_c(0)$. Eventhough these salts are very clean materials, $[1/2\pi T_c(0)\tau \simeq 0.016]^{1}$, in the intermediate field regime the impurity effects may be very dramatic and destroy superconductivity, since $T_c(H)$ is strongly suppressed $[1/2\pi T_c(H)\tau \gg 1]$. At least the last reentrant phases $M = 1$ and $M = 2$ are expected to survive small disorder effects. Thus, the effects discussed here should be observable in quasi-1D superconductors.

6. Acknowledgements

7. References

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